American Academic Scientific Research Journal for Engineering, Technology, and Sciences
ISSN (Print) 2313-4410, ISSN (Online) 2313-4402
http://asrjetsjournal.org/

Preparation of MoS_2 Microspheres with Different Proportions by Hydrothermal Method and their Gas Sensing Performance

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Abstract

MoS_2 microspheres with three different proportions were prepared by hydrothermal method. The effects of different proportions on the morphology, purity and sensing performance of MoS_2 were studied. The morphology and structure of MoS_2 were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results show that the MoS_2 microspheres with the best morphology and the highest purity can be obtained when the ratio of Mo to S is 1:2. The results of gas sensitivity test show that the optimum working temperature of the three samples is 175°C. When the ratio of Mo to S is 1:2, the sensitivity to 100ppm-500ppm ethanol gas is obviously better than other ratios.

Keywords: MoS_2; Different proportions; Gas sensing performance.

1. Introduction

In recent years, the research on the preparation and application of two-dimensional graphene and its derivatives has led to the exploration of a new class of two-dimensional materials. [1-3] Among them, MoS_2 has become a promising candidate material for constructing gas sensors because of its superior semiconductor properties and high specific surface area. [4-5] The research and application of nano MoS_2 is still the development direction in the future. The micro morphology has a great influence on the gas sensing performance. The authors in [6] noted that molecular adsorbates are well adsorbed at the edge of MoS_2 than on the surface of MoS_2. Therefore, the preparation of nano MoS_2 with clear edge exposure and large specific surface area is beneficial to improve the gas sensing characteristics.

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At present, many preparation methods have been reported, such as micromechanical stripping method, lithium ion intercalation method, template method, hydrothermal method and so on. [7-8] The authors in [9] prepared mesostructured MoS_2 with a rod-shaped morphology by a nanocasting approach. The authors in [10] fabricated the ultrathin two dimensional (2D) lamellar nanofiltration membranes by layer-by-layer stacking MoS_2 nanosheet building blocks. Among them, the hydrothermal method has the advantages of simple operation, low pollution, flexibility and controllability. Nano sensing materials with different morphology can be prepared by hydrothermal method [11-14] .

In this paper, sodium molybdate and thiourea were used as reaction media to prepare MoS_2. MoS_2 microspheres with three different proportions were prepared by hydrothermal method. The ratio of Mo to S is 1:2, 1:1 and 2:1 respectively. The three samples were characterized by XRD and SEM and the gas sensing performance were analyzed. The results show that the MoS_2 microspheres have better morphology, higher purity and better sensing characteristics when the ratio of Mo to S is 1:2.

2. Materials and Methods

2.1. Chemicals

Sodium Molybdate ($Na_2MoO_4{\cdot}2H_2O$) were purchased from Shanghai Macklin Biochemical Co.,Ltd. Thiourea (H_2NCSNH_2) and Citric Acid ($C_6H_8O_7{\cdot}H_2O$) were purchased from Tianjin Fengchuan chemical reagent Technology Co., Ltd. Unless otherwise specified, all materials in the experiment are used directly without further purification.

2.2. Synthesis of MoS_2 microspheres

The MoS_2 microspheres was synthesized by a simple hydrothermal method. Sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$) and thiourea (CH_4N_2S) were mixed and dissolved in 70ml of deionized water. The ratio of Mo to S is 1:2, 1:1 and 2:1 respectively. The samples were labeled MoS_2-1、MoS_2-2 and MoS_2-3 respectively. After stirring to a transparent solution, added 0.46 g citric acid to the above solution. After magnetic stirring for 10min, the uniform solution was transferred to 100 ml stainless steel autoclave with teflon-lined, tightly sealed and maintained at 200 ℃ for 21 hours. After the hydrothermal process, the autoclave automatically cooled to room temperature. Collected the black sediment through centrifuge, washed it with deionized water for 3 times and ethanol for 2 times. Finally, it was dried under vacuum at 60 ℃ for 4 h to obtain black powder.

2.3. Characterization

Scanning electron microscopy (SEM, JEOL JSM-7200F) were used to characterize the samples' surface morphologies and microstructures. X-ray diffraction (XRD, Rigaku D/MAX 2550 diffractometer with Cu Kα radiation: λ =1.5418 Å) was performed to investigate the crystallographic structure of the samples from 10° to 80°.

3. Structural, Surface and Morphological Studies

Morphology is the key factor affecting the gas sensing characteristics of the sensor [15-17]. The microstructure of the MoS_2-2、MoS_2-3 and MoS_2-1 can be observed by SEM. As shown in Figure. 1(a), MoS_2-2 nanosheets agglomerated into microspheres with a diameter of 2μm. The agglomeration phenomenon is so serious that most of the nanosheets edges are almost covered, which will greatly reduce the active sites. Figure. 1(b) shows the micro morphology of MoS_2-3. The microsphere structure has not been formed. Heterogeneous nanosheets and nanostructures can be observed in the Figure. 1(b). Figure. 1(c) shows the micro morphology of MoS_2-1. It can be seen that the microsphere MoS_2 is assembled from two-dimensional nanosheets. The microsphere grow evenly and the edges are exposed clearly. In general, the micro morphologies of the three samples are quite different due to different ratios. Compared with MoS_2-2 and MoS_2-3, the morphology of MoS_2-1 is better.

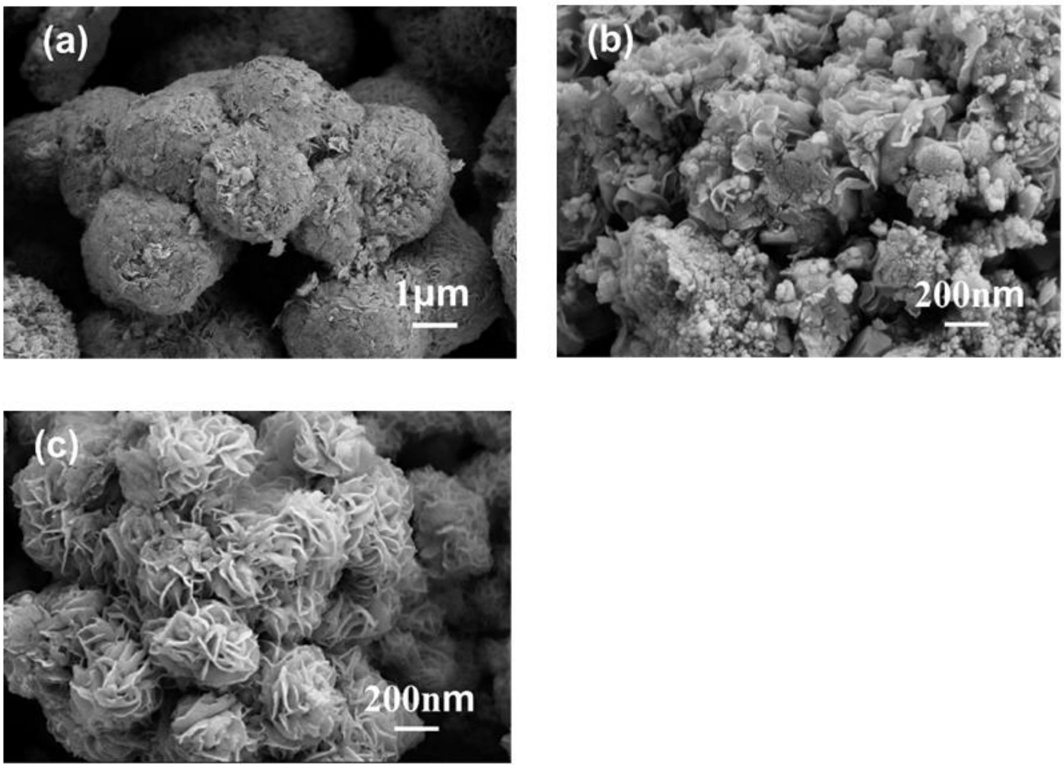

Figure 1: (a) SEM images of MoS_2-2; (b) SEM images of MoS_2-3; (c) SEM images of MoS_2-1.

The crystal structure and phase composition of the MoS_2-1、MoS_2-2 and MoS_2-3 were examined by XRD. As shown in Figure. 2, the diffraction peaks at 2θ = 14.00°、32.22°、35.83°、58.10° are assigned to the (003), (100), (102) and (110) plane of the MoS_2 (JCPDS No.01-074-0932). In the spectrum of MoS_2-2, it can be seen that the corresponding peaks of (003) crystal plane and (102) crystal plane are not prominent enough. In the spectrum of MoS_2-3, the position of the main peak obviously shifted, and the corresponding peak of (110) crystal plane could not be found. Compared with MoS_2-2 and MoS_2-3, the main peak of MoS_2-2 is relatively complete and prominent and the diffraction peak can also correspond to the crystal plane. MoS_2-1 has high purity molybdenum disulfide crystal structure.

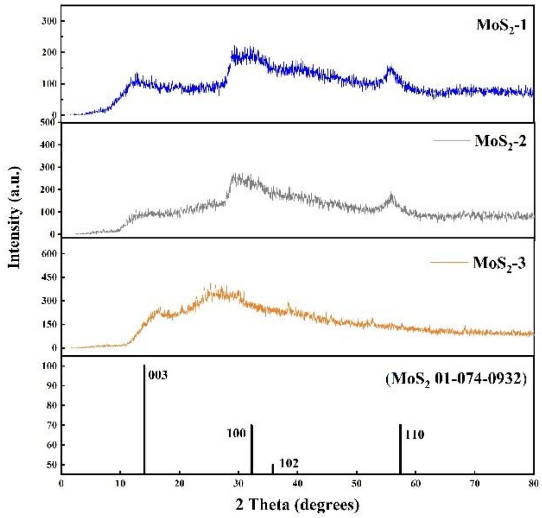

Figure 2: XRD patterns of MoS_2-1、MoS_2-2 and MoS_2-3.

4. Gas-sensing performance

The operating temperature will significantly affect the conductivity and electron mobility of semiconductors, resulting in different responses to gas sensors. [18-20] During the test, 100ppm ethanol was introduced into MoS_2-1、MoS_2-2 and MoS_2-3 at the same time. The resistance change of the acquisition system was observed by changing the temperature. The relationship curve between working temperature and sensitivity is shown in Figure. 3. The results show that the optimum operating temperature of the three samples is 175℃. The sensitivity of MoS_2-1 is about 3.25, while the sensitivity of MoS_2-2 and MoS_2-3 is 1.17 and 1.16. Different proportions have no effect on the optimum working temperature, but have a great effect on the sensitivity.

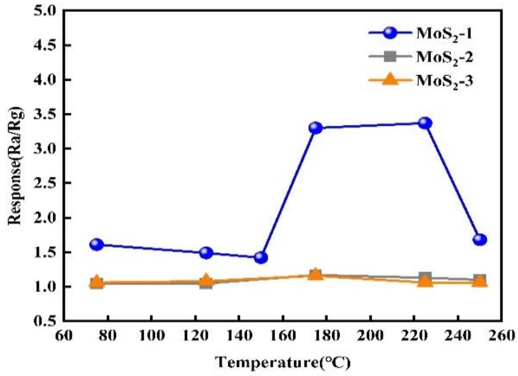

Figure 3: Response of MoS_2-1、MoS_2-2 and MoS_2-3 towards 100 ppm ethanol at different temperature.

In order to further explore the improvement of sensitivity, the sensitivity of MoS_2-1、MoS_2-2 and MoS_2-3 exposed to different ethanol concentrations were tested at the optimum working temperature of 175℃. As shown in Figure. 4, the responses of MoS_2-1 were significantly higher than that of MoS_2-2 and MoS_2-3 with the increase of ethanol concentration from 100 ppm to 500 ppm ethanol.

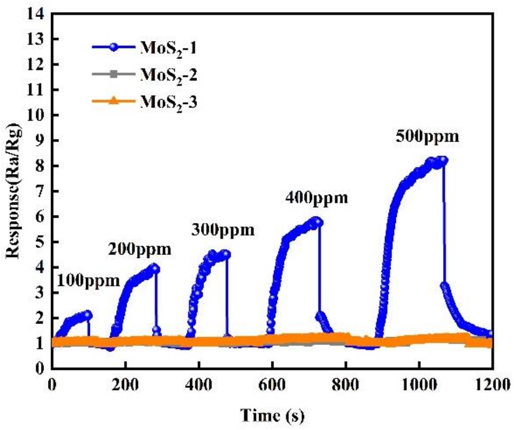

Figure 4: The response of MoS_2-1、MoS_2-2 and MoS_2-3 to 100ppm-500ppm ethanol at 175 ℃.

There are abundant active sites on the surface of MoS_2. When the measured gas is introduced, it will adsorb gas molecules to produce charge transfer, resulting in the change of resistance. The higher sensitivity of MoS_2-1 may be due to its better morphology. The edge of MoS_2-1 is clearly exposed, which provides more active sites for the adsorbed gas. Compared with MoS_2-2 and MoS_2-3, MoS_2-1 can adsorb more gas molecules, and the adsorbed gas molecules will generate charge transfer with MoS_2-1. With the increase of carrier mobility, the sensitivity will also increase [21-23].

5. Conclusions

In conclusion, three different proportions of MoS_2 microspheres were prepared by hydrothermal method, which were recorded as MoS_2-1、MoS_2-2 and MoS_2-3. The morphology and structure were characterized. The results show that different proportions have a great influence on the purity and morphology of the final samples. When the ratio of molybdenum to sulfur is 1:2, MoS_2 with the best morphology and the highest purity can be obtained. The gas sensitivity test results show that different ratios have no effect on the optimal working temperature. The optimal working temperature of the three samples is 175 ℃, but the sensitivity of MoS_2-1 to 100ppm-500ppm ethanol gas is significantly higher than that of MoS_2-2 and MoS_2-3. This may be because the surface of MoS_2-1 has more active sites that can adsorb ethanol gas.

Acknowledgements

Thanks to Professor Haiming Zhang for his guidance during the research process.

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