Notice

DESCRIPTION CN118255392A

A three-dimensional molybdenum disulfide nanoflower composite material, its preparation method and application

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一种三维二硫化钼纳米花复合材料及其制备方法与应用

[0001]

Technical Field

技术领域

[n0001]

This invention belongs to the field of gas-sensitive materials technology, and particularly relates to a three-dimensional molybdenum disulfide nanoflower composite material, its preparation method and application.

本发明属于气敏材料技术领域，尤其涉及一种三维二硫化钼纳米花复合材料及其制备方法与应用。

[0003]

Background Technology

背景技术

[n0002]

NO and NER1 gases are one of the causes of acid rain and ozone. They can trigger various environmental effects such as surface water acidification and photochemical smog, and can also have adverse effects on human health.

NO₂气体是酸雨和臭氧的成因之一，可以引发地表水的酸化、光化学烟雾等多种环境效应，对人体健康也会造成不良影响。

Therefore, comprehensive monitoring of NO and NER2 emissions within the region is of great significance for monitoring air pollution and air quality.

因此，全面监测区域内NO₂气体的排放情况对监测大气污染和空气质量具有重要意义。

Resistive gas sensors are one of the commonly used methods for detecting NO₂ gas. The main principle is that NO₂ in the gas to be measured will capture electrons from the surface of the gas-sensitive material, causing a change in the carrier concentration on the surface, which in turn causes a change in resistance.

电阻型气敏传感器是NO₂气体检测的常用方法之一，其主要原理是待测气体中的NO₂会夺取气敏材料表面的电子使其表面的载流子浓度发生变化，进而引起电阻变化。

When the gas-sensitive element is exposed to a NO₂ gas environment, the composite material will adsorb and desorb NO₂, which will cause the resistance value of the gas-sensitive element to change. Effective monitoring of NO₂ concentration can be achieved by monitoring this resistance change. Two-dimensional nanomaterials have attracted much attention in fields such as flexible electronic devices, batteries, and sensors due to their abundant active sites, high specific surface area, and unique physicochemical properties. Using two-dimensional nanomaterials to prepare gas-sensitive materials for gas sensors is an important approach to developing high-performance sensors.

当气敏元件暴露于NO₂气体环境中时，复合材料会与NO₂发生吸附、脱附，这一过程会导致气敏元件的电阻值发生变化。 通过监测这种电阻变化实现对NO₂浓度的有效监测。 二维纳米材料因为具有丰富的活性位点、高比表面积、独特的物理化学性质，在柔性电子器件、电池、传感器等领域备受关注。 利用二维纳米材料制备气敏传感器的气敏材料是开发高性能传感器的重要途径。

[n0003]

Molybdenum disulfide nanosheets are a typical transition metal dichalcogenide compound. They have high adsorption strength for NO₂ gas and a high surface area ratio, and are considered to be a gas-sensitive material with great potential.

二硫化钼纳米片是一种典型的过渡金属二硫族化合物，其表面对NO₂气体吸附强度高、拥有高表面积比，被认为是拥有巨大潜力的气敏传感材料。

However, the low conductivity and strong Mo-S bonds limit the development of molybdenum disulfide as a gas-sensitive material. Two-dimensional molybdenum disulfide nanosheets as gas-sensitive materials suffer from slow response speed, slow recovery speed, and poor repeatability. Molybdenum disulfide nanosheets, as gas-sensitive materials, can have their properties improved through modification and functionalization strategies such as element doping, defect engineering, surface functionalization, and the formation of heterostructures. However, these modification and functionalization methods usually complicate the synthesis process of gas-sensitive materials and increase the cost accordingly.

但是低导电性、强Mo-S键限制了二硫化钼作为气敏材料的发展，二维二硫化钼纳米片作为气敏材料存在响应速度慢、恢复速度慢，重复性差的问题。 作为气敏材料的二硫化钼纳米片，其性能能够通过元素掺杂、缺陷工程、表面官能化以及形成异质结构等改性和功能化策略得到提升，然而，这些改性和功能化方法通常也会使气敏材料的合成工艺变得复杂，且成本相应增高。

[0006]

Summary of the Invention

发明内容

[n0004]

To address the problems of slow response speed, low sensitivity, and poor repeatability of existing two-dimensional molybdenum disulfide nanosheets as gas-sensitive materials, this invention provides a three-dimensional molybdenum disulfide nanoflower composite material, its preparation method, and its application.

为解决现有二维二硫化钼纳米片作为气敏材料存在响应速度慢、灵敏度低及重复性差的问题，本发明提供了一种三维二硫化钼纳米花复合材料及其制备方法与应用。

[n0005]

The technical solution of the present invention:

本发明的技术方案：

[0009]

A three-dimensional molybdenum disulfide nanoflower composite material, wherein the material is a nanoscale three-dimensional flower structure, the three-dimensional flower structure is composed of several layered structures, the diameter of the overall three-dimensional flower structure is 150 nm to 200 nm, and the specific surface area is 20 mNER9 / g to 60 mNER10 / g.

一种三维二硫化钼纳米花复合材料，所述材料为纳米级三维花状结构，所述三维花状结构由若干片层结构组成，整体三维花状结构的直径为150 nm~200 nm，比表面积为20m²/g~60 m²/g。

[n0006]

A method for preparing a three-dimensional molybdenum disulfide nanoflower composite material includes the following steps:

一种三维二硫化钼纳米花复合材料的制备方法，包括如下步骤：

[0011]

Step 1: Preparation of molybdenum disulfide precursor:

步骤一、制备二硫化钼前驱体：

[0012]

Sodium molybdate dihydrate and L-cysteine were dissolved in deionized water and stirred to obtain mixed solution I. Mixed solution I was placed in an autoclave and heated. After cooling, mixed solution II was obtained. Mixed solution II was centrifuged to collect the precipitate. After washing and drying, molybdenum disulfide precursor was obtained.

将二水钼酸钠和L-半胱氨酸溶于去离子水，搅拌后得到混合溶液Ⅰ，将所述混合溶液Ⅰ置于高压釜中加热处理，冷却后得到混合溶液II，将所述混合溶液II离心收集沉淀，清洗、干燥后得到二硫化钼前驱体；

[0013]

Step 2: Preparation of three-dimensional molybdenum disulfide nanoflower composite material:

步骤二、制备三维二硫化钼纳米花复合材料：

[0014]

The molybdenum disulfide precursor obtained in step one and selenium powder were placed in a tube furnace and heated in an atmosphere of mixed hydrogen and argon gas. The product was collected to obtain the Se-doped three-dimensional molybdenum disulfide nanoflower composite material.

将步骤一所得二硫化钼前驱体与硒粉置于管式炉中，在氢气与氩气混合气体的气氛下加热处理，收集产物即得到Se掺杂的三维二硫化钼纳米花复合材料。

[n0007]

Furthermore, in step one, the mass ratio of sodium molybdate dihydrate to L-cysteine is 1~10: 1; the total mass of sodium molybdate dihydrate and L-cysteine to the mass-volume ratio of deionized water is 1.0 g~2.5 g: 35 mL~65 mL; and the stirring time is 30 min~60 min.

进一步的，步骤一所述二水钼酸钠和L-半胱氨酸的质量比为1~10:1；二水钼酸钠和L-半胱氨酸的总质量与去离子水的质量体积比为1.0 g~2.5 g：35 mL~65 mL；所述搅拌的搅拌时间为30 min~60 min。

[n0008]

Furthermore, the heating treatment described in step one involves heating a stainless steel autoclave in a water bath at 160 °C to 220 °C for 18 h to 24 h.

进一步的，步骤一所述加热处理为160 °C~220 °C条件下水浴加热不锈钢高压釜18 h~24 h。

[n0009]

Furthermore, the centrifugation conditions in step one are 5000 r/min to 8000 r/min for 5 min to 15 min; the washing involves washing the precipitate with deionized water and anhydrous ethanol successively and then centrifuging to collect the precipitate; the drying involves drying at 60 °C to 90 °C for 12 h to 24 h.

进一步的，步骤一所述离心的条件为5000 r/min~8000 r/min离心5 min~15 min；所述清洗为先后用去离子水和无水乙醇清洗沉淀并离心收集沉淀；所述干燥为60 °C~90°C下干燥12 h~24 h。

[n0010]

Furthermore, in step two, the mass ratio of the molybdenum disulfide precursor to selenium powder is 1:1 to 10, and the volume percentage of hydrogen in the hydrogen and argon mixture is 5% to 8%.

进一步的，步骤二所述二硫化钼前驱体与硒粉的质量比为1:1~10，所述氢气与氩气混合气体中氢气的体积百分含量为5%~8%。

[n0011]

Furthermore, the heating treatment in step two is carried out at a constant temperature of 300 °C to 600 °C for 0.5 h to 3.5 h.

进一步的，步骤二所述加热处理为300 °C~600 °C恒温0.5 h~3.5 h。

[n0012]

Application of a three-dimensional molybdenum disulfide nanoflower composite material in NO_NER11 gas detection.

一种三维二硫化钼纳米花复合材料在NO₂气体检测中的应用。

[n0013]

Furthermore, the application is to prepare a gas-sensitive element using a three-dimensional molybdenum disulfide nanoflower composite material. The preparation method of the gas-sensitive element is to ultrasonically disperse the molybdenum disulfide nanoflower composite material according to claim 1 in 1 to 10 times the volume of ethanol solution to obtain a uniformly dispersed suspension. Then, the suspension is coated on an Au interdigitated electrode that has been cleaned with ethanol and dried at 50 °C to 90 °C for 2 h to 5 h to obtain the gas-sensitive element.

进一步的，所述应用为以三维二硫化钼纳米花复合材料制备气敏元件，所述气敏元件的制备方法为将权利要求1所述的二硫化钼纳米花复合材料超声分散于1倍~10倍体积的乙醇溶液中，得到分散均匀的

悬浊液，然后将悬浊液涂覆在乙醇清洗过的Au叉指电极上，并置于50 ℃~90 ℃下干燥2 h~5 h，得到气敏元件。

[n0014]

Furthermore, the application involves placing the gas-sensitive element prepared from the three-dimensional molybdenum disulfide nanoflower composite material as described in claim 1 at 15 ℃~35 ℃ and 20%~80% humidity to detect the NO₂ gas concentration in the gas to be tested.

进一步的，所述应用是将由权利要求1所述的三维二硫化钼纳米花复合材料制备的气敏元件置于15 ℃~35 ℃、20%~80%湿度条件下对待测气体中NO₂气体浓度进行检测。

[n0015]

The beneficial effects of this invention are:

本发明的有益效果：

[0024]

This invention uses Se as an anionic dopant to prepare three-dimensional molybdenum disulfide nanoflower composite materials, achieving control over the morphology and interplanar spacing of the composite material, thereby forming channels that are more conducive to gas adsorption and desorption, making it easier for NO₂ gas to enter the interior of the composite material and improving the adsorption reversibility of the composite material.

本发明以Se作为阴离子掺杂剂制备三维二硫化钼纳米花复合材料，实现了对复合材料形貌和晶面间距的控制，以此形成更利于气体吸脱附的通道，使NO₂气体更容易进入复合材料内部，提高了复合材料的吸附可逆性。

During the reaction, Se doping causes structural distortion, generating abundant sulfur defects that provide more active sites, increasing the contact probability between the composite material and NO₂ molecules, improving the gas sensitivity of the composite material and its selectivity to NO₂ molecules, and further shortening the response time.

在反应过程中Se掺杂引起结构畸变，产生丰富的硫缺陷提供了更多的活性位点，增加了复合材料与NO₂分子之间的接触几率，提高了复合材料的气体敏感性和对NO₂分子的选择性，进一步缩短了响应时间。

[n0016]

A gas-sensitive element was prepared using the three-dimensional molybdenum disulfide nanoflower composite material provided by the present invention, and it was used to detect the concentration of NO₂ gas in the test gas at room temperature. The sensitivity of NO₂ gas with a concentration of 100 ppm reached 40.82, and the response time was 5.8 seconds.

采用本发明提供的三维二硫化钼纳米花复合材料制备气敏元件，并在室温下将其用于检测待测气体中NO₂气体浓度，对浓度为100 ppm 的NO₂气体灵敏度达40.82，响应时间为5.8秒。

As the NO₂ concentration decreases, the response value also decreases accordingly. The lowest detection limit is 0.1 ppm, corresponding to a response value of 1.2 and a response time of 14.7 seconds.

当NO₂浓度下降时，响应值亦随之递减，最低检测限为0.1ppm，对应的响应值为1.2，响应时间为14.7秒。

After multiple NO_NER19 adsorption-desorption tests, the three-dimensional molybdenum disulfide nanoflower composite material still showed excellent repeatability, indicating that the composite material has high sensitivity and good repeatability, which can reduce the cost of gas sensors.

经过多次NO₂吸附脱附试验后，三维二硫化钼纳米花复合材料的重复性仍表现出色，说明该复合材料灵敏度高、重复性好，能够降低气敏传感器的成本。

[n0017]

The method for preparing three-dimensional molybdenum disulfide nanoflower composite materials provided by this invention has the characteristics of simple process, low cost and environmentally friendly and non-toxic production process. The prepared three-dimensional molybdenum disulfide nanoflower composite materials can significantly improve the performance of gas sensors and have important application prospects in the field of NO and NER2O gas detection.

本发明提供的三维二硫化钼纳米花复合材料制备方法具有工艺简单、成本低廉、制作过程环保无毒的特点，所制备的三维二硫化钼纳米花复合材料能够显著提升气敏传感器的性能，在NO₂气体检测领域具有重要应用前景。

[0027]

Attached Figure Description

附图说明

[n0018]

Figure 1 is a scanning electron microscope image of the three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 1;

图1为实施例一制备的三维二硫化钼纳米花复合材料的扫描电镜图；

[0029]

Figure 2 is an X-ray diffraction pattern of the three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 1;

图2为实施例一制备的三维二硫化钼纳米花复合材料的X射线衍射图；

[0030]

Figure 3 is a sensitivity curve of the gas-sensitive element prepared in Example 7 for detecting NO_2;

图3为实施例七制备的气敏元件检测NO_2的灵敏度曲线图；

[0031]

Figure 4 shows the gas selectivity test results of the gas-sensitive element prepared in Example 7 at room temperature;

图4为实施例七制备的气敏元件在室温下的气体选择性测试图；

[0032]

Figure 5 is a sensitivity curve of the gas-sensitive element prepared in Example 8 for detecting NO₂;

图5为实施例八制备的气敏元件检测NO₂的灵敏度曲线图；

[0033]

Figure 6 shows the repeatability test results of the gas-sensitive element prepared in Example 8 at room temperature for 100 ppm NO₂.

图6为实施例八制备的气敏元件在室温下对100 ppmNO₂的重复性测试结果图。

[0034]

Detailed Implementation

具体实施方式

[n0019]

The technical solution of the present invention will be further described below with reference to the embodiments, but it is not limited thereto. Any modifications or equivalent substitutions to the technical solution of the present invention without departing from the spirit and scope of the technical solution of the present invention should be covered within the protection scope of the present invention.

下面结合实施例对本发明的技术方案做进一步的说明，但并不局限于此，凡是对本发明技术方案进行修改或者等同替换，而不脱离本发明技术方案的精神和范围，均应涵盖在本发明的保护范围中。

Unless otherwise specified, the process equipment or apparatus used in the following embodiments are all conventional equipment or apparatus in the art. Unless otherwise specified, the raw materials used in the embodiments of the present invention are all commercially available. Unless otherwise specified, the technical means used in the embodiments of the present invention are all conventional means well known to those skilled in the art.

下列实施例中未具体注明的工艺设备或装置均采用本领域内的常规设备或装置，若未特别指明，本发明实施例中所用的原料等均可市售获得；若未具体指明，本发明实施例中所用的技术手段均为本领域技术人员所熟知的常规手段。

[n0020]

Example 1

实施例一

[0037]

This embodiment provides a method for preparing a three-dimensional molybdenum disulfide nanoflower composite material, including the following steps:

本实施例提供了一种三维二硫化钼纳米花复合材料的制备方法，包括如下步骤：

[0038]

Step 1: Preparation of molybdenum disulfide precursor:

步骤一、制备二硫化钼前驱体：

[0039]

1 g of sodium molybdate dihydrate and 0.2 g of L-cysteine were dissolved in 50 mL of deionized water and stirred for 40 min to obtain mixed solution I. Mixed solution I was placed in a stainless steel autoclave and heated in a water bath at 200 °C for 20 h. Then the stainless steel autoclave was cooled to room temperature to obtain mixed solution II. Mixed solution II was centrifuged at 6000 r/min for 10 min to collect the precipitate. The precipitate was washed with deionized water and anhydrous ethanol, and centrifuged at 6000 r/min for 10 min to collect the precipitate. The washed precipitate was placed in a vacuum drying oven and dried at 65 °C for 15 h to obtain the molybdenum disulfide precursor.

将1 g二水钼酸钠和0.2 g L-半胱氨酸溶于50 mL去离子水，搅拌40 min后得到混合溶液Ⅰ，将所得混合溶液Ⅰ置于不锈钢高压釜中，在200 °C条件下水浴加热不锈钢高压釜20 h，然后将不锈钢高压釜冷却到室温，得到混合溶液II；所得混合溶液II以6000 r/min离心10 min收集沉淀，先后用去离子水和无水乙醇清洗离心所得沉淀，以6000 r/min离心10min收集沉淀，将清洗后的沉淀置于真空干燥箱中65 °C下干燥15 h得到二硫化钼前驱体;

[0040]

Step 2: Preparation of three-dimensional molybdenum disulfide nanoflower composite material:

步骤二、制备三维二硫化钼纳米花复合材料：

[0041]

The 0.5 g molybdenum disulfide precursor obtained in step one and 1.5 g selenium powder were placed in a tube furnace and kept at 500 °C for 3 h in an atmosphere of hydrogen and argon mixed gas with a hydrogen volume percentage of 6%. The product was then collected to obtain Se-doped three-dimensional molybdenum disulfide nanoflower composite material.

将步骤一所得0.5 g 二硫化钼前驱体与1.5 g硒粉置于管式炉中，在氢气的体积百分含量为6%的氢气与氩气混合气体的气氛下，500 °C 恒温3 h后收集产物，得到Se掺杂的三维二硫化钼纳米花复合材料。

[n0021]

Figure 1 is a scanning electron microscope image of the three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 1. It can be clearly seen from the figure that the three-dimensional flower-like structure is composed of several lamellar structures, with abundant lamellar structures. The diameter of the overall three-dimensional flower-like structure is 150 nm to 200 nm, the interlayer spacing is 0.5 nm to 0.8 nm, and the specific surface area is 20 mNER24 g to 60 mNER25 g.

图1为实施例一制备的三维二硫化钼纳米花复合材料的扫描电镜图；从图中可以清晰地看到三维花状结构由若干片层结构组成，具有丰富的片层结构，整体三维花状结构的直径为150 nm~200 nm，层间距为0.5 nm~0.8 nm, 比表面积为20 m²/g~60 m²/g。

Using Se as an anionic dopant to prepare three-dimensional molybdenum disulfide nanoflower composites enabled control over the morphology and interplanar spacing of the composite material, thereby forming channels that are more conducive to gas adsorption and desorption, making it easier for NO₂ gas to enter the interior of the composite material and improving the adsorption reversibility of the composite material.

Se作为阴离子掺杂剂制备三维二硫化钼纳米花复合材料实现了对复合材料形貌和晶面间距的控制，以此形成更利于气体吸脱附的通道，使NO₂气体更容易进入复合材料内部，提高了复合材料的吸附可逆性。

[n0022]

Figure 2 shows the X-ray diffraction pattern of the three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 1. As can be seen from the figure, the diffraction peaks of the compound, i.e., the 2θ angle values of 14.4°, 39.5°, 49.8°, 60.1°, and 70.1°, are consistent with the (002), (103), (105), (008), and (108) crystal planes of the standard card of molybdenum disulfide, respectively, confirming the successful synthesis of Se-doped molybdenum disulfide composite material.

图2为实施例一制备的三维二硫化钼纳米花复合材料的X射线衍射图；从图中可以看出，化合物的衍射峰即2θ角值为14.4°、39.5°、49.8°、60.1°、70.1°分别与二硫化钼的标准卡片的(002), (103), (105), (008), (108) 晶面相吻合，证实成功合成Se掺杂二硫化钼复合材料。

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The 2θ angle value of 33.1° is offset from the (100) crystal plane of the standard card of molybdenum disulfide, which is due to Se doping.

θ角的值为33.1° 处与二硫化钼的标准卡片的(100)晶面相比有所偏移，这是由于Se掺杂引起的。

During the reaction, Se doping causes structural distortion, generating abundant sulfur defects that provide more active sites, increasing the contact probability between the composite material and NO₂ molecules, improving the gas sensitivity of the composite material and its selectivity to NO₂ molecules, and further shortening the response time.

在反应过程中Se掺杂引起结构畸变，产生丰富的硫缺陷提供了更多的活性位点，增加了复合材料与NO₂分子之间的接触几率，提高了复合材料的气体敏感性和对NO₂分子的选择性，进一步缩短了响应时间。

[n0023]

Example 2

实施例二

[0045]

This embodiment provides a method for preparing a three-dimensional molybdenum disulfide nanoflower composite material, including the following steps:

本实施例提供了一种三维二硫化钼纳米花复合材料的制备方法，包括如下步骤：

[0046]

Step 1: Preparation of molybdenum disulfide precursor:

步骤一、制备二硫化钼前驱体：

[0047]

1 g of sodium molybdate dihydrate and 0.2 g of L-cysteine were dissolved in 50 mL of deionized water and stirred for 40 min to obtain mixed solution I. Mixed solution I was placed in a stainless steel autoclave and heated in a water bath at 210 °C for 20 h. Then the stainless steel autoclave was cooled to room temperature to obtain mixed solution II. Mixed solution II was centrifuged at 6000 r/min for 10 min to collect the precipitate. The precipitate was washed with deionized water and anhydrous ethanol, and centrifuged at 6000 r/min for 10 min to collect the precipitate. The washed precipitate was placed in a vacuum drying oven and dried at 65 °C for 15 h to obtain the molybdenum disulfide precursor.

将1 g二水钼酸钠和0.2 g L-半胱氨酸溶于50 mL去离子水，搅拌40 min后得到混合溶液Ⅰ，将所得混合溶液Ⅰ置于不锈钢高压釜中，在210 °C条件下水浴加热不锈钢高压釜20 h，然后将不锈钢高压釜冷却到室温，得到混合溶液Ⅱ；所得混合溶液Ⅱ以6000 r/min离心10 min收集沉淀，先后用去离子水和无水乙醇清洗离心所得沉淀，以6000 r/min离心10min收集沉淀，将清洗后的沉淀置于真空干燥箱中65 °C下干燥15 h得到二硫化钼前驱体；

[0048]

Step 2: Preparation of three-dimensional molybdenum disulfide nanoflower composite material:

步骤二、制备三维二硫化钼纳米花复合材料：

[0049]

The 0.5 g molybdenum disulfide precursor obtained in step one and 3 g selenium powder were placed in a tube furnace and kept at 550 °C for 2 h in an atmosphere of hydrogen and argon mixed gas with a hydrogen volume percentage of 7%. The product was then collected to obtain Se-doped three-dimensional molybdenum disulfide nanoflower composite material.

将步骤一所得0.5 g 二硫化钼前驱体与3 g硒粉置于管式炉中，在氢气的体积百分含量为7%的氢气与氩气混合气体的气氛下，550 °C 恒温2 h后收集产物，得到Se掺杂的三维二硫化钼纳米花复合材料。

[n0024]

Example 3

实施例三

[0051]

This embodiment provides a method for preparing a three-dimensional molybdenum disulfide nanoflower composite material, including the following steps:

本实施例提供了一种三维二硫化钼纳米花复合材料的制备方法，包括如下步骤：

[0052]

Step 1: Preparation of molybdenum disulfide precursor:

步骤一、制备二硫化钼前驱体：

[0053]

1 g of sodium molybdate dihydrate and 1.0 g of L-cysteine were dissolved in 65 mL of deionized water and stirred for 60 min to obtain mixed solution I. Mixed solution I was placed in a stainless steel autoclave and heated in a water bath at 180 °C for 24 h. The autoclave was then cooled to room temperature to obtain mixed solution II. Mixed solution II was centrifuged at 5000 r/min for 15 min to collect the precipitate. The precipitate was washed

with deionized water and anhydrous ethanol, and centrifuged at 5000 r/min for 15 min to collect the precipitate. The washed precipitate was placed in a vacuum drying oven and dried at 70 °C for 12 h to obtain the molybdenum disulfide precursor.

将1 g二水钼酸钠和1.0 g L-半胱氨酸溶于65 mL去离子水，搅拌60 min后得到混合溶液Ⅰ，将所得混合溶液Ⅰ置于不锈钢高压釜中，在180 °C条件下水浴加热不锈钢高压釜24 h，然后将不锈钢高压釜冷却到室温，得到混合溶液II；所得混合溶液II以5000 r/min离心15 min收集沉淀，先后用去离子水和无水乙醇清洗离心所得沉淀，以5000 r/min离心15min收集沉淀，将清洗后的沉淀置于真空干燥箱中70 °C下干燥12 h得到二硫化钼前驱体；

[0054]

Step 2: Preparation of three-dimensional molybdenum disulfide nanoflower composite material:

步骤二、制备三维二硫化钼纳米花复合材料：

[0055]

The 0.5 g molybdenum disulfide precursor obtained in step one and 0.5 g selenium powder were placed in a tube furnace and kept at 600 °C for 3.5 h in an atmosphere of hydrogen and argon mixed gas with a hydrogen volume percentage of 5%. The product was then collected to obtain Se-doped three-dimensional molybdenum disulfide nanoflower composite material.

将步骤一所得0.5 g 二硫化钼前驱体与0.5 g硒粉置于管式炉中，在氢气的体积百分含量为5%的氢气与氩气混合气体的气氛下，600 °C 恒温3.5 h后收集产物，得到Se掺杂的三维二硫化钼纳米花复合材料。

[n0025]

Example 4

实施例四

[0057]

This embodiment provides a method for preparing a three-dimensional molybdenum disulfide nanoflower composite material, including the following steps:

本实施例提供了一种三维二硫化钼纳米花复合材料的制备方法，包括如下步骤：

[0058]

Step 1: Preparation of molybdenum disulfide precursor:

步骤一、制备二硫化钼前驱体：

[0059]

1 g of sodium molybdate dihydrate and 0.3 g of L-cysteine were dissolved in 60 mL of deionized water and stirred for 50 min to obtain mixed solution I. Mixed solution I was placed in a stainless steel autoclave and heated in a water bath at 190 °C for 22 h. The autoclave was then cooled to room temperature to obtain mixed solution II. Mixed solution II was centrifuged at 5000 r/min for 15 min to collect the precipitate. The precipitate was washed with deionized water and anhydrous ethanol, and then centrifuged at 7000 r/min for 15 min to collect the precipitate. The washed precipitate was placed in a vacuum drying oven and dried at 80 °C for 18 h to obtain the molybdenum disulfide precursor.

将1 g二水钼酸钠和0.3 g L-半胱氨酸溶于60 mL去离子水，搅拌50 min后得到混合溶液Ⅰ，将所得混合溶液Ⅰ置于不锈钢高压釜中，在190 °C条件下水浴加热不锈钢高压釜22 h，然后将不锈钢高压釜冷却到室温，得到混合溶液II；所得混合溶液II以5000 r/min离心15 min收集沉淀，先后用去离子水和无水乙醇清洗离心所得沉淀，以7000 r/min离心15min收集沉淀，将清洗后的沉淀置于真空干燥箱中80 °C下干燥18 h得到二硫化钼前驱体；

[0060]

Step 2: Preparation of three-dimensional molybdenum disulfide nanoflower composite material:

步骤二、制备三维二硫化钼纳米花复合材料：

[0061]

The 0.5 g molybdenum disulfide precursor obtained in step one and 2.5 g selenium powder were placed in a tube furnace and kept at 550 °C for 3 h in an atmosphere of hydrogen and argon mixed gas with a hydrogen volume percentage of 6%. The product was then collected to obtain Se-doped three-dimensional molybdenum disulfide nanoflower composite material.

将步骤一所得0.5 g 二硫化钼前驱体与2.5 g硒粉置于管式炉中，在氢气的体积百分含量为6%的氢气与氩气混合气体的气氛下，550 °C 恒温3 h后收集产物，得到Se掺杂的三维二硫化钼纳米花复合材料。

[n0026]

Example 5

实施例五

[0063]

This embodiment provides a method for preparing a three-dimensional molybdenum disulfide nanoflower composite material, including the following steps:

本实施例提供了一种三维二硫化钼纳米花复合材料的制备方法，包括如下步骤：

[0064]

Step 1: Preparation of molybdenum disulfide precursor:

步骤一、制备二硫化钼前驱体：

[0065]

1 g of sodium molybdate dihydrate and 0.15 g of L-cysteine were dissolved in 40 mL of deionized water and stirred for 40 min to obtain mixed solution I. Mixed solution I was placed in a stainless steel autoclave and heated in a water bath at 220 °C for 18 h. The autoclave was then cooled to room temperature to obtain mixed solution II. Mixed solution II was centrifuged at 8000 r/min for 5 min to collect the precipitate. The precipitate was washed with

deionized water and anhydrous ethanol, and then dried in a vacuum drying oven at 70 °C for 20 h to obtain the molybdenum disulfide precursor.

将1 g二水钼酸钠和0.15 g L-半胱氨酸溶于40 mL去离子水，搅拌40 min后得到混合溶液Ⅰ，将所得混合溶液Ⅰ置于不锈钢高压釜中，在220 °C条件下水浴加热不锈钢高压釜18 h，然后将不锈钢高压釜冷却到室温，得到混合溶液Ⅱ；所得混合溶液Ⅱ以8000 r/min离心5 min收集沉淀，先后用去离子水和无水乙醇清洗离心所得沉淀，将清洗后的沉淀置于真空干燥箱中70 °C下干燥20 h得到二硫化钼前驱体；

[0066]

Step 2: Preparation of three-dimensional molybdenum disulfide nanoflower composite material:

步骤二、制备三维二硫化钼纳米花复合材料：

[0067]

The 0.5 g molybdenum disulfide precursor obtained in step one and 4 g selenium powder were placed in a tube furnace and kept at 500 °C for 2 h in an atmosphere of hydrogen and argon mixed gas with a hydrogen volume percentage of 7%. The product was then collected to obtain Se-doped three-dimensional molybdenum disulfide nanoflower composite material.

将步骤一所得0.5 g 二硫化钼前驱体与4 g硒粉置于管式炉中，在氢气的体积百分含量为7%的氢气与氩气混合气体的气氛下，500 °C 恒温2 h后收集产物，得到Se掺杂的三维二硫化钼纳米花复合材料。

[n0027]

Example 6

实施例六

[0069]

This embodiment provides a method for preparing a three-dimensional molybdenum disulfide nanoflower composite material, including the following steps:

本实施例提供了一种三维二硫化钼纳米花复合材料的制备方法，包括如下步骤：

[0070]

Step 1: Preparation of molybdenum disulfide precursor:

步骤一、制备二硫化钼前驱体：

[0071]

1 g of sodium molybdate dihydrate and 0.1 g of L-cysteine were dissolved in 35 mL of deionized water and stirred for 30 min to obtain mixed solution I. Mixed solution I was placed in a stainless steel autoclave and heated in a water bath at 170 °C for 22 h. The autoclave was then cooled to room temperature to obtain mixed solution II. Mixed solution II was centrifuged at 8000 r/min for 5 min to collect the precipitate. The precipitate was washed with deionized water and anhydrous ethanol, and centrifuged at 8000 r/min for 5 min to collect the precipitate. The washed precipitate was placed in a vacuum drying oven and dried at 60 °C for 24 h to obtain the molybdenum disulfide precursor.

将1 g二水钼酸钠和0.1 g L-半胱氨酸溶于35 mL去离子水，搅拌30 min后得到混合溶液Ⅰ，将所得混合溶液Ⅰ置于不锈钢高压釜中，在170 °C条件下水浴加热不锈钢高压釜22 h，然后将不锈钢高压釜冷却到室温，得到混合溶液II；所得混合溶液II以8000 r/min离心5 min收集沉淀，先后用去离子水和无水乙醇清洗离心所得沉淀，以8000 r/min离心5min收集沉淀，将清洗后的沉淀置于真空干燥箱中60 °C下干燥24 h得到二硫化钼前驱体；

[0072]

Step 2: Preparation of three-dimensional molybdenum disulfide nanoflower composite material:

步骤二、制备三维二硫化钼纳米花复合材料：

[0073]

The 0.5 g molybdenum disulfide precursor obtained in step one and 5 g selenium powder were placed in a tube furnace and kept at 600 °C for 0.5 h in an atmosphere of hydrogen and argon mixed gas with a hydrogen volume percentage of 8%. The product was then collected to obtain Se-doped three-dimensional molybdenum disulfide nanoflower composite material.

将步骤一所得0.5 g 二硫化钼前驱体与5 g硒粉置于管式炉中，在氢气的体积百分含量为8%的氢气与氩气混合气体的气氛下，600 °C 恒温0.5 h后收集产物，得到Se掺杂的三维二硫化钼纳米花复合材料。

[n0028]

Example 7

实施例七

[0075]

This embodiment provides a gas-sensitive element made from a three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 1 as a gas-sensitive material.

本实施例提供了一种由实施例一制备的三维二硫化钼纳米花复合材料作为气敏材料制作的气敏元件。

[n0029]

The specific preparation method of the gas-sensitive element in this embodiment is as follows:

本实施例气敏元件的具体制备方法为：

[0077]

The three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 1 was ultrasonically dispersed in 5 times its volume of anhydrous ethanol solution to obtain a uniformly dispersed suspension. The suspension was then spin-coated onto an Au interdigitated electrode that had been cleaned with ethanol and dried at 60 °C for 4 h to obtain a gas-sensitive element.

将实施例一制备的三维二硫化钼纳米花复合材料超声分散于5 倍体积的无水乙醇溶液中，得到分散均匀的悬浊液，然后将悬浊液旋涂在乙醇清洗过的Au叉指电极上，并置于60 °C下干燥4 h，得到气敏元件。

[n0030]

The prepared gas-sensitive element was subjected to gas-sensitive detection using a static gas mixing method. The specific steps were as follows: First, the gas-sensitive element to be tested was installed in the gas chamber and connected to the information acquisition and analysis equipment. At a detection temperature of 25 °C and a detection humidity of 25%, 100 ppm of NO₂ was injected. When the gas-sensitive response stabilized according to the feedback from the data acquisition system, a gas pump was used to evacuate the gas, causing NO₂ to desorb and the device to return to its initial state, thus completing one gas injection cycle. Then, NO₂ gas injection cycles were performed sequentially at concentrations of 100 ppm, 50 ppm, 30 ppm, 10 ppm, 5 ppm, 3 ppm, 1 ppm, 0.5 ppm, 0.3 ppm, and 0.1 ppm. After completing the gas injection cycles, the sensitivity curve for detecting nitrogen dioxide by the gas-sensitive element prepared in this embodiment was obtained, as shown in Figure 3. The sensitivity for NO₂ at a concentration of 100 ppm reached 40.82, and the sensitivity for NO₂ concentration was as low as 0.1. The material has a sensitivity of 1.2 for gases at ppm, and exhibits fast response and good adsorption reversibility.

采用静态配气法对制备的气敏元件进行气敏检测，具体步骤为：首先将待测气敏元件安装到气室中并与信息采集及分析设备连接，在检测温度25 °C、检测湿度为25%下，开始注入100 ppm的NO₂，当根据数据采集系统反馈的信息观察到气敏响应稳定时，则利用气泵抽气，使NO₂脱附，待测器件回归初始状态，即完成一个注气循环；然后依次进行100 ppm、50 ppm、30 ppm、10 ppm、5 ppm、3 ppm、1 ppm、0.5 ppm和0.3 ppm、0.1ppm的NO₂注气循环；完成注气循环后得到如图3所示的本实施例制备的气敏元件检测二氧化氮的灵敏度曲线，对NO₂浓度为100 ppm气体的灵敏度达40.82，对NO₂浓度低至0.1 ppm的气体的灵敏度为1.2，并且材料的响应速度快、吸附可逆性好。

[n0031]

Table 1 shows the sensitivity and response time of the gas-sensitive element prepared in this embodiment under different nitrogen dioxide concentrations, where the sensitivity S = R_a/R_g, R_a is the resistance of the sensor in air, and R_g is the resistance of the sensor in NO₂ atmosphere.

表1为测试本实施例制备的气敏元件在不同二氧化氮浓度下的灵敏度和响应时间，其中灵敏度S=R_a/R_g，R_a为传感器在空气中的电阻，R_g为传感器在NO₂气氛中的电阻。

The time required for the resistance to change by 90% during gas adsorption and desorption is the response time.

在气体吸附和解析过程中，电阻变化90%所需要的时间是响应时间。

[n0032]

Table 1

表1

[n0033]

Figure 4 is a gas selectivity test diagram of the gas-sensitive element prepared in this embodiment at room temperature. The test gases include NO₂, H₂S, NH₃, SO₂ and N₂O. Except for NO₂, which is injected at a concentration of 100 ppm, the injection concentration of the other gases is 10000 ppm.

图4是本实施例制备的气敏元件在室温下的气体选择性测试图，其中测试气体包括：NO₂、H₂S、NH₃、SO₂和N₂O，除NO₂注入浓度为100 ppm外，其余气体的注入浓度为10000 ppm。

As shown in Figure 4, the gas-sensitive element made from the three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 1 exhibits excellent selectivity for NO₂ at room temperature.

图4结果可知，由实施例一制备的三维二硫化钼纳米花复合材料作为气敏材料制作的气敏元件在室温下对NO₂具有优异的选择性。

[n0034]

Example 8

实施例八

[0084]

This embodiment provides a gas-sensitive element made from a three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 2 as a gas-sensitive material.

本实施例提供了一种由实施例二制备的三维二硫化钼纳米花复合材料作为气敏材料制作的气敏元件。

[n0035]

The specific preparation method of the gas-sensitive element in this embodiment is as follows:

本实施例气敏元件的具体制备方法为：

[0086]

The three-dimensional molybdenum disulfide nanoflower composite material prepared in Example 2 was ultrasonically dispersed in 5 times its volume of anhydrous ethanol solution to obtain a uniformly dispersed suspension. The suspension was then spin-coated onto an Au interdigitated electrode that had been cleaned with ethanol and dried at 60 °C for 4 h to obtain a gas-sensitive element.

将实施例二制备的三维二硫化钼纳米花复合材料超声分散于5 倍体积的无水乙醇溶液中，得到分散均匀的悬浊液，然后将悬浊液旋涂在乙醇清洗过的Au叉指电极上，并置于60 ℃下干燥4 h，得到气敏元件。

[n0036]

The prepared gas-sensitive element was tested using a static gas mixing method. The specific steps were as follows: First, the gas-sensitive element was installed in the gas chamber and connected to the information acquisition and analysis equipment. At a detection temperature of 30 °C and a detection humidity of 35%, 100 ppm of NO_NER46 was injected. When the gas-sensitive response stabilized according to the feedback from the data acquisition system, a gas pump was used to desorb NO_NER47, returning the device to its initial state, thus completing one gas injection cycle. Then, NO_NER48 gas injection cycles were performed sequentially at concentrations of 100 ppm, 50 ppm, 30 ppm, 10 ppm, 5 ppm, 3 ppm, 1 ppm, 0.5 ppm, 0.3 ppm, and 0.1 ppm. After completing the gas injection cycles, the sensitivity curve of the gas-sensitive element for detecting nitrogen dioxide, as shown in Figure 5, was obtained. The results showed that the sensitivity was high for NO_NER49 at a concentration of 100 ppm. The sensitivity for ppm gases is 24.1, and the sensitivity for NO₂ concentrations as low as 0.1 ppm is 1.2.

采用静态配气法对制备的气敏元件进行气敏检测，具体步骤为：首先将待测气敏元件安装到气室中并与信息采集及分析设备连接，在检测温度30 °C、检测湿度为35%下，开始注入100 ppm的NO₂，当根据数据采集系统反馈的信息观察到气敏响应稳定时，则利用气泵抽气，使NO₂脱附，待测器件回归初始状态，即完成一个注气循环；然后依次进行100 ppm、50 ppm、30 ppm、10 ppm、5 ppm、3 ppm、1 ppm、0.5 ppm和0.3 ppm、0.1ppm的NO₂注气循环；完成注气循环后得到如图5所示的本实施例制备的气敏元件检测二氧化氮的灵敏度曲线，结果显示，对NO₂浓度为100 ppm气体的灵敏度达24.1，对NO₂浓度低至0.1 ppm的气体的灵敏度为1.2。

[n0037]

Figure 6 shows the repeatability test results of the gas-sensitive element prepared in this embodiment at room temperature for 100 ppm NO₂.

图6为本实施例制备的气敏元件在室温下对100 ppm NO₂的重复性测试结果图。

As shown in the figure, the resistance of the sensitive membrane formed by the three-dimensional molybdenum disulfide nanoflower composite material prepared by Se doping decreases rapidly after adsorbing NO₂, and the repeatability is good after seven consecutive cycles of adsorption-desorption of 100 ppm NO₂.

从图可知，Se掺杂制备的三维二硫化钼纳米花复合材料所形成的敏感膜吸附NO₂后，电阻阻值较迅速地降低，连续7个循环吸附-脱附100 ppm NO₂后，重复性较好。