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Research Progress of SnS_2/rGO Material in Gas Sensor

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Abstract. The material formed by combining two kinds of materials in a certain way is called composited material. Although reduced graphene oxide (rGO) has extremely high electron mobility, good chemical stability and high specific surface area, rGO sensors have problems such as slow recovery kinetics and poor selectivity. Tin disulfide (SnS_2)as a two-dimensional metal chalcogenide in the middle gap has excellent gas sensitivity and recovery kinetics, but the resistance is too large when working at room temperature. Therefore, the combination of SnS_2 and rGO can have both high electron mobility and excellent gas sensitivity. Therefore, the research of gas sensors based on SnS2/rGO has also become a hot spot. This article reviews the research progress of SnSn/rGO in the field of gas sensors.

1 Introduction

The semiconductor gas sensor device includes a semiconductor gas sensitive material, a connecting electrode and an inert substrate. Among them, the semiconductor gas-sensitive material is the core of the semiconductor gas sensor. The quality of a sensor depends largely on the nature of the gas-sensitive material. In 2004, Novoselov[1] research group first reported the use of mechanical exfoliation to prepare micrometer-scale graphene. Since then, many other two-dimensional materials with similar properties to graphene have also been synthesized and studied. These materials are called graphene-like materials such as two-dimensional metal chalcogenides (2D-TMD). 2D-TMD is a class of compounds with the molecular formula MX2. M represents a metal element (including Ti, Hf, V, Nb, Ta, Mo, W, Re, etc.), and X represents a chalcogen element (Se, S or Te) [2]. 2D-TMD not only has various excellent properties similar to graphene, but its band gap changes significantly as the number of layers decreases. The nature of this adjustable band gap makes single-layer or few-layer 2D-TMD has a wide range of applications in various fields, especially sensors. In short, two-dimensional materials represented by graphene and 2D-TMD have quickly become ideal gas-sensing materials for semiconductor gas sensors due to their inherent high specific surface volume and electron mobility. The following introduces reduced graphene oxide materials, SnS_2 materials, SnS_2/rGO materials and their applications in the field of gas sensors[3].

2 rGO

In 1947, Wallace, P.R[4]first proposed that single-layer graphene is a thin film composed of sp^2 carbon atoms (as shown in Figure 1), and conducted research on its electronic properties. Graphene has the thinnest thickness, the highest strength, and the best electrical conductivity among the existing nanomaterials. It is known as the "black gold", the "king of new materials", etc., and has therefore become a research hotspot in the field of materials science. Due to graphene's stable mechanical structure, excellent electrical conductivity, excellent optical properties, and extremely high electron mobility, graphene has a huge application prospect in various fields[5].

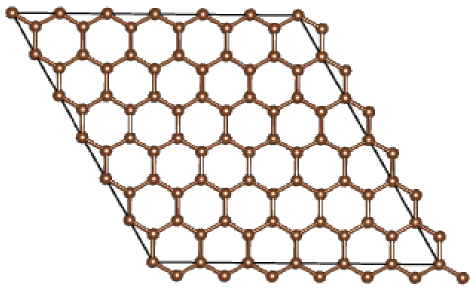

Fig 1. Schematic diagram of single-layer graphene

In 2007, Novoselov[6]made a micron-level graphene gas sensor through a micro-mechanical peeling method, and its detection limit was as low as ppb. The gas adsorbed on the surface of graphene can cause a significant change in its resistance, which indicates that graphene can be used as a sensitive material for gas detection[7]. Although graphene has attracted widespread attention in the field of gas sensors with its excellent performance. However, its zero band gap limits its development to a certain extent. Therefore, many researchers have proposed to functionalize or modify graphene [8]. rGO is one of the simplest and the first two-dimensional graphene materials to be studied. It is widely used due to its easy processing, high solubility in various

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solvents, oxygen-containing functional groups or defects, etc. Research on gas sensors. Hydrazine is a commonly used reducing agent for reducing graphene oxide (GO). Robinson et al[9] controlled the reduction degree of GO by changing the reaction time of GO in the hydrazine vapor, thereby adjusting the performance of the rGO-based gas sensor. The results show that the rGO gas sensor can detect HCN, DMMP, etc. at the ppb level at room temperature. In addition, sodium borohydride can also be used to reduce GO to make gas sensors for the detection of NH_3[10]. In a dry N_2 atmosphere, the sensor is exposed to different concentrations of NH_3, showing a very high selectivity to NH3. Annealing in an inert gas can also reduce GO. Lu G et al.[11] prepared rGO by annealing in argon gas to detect harmful gases such as NO_2 and NH3 at room temperature, and the higher the annealing temperature, the faster the response of the rGO sensor. The rGO prepared by the hydrothermal method at 150˚C can measure NO_2 at 60 ppb. This may be due to the presence of nanostructured pores on the surface of the rGO material, which increases the specific surface area and provides many adsorption sites for NO_2, resulting in its high response. rGO can also be used as a gas-sensitive material for CO_2 detection. Syed Muhammad Hafiz[12] studied a semiconductor gas sensor based on rGO for CO_2 detection. The lower amount of charge transfer between CO_2 and rGO results in a weaker adsorption strength of CO_2, and at the same time, the recovery time of CO_2 is also greatly shortened. Hu N et al.[13] reduced GO with p-phenylenediamine and prepared rGO for the detection of DMMP. The gas sensitivity test is carried out in room temperature and humid environment (RH <20%). The research results show that the response of rGO-based gas sensor can reach 4% when the DMMP concentration is 5 ppm; and the sensor response is directly proportional to the DMMP concentration , Has good repeatability and stability. In addition to the above-mentioned research on rGO alone as a gas-sensitive material, there are a large number of reports of rGO compounded with other gas-sensitive materials such as metal oxides [14] as gas-sensitive materials for the detection of toxic and harmful gases. Studies have found that the gas-sensing performance of rGO composite metal oxide is better than that of pure rGO or metal oxide, including selectivity, sensitivity and stability. This shows the importance of rGO in gas sensing reactions. Although rGO may help the gas and charge transport between materials in these composites. However, there are still some problems to be solved, such as poor recovery.

3 SnS2

Among the two-dimensional metal chalcogenides, the earliest, most extensive and representative one is molybdenum disulfide (MoS_2) [15]. Although gas sensors based on MoS_2 have great advantages in sensitivity and response time, their selectivity and recovery are still not ideal[16]. With the gradual deepening of research, the cations of two-dimensional transition metal chalcogenides are not limited to the traditional transition groups. The sulfides of III-VI A metals such as Ga, Sn, Pb, In, etc. also have similar properties to MoS2. Therefore, Ga, Sn, Pb, In, etc. are called post-transition metals, and the layered semiconductors formed by them and S group atoms are due to their two-dimensional properties induced by anisotropic crystallography, coupled with excellent electrical, Optical and mechanical properties have also entered the field of vision of researchers. Tin disulfide (SnS_2) is one of the late transition metal sulfides. A large number of studies have shown that SnS_2 materials exhibit excellent gas sensitivity in gas sensors. Although tin is not a member of the transition metal family, SnS_2 exists in a two-dimensional planar crystal structure similar to transition metal sulfides. The Sn atomic layer is sandwiched between two layers of S atoms, and the adjacent S atomic layers are connected by weak van der Waals forces. The schematic diagram of the molecular structure is shown in Figure 3. It is an n-type semiconductor and a typical two-dimensional metal chalcogenide with an intermediate gap (Eg=2.35eV), crystallized into a hexagonal CdI2 structure, and has good chemical stability, low cost and excellent Electrical and optical properties[17]. Compared with MoS_2, SnS_2 has greater electronegativity, which may enhance gas adsorption sites, thereby optimizing the sensing response and recovery, which provides potential for gas-sensing applications.

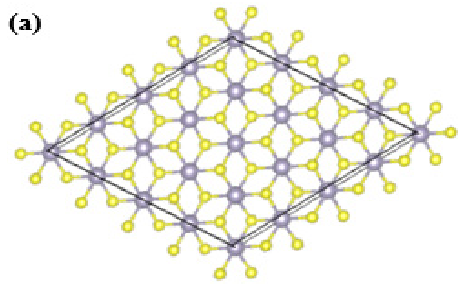

Fig 2. SnS_2 molecular structure diagram

In the research of gas sensors based on SnS_2, NO_2 and NH_3 are two kinds of small molecules of harmful gases that are widely studied. Young-Ho Kim et al. [18] reported the study of SnS2 to detect ppm level NO_2. The gas sensitivity test results showed that SnS_2 material can detect ppb to ppm level NO_2 with high sensitivity and rapid response at the optimal working temperature of 250℃. And under the condition of gas concentration of 10 ppm NO_2, the sensor's response degree>2000%, the response time is 6s, the recovery time is 40s, and it has good stability. Jian Zhen Ou et al. [16] prepared SnS2 material under low temperature conditions and developed a high-sensitivity, high-response NO_2 gas sensor. The research results show that the sensor exhibits high sensitivity at the operating temperature of 80-160ºC, and has the highest response at 120℃, and the shortest response time. With the increase of NO_2 concentration, its response is also increasing, at the best Under the conditions, the lower limit of detection can reach 30ppb. Ya Xiong et al. [19] studied NH_3. They synthesized thin nanosheets through a simple hydrothermal method to assemble into three-dimensional SnS_2 nanostructures. When detecting 100ppm NH_3 at an ambient temperature of 200°C, the SnS_2-based sensor showed a response value of 7.4, with a response time of 40.6s and a recovery time of 624s. In addition, the lowest detection limit of this sensor for NH_3 is 0.5 ppm. Compared with CO_2, CH_4, H_2, ethanol and acetone, it has a unique selectivity to NH_3. The analysis results show that the excellent performance of the NH_3 sensor may be due to the unique thin-layer assembly of the flower-like nanostructure of SnS_2, which is conducive to the carrier charge transfer process and the adsorption/desorption reaction. Bo Zhang et al. [20] studied the sensing performance of defective SnS_2 nanosheets. They prepared SnS_2 by hydrothermal synthesis and irradiated it with argon plasma within a few seconds to obtain defective SnS_2 nanosheets for use in NH_3 gas sensors. The study found that the electronic structure of the material can be adjusted by the argon plasma irradiation time. The SnS_2 material exhibits ideal gas sensitivity to NH_3 after being irradiated with argon plasma for 4 seconds, including high sensitivity, excellent selectivity and sensing kinetics, and low operating temperature. Based on the above research and analysis, it is concluded that the best working temperature of gas sensors based on pure SnS_2 is mostly at 100-200°C. SnS_2 has a strong thermal dependence, that is, gas sensitivity can be increased by appropriately increasing the working temperature [21]. However, increasing the operating temperature will increase the power consumption of the gas sensor, which is not conducive to its practical application. Therefore, many researchers solve this problem by compounding another material.Compounding with other materials is an effective way to solve the excessive working resistance of pure SnS_2 at room temperature.

4 Application of materials in gas sensors

At present, the more extensive research is the NO_2 gas sensor. Ming Cheng et al.[22] found that SnS_2/rGO materials exhibit unique selectivity to NO_2. The existence of rGO effectively reduces the optimal working temperature of the gas sensor. Compared with the SnS2 gas sensor, the response of the rGO/SnS_2 gas sensor to NO_2 has increased by almost an order of magnitude, with a response time of 50s and a recovery time of 48s, showing good response/recovery dynamics. This remarkable sensing The performance improvement may be due to the synergy of composite materials. Mahnaz Shafiei et al.[23] tested different target gases (including NO_2, CH_4, NH_3, ethanol, and acetone) at a working temperature of 25-100ºC. Compared with other intrinsic materials, the gas sensor exhibits unique selectivity and recovery to NO_2. The three-dimensional structure of SnS_2/rGO material can also show good NO_2 sensitivity, including high sensitivity, excellent selectivity, low detection limit (8.7 ppb), and good recovery [24]. The response of SnS_2/rGO to NO_2 is 4 times that of pure rGO, indicating that the composite material has a significant role in enhancing the gas-sensitivity of rGO. The high sensitivity may be due to the formation of heterostructures and 3D porous structures. These heterojunctions and 3D porous structures promote the adsorption, desorption and charge transfer of NO_2 by providing alternative adsorption sites and charge transport pathways.

In addition, humidity sensors and NH_3 sensors based on SnS_2/rGO are also research hotspots in this field. Dongzhi Zhang et al.[25] prepared a SnS_2/GO humidity sensor with ultra-high response, negligible hysteresis, good repeatability and extremely fast response/recovery characteristics, and its gas sensitivity is better than pure SnS_2 or GO gas sensors. Yifan Huang et al.[26] synthesized a high-sensitivity gas sensor based on SnS_2/rGO for the detection of NH_3 at room temperature. This gas sensor shows excellent sensitivity to ppm-level NH_3 (11% response to 1 ppm). The unique gas sensitivity of SnS_2 makes the composite material more sensitive to NH_3 than pure rGO by 55 times.

5 Conclusion

In summary, the previous article summarized rGO materials, SnS_2 materials, SnS_2/rGO materials and their applications in the field of gas sensors with two-dimensional semiconductor gas sensing materials as the object. Both rGO and SnS_2 materials alone can be used as gas-sensing materials for semiconductor gas sensors, but rGO materials have poor recovery properties, and SnS_2 materials have problems such as large electrical resistance at room temperature. The SnS_2/rGO material not only solves the problem of poor recovery due to the synergy between the materials, but also reduces the resistance of SnS_2. SnS_2/rGO materials have been widely used in the research of gas sensors for small molecule harmful gases (especially NO_2 and NH_3).

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