Notice

DESCRIPTION CN104857976A

A three-dimensional molybdenum disulfide nanoflower-graphene composite material and its application

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一种三维二硫化钼纳米花-石墨烯复合材料及其应用

[0001]

Technical Field

技术领域

[0002]

This invention belongs to the field of clean and sustainable new energy preparation and application, and specifically relates to a three-dimensional molybdenum disulfide nanoflower-graphene composite material and its application.

本发明属于清洁可持续新型能源制备应用领域，特别涉及一种三维二硫化钼纳米花-石墨烯复合材料及其应用。

[0003]

Background Technology

背景技术

[0004]

With the rapid development of the world economy, the excessive consumption of traditional energy sources such as oil and natural gas, as well as the environmental problems caused by the use of traditional energy sources, are hindering the rapid and effective further development of today's society.

伴随着世界经济的高速发展，传统能源如石油、天然气等过度消耗以及使用传统能源所引起的环境问题制约着当今社会快速有效的进一步发展。

Therefore, finding an inexhaustible, green, and clean energy source to replace traditional energy sources has become the top priority in solving the energy crisis.

因此找到一种取之不尽用之不竭绿色清洁能源替代传统能源成为解决能源危机的重中之重。

Hydrogen, as a renewable resource, has the characteristics of being green and pollution-free, and therefore it can be used as an ideal new type of green energy to replace traditional non-renewable resources.

氢气作为一种可再生资源具有绿色无污染等特点，因此其可以作为一种理想的新型绿色能源去取代传统的非可再生资源。

Traditional electrochemical hydrogen evolution catalysts include platinum-based noble metal catalysts. Although these catalysts exhibit superior electrochemical hydrogen evolution catalytic activity, their high preparation cost and limited earth reserves restrict their further development and practical application.

传统的电化学析氢催化剂包括铂在类的贵金属催化剂，这些催化虽然表现出较为优越的电化学析氢催化活性，但是贵金属催化剂制备成本高、地球储存量少，限制了其进一步发展和实际应用。

[0005]

Molybdenum disulfide is a typical transition metal sulfide with a layered structure similar to graphene.

二硫化钼一种典型的过度金属硫化物，具有类似于石墨烯的层状结构。

In recent years, theoretical calculations and experimental results have shown that the catalytic active centers of molybdenum disulfide exist on the active sites at the edges of the 002 facet rather than on the inert 002 facet itself. Meanwhile, molybdenum disulfide, as a semiconductor, has poor conductivity, resulting in a large resistance value between the two phases at the catalyst interface, thereby reducing the catalytic efficiency of the catalyst itself. On the other hand, during long-term use, catalysts inevitably dissolve in the solution, directly leading to a decrease in catalyst activity, thus failing to meet the requirements for long-term use. Therefore, improving the stability of the ultra-short skirt of electrochemical catalytic hydrogen evolution catalysts has become another practical issue that needs to be considered to improve catalytic performance. The preparation of molybdenum disulfide-graphene composite materials has been reported for applications in electrochemical hydrogen evolution, supercapacitors, lithium-ion batteries, and other fields. To date, the synthesis of molybdenum disulfide nanosheets with a three-dimensional nanoflower structure perpendicular to graphene via a one-step hydrothermal method, with the lattice spacing on the 002 plane expanded to 0.85 nm, has never been reported.

近些年来，理论计算和实验结果表明二硫化钼的催化活性中心存在于002面上的边缘的活性点上而不是惰性的002面本身。 与此同时二硫化钼作为一种半导体，具有导电性差特点，使得催化剂界面两相间存在较大的电阻值，从而降低了催化剂本身的催化效率。 另一方面，催化剂长期使用过程不可避免的会发生其本身溶解在溶液里面，直接导致催化剂的活性降低，从而不能满足对于催化剂长时间使用的需求，因此提高电化学催化析氢催化剂超短裙稳定性成为了提高催化能力另一面需要考虑的实际问题。 二硫化钼-石墨烯复合材料的制备已被报道应用于电化学析氢，超级电容器，锂离子电池等当面。 到目前为止，通过一步水热法合成具有三维纳米花结构的二硫化钼纳米片垂直于石墨烯上，并且其002面上的晶格间距扩大到0.85nm还未曾报道过。

[0006]

The purpose of this invention is to address the shortcomings of existing technologies by providing a compound of a three-dimensional molybdenum disulfide nanoflower-graphene composite.

本发明的目的是针对现有技术的不足，提供一种三维二硫化钼纳米花-石墨烯复合物的化合物。

It is also applied in the field of electrochemical hydrogen evolution catalysis. This three-dimensional molybdenum disulfide nano-graphene exhibits characteristics such as low catalyst loading, high catalytic activity, and good stability.

并应用于电化学析氢催化领域。 该三维二硫化钼纳米化-石墨烯具有催化剂负载量底、催化活性高、稳定性好等特点。

[0007]

Summary of the Invention

发明内容

[0008]

The purpose of this invention is to address the shortcomings of existing technologies by providing a three-dimensional molybdenum disulfide nanoflower-graphene composite material and its applications.

本发明的目的在于针对现有技术的不足，提供一种三维二硫化钼纳米花-石墨烯复合材料及其应用。

[0009]

The objective of this invention is achieved through the following technical solution: a three-dimensional molybdenum disulfide nanoflower-graphene composite material, prepared by the following method:

本发明的目的是通过以下技术方案实现的：一种三维二硫化钼纳米花-石墨烯复合材料，通过以下方法制备得到：

[0010]

(1) 10 mg of graphene oxide (GO) was uniformly dispersed in 10 mL of N,N-dimethylformamide (DMF) to obtain a graphene oxide suspension;

（1）将10mg氧化石墨烯（GO）均匀分散于10mL,N二甲基甲酰胺（DMF）中，得到氧化石墨烯悬浮液；

[0011]

(2) Dissolve 20 mg of ammonium thiomolybdate in the graphene oxide suspension from step 1;

（2）将20mg硫代钼酸胺溶于步骤1的氧化石墨烯悬浮液中；

[0012]

(3) Transfer the mixed solution obtained in step 2 to a reaction vessel and react at 190°C for 15 h to obtain a black product;

（3）把步骤2中得到的混合溶液转移到反应釜中，并在190°C下反应15h，得到黑色产物；

[0013]

(4) The black product obtained in step 3 was washed with ethanol and then vacuum dried at 60°C for 24 h to obtain a three-dimensional molybdenum disulfide nanoflower-graphene composite material.

（4）将步骤3中反应得到的黑色产物用乙醇清洗后，并在60°C下真空干燥24h，得到三维二硫化钼纳米花-石墨烯复合材料。

[0014]

An application of a three-dimensional molybdenum disulfide nanoflower-graphene composite material is disclosed, wherein the material is used to prepare an electrode, the electrode consisting of a glassy carbon electrode and a three-dimensional molybdenum disulfide nanoflower-graphene composite material coated on the glassy carbon electrode.

一种三维二硫化钼纳米花-石墨烯复合材料的应用，该应用为将所述材料应用于制备电极，所述电极由玻碳电极和涂于玻碳电极上的三维二硫化钼纳米花-石墨烯复合材料组成。

[0015]

Further, the electrode is prepared as follows: 3 mg of three-dimensional molybdenum disulfide nanoflower-graphene composite material is dispersed in a mixed solution of 1.5 mL of deionized water and ethanol (volume ratio of deionized water to ethanol is 3:1), and then 120 μL of Nafion solution with a mass fraction of 5 wt% is added. After uniform dispersion, a suspension is obtained; the suspension is coated on a glassy carbon electrode and naturally dried to obtain a glassy carbon electrode modified with three-dimensional molybdenum disulfide nanoflower-graphene.

进一步地，所述电极的制备方法为： 将3mg三维二硫化钼纳米花-石墨烯复合材料分散于1.5mL去离子水和乙醇的混合溶液中（离子水和乙醇的体积比为3：1），然后加入120μL质量分数为5wt%的Nafion溶液中，分散均匀后，得到悬浮液；将悬浮液涂在玻碳电极上，自然干燥后得到三维二硫化钼纳米花-石墨烯修饰的玻碳电极。

[0016]

The beneficial effects of this invention are: this invention obtains a three-dimensional molybdenum disulfide nanoflower-graphene composite material through a simple one-step hydrothermal method, and the electrode prepared using this material can be applied to electrochemical catalytic hydrogen evolution.

本发明的有益效果是：本发明通过简单的一步水热法得到了三维二硫化钼纳米花-石墨烯复合材料，采用该材料制备的电极可以应用于电化学催化析氢中。

In terms of catalytic activity, since these three-dimensional molybdenum disulfide nanoflowers are perpendicular to the graphene substrate, the active centers at the edges of the catalytically active 002 surface are more likely to come into contact with hydrogen ions in the solution.

在催化活性方面，由于这种三维二硫化钼纳米花片是垂直于石墨烯基底上的，因此及具有催化活性的002面上边缘活性中心就更容易和溶液中的氢离子接触。

Compared to flat molybdenum disulfide nanosheets, this reduces the resistance to electron transport between molybdenum disulfide layers.

相对于平躺的二硫化钼纳米片降低了电子在二硫化钼层与层之间传输的阻力。

In addition, graphene has good electron conduction and transport properties, which effectively reduces the resistance between the two phases of the catalyst.

另外石墨烯具有较好的电子传导和运输作用，有效的降低了催化剂两相间的电阻。

It improved catalytic activity.

提高了催化活性。

In terms of catalytic stability, the increased interlayer spacing on the 002 surface and the formation of the three-dimensional structure in the three-dimensional molybdenum disulfide nanoflower-graphene composite material help reduce the volume change of the catalyst during long-term use, thus enhancing the stability of the catalyst.

在催化稳定性方面，由于002面上的层间距的扩大，以及三维二硫化钼纳米花-石墨烯复合材料中三维结构的形成有利于减少催化剂在长时间使用过程中体积的改变，因此增强了催化剂的稳定性。

[0017]

Attached Figure Description

附图说明

[0018]

Figure 1 is a scanning electron microscope (SEM) image of the three-dimensional molybdenum disulfide nanoflower-graphene composite prepared in this invention.

图1是本发明制备的三维二硫化钼纳米花-石墨烯复合物扫描电子显微镜图片（SEM）。

[0019]

Figure 2 is a high-resolution transmission electron microscope (HRTEM) image of the three-dimensional molybdenum disulfide nanoflower-graphene composite prepared according to the present invention.

图2是本发明制备三维二硫化钼纳米花-石墨烯复合物高分辨透射电子显微镜图片（HRTEM）。

[0020]

Figure 3 shows the polarization curves of the electrochemical hydrogen evolution of the three-dimensional molybdenum disulfide nanoflower-graphene composite prepared in this invention in 0.5M sulfuric acid solution.

图3是本发明制备三维二硫化钼纳米花-石墨烯复合物在0.5M硫酸溶液中电化学析氢的极化曲线（Polarization curves）。

[0021]

Figure 4 shows the stability test curve of the three-dimensional molybdenum disulfide nanoflower-graphene composite prepared in this invention in 0.5M sulfuric acid (Durability test).

图4 是本发明制备三维二硫化钼纳米花-石墨烯复合物在0.5M硫酸中的稳定性测试曲线（Durability test）。

[0022]

Detailed Implementation

具体实施方式

[0023]

The technical solutions of the present invention will be further described below with reference to the embodiments. These embodiments should not be construed as limiting the technical solutions.

下面结合实施例对本发明作进一步说明本发明的技术解决方案，这些实施例不能理解为是对技术解决方案的限制。

[0024]

Example 1: This example describes the preparation of a three-dimensional molybdenum disulfide nanoflower-graphene composite material, specifically including the following steps:

实施例1：本实施例制备三维二硫化钼纳米花-石墨烯复合材料，具体包括以下步骤：

[0025]

(1) Add 10 mg of the prepared graphene oxide powder (GO) to a reagent bottle containing 10 mL of N,N-dimethylformamide and sonicate for half an hour to uniformly disperse the graphene in N,N-dimethylformamide (DMF) to obtain a graphene oxide suspension:

（1）将10mg已经制备好的氧化石墨烯粉末（GO）加入到含有10mL的N,N二甲基甲酰胺试剂瓶中，超声半个小时，使石墨烯均匀分散在N,N二甲基甲酰胺（DMF）中，得到氧化石墨烯悬浮液：

[0026]

(2) Weigh 20 mg of thiomolybdate using an electronic balance and add it to the graphene oxide suspension in step one.

（2）用电子天平称取20mg硫代钼酸胺，并加入到步骤一中的氧化石墨烯悬浮液中。

Dissolve it by sonication for 10 minutes;

超声10分钟使其溶解；

[0027]

(3) Add the solution from step 2 to a 25 mL tetrafluoroethylene reaction vessel and react at 190 °C for 15 h;

（3）把步骤2中的溶液加入到25mL四氟乙烯的反应釜中，并在190°C下反应15h；

[0028]

(4) Add the black product obtained in step 3 to ethanol, centrifuge and wash, repeat 5 times for 8 min each time, at a speed of 8000 rpm/min, and vacuum dry at 60°C for 24 h to obtain a three-dimensional molybdenum disulfide nanoflower-graphene composite material.

（4）将步骤3中反应得到的黑色产物加入乙醇，离心洗涤，每次8min重复5次，转速为8000rpm /min 并在60°C下真空干燥24h，得到三维二硫化钼纳米花-石墨烯复合材料。

[0029]

Figure 1 is a scanning electron microscope (SEM) image of the three-dimensional molybdenum disulfide nanoflower-graphene composite prepared in this invention. It can be seen from the figure that the three-dimensional molybdenum disulfide flowers are self-assembled from ultrathin molybdenum disulfide nanosheets that are perpendicular to the graphene substrate. It can be seen from Figure 1 that the lateral size of the molybdenum disulfide nanosheets is 100-200 nm.

图1为本发明制备的三维二硫化钼纳米花-石墨烯复合物的扫描电子显微镜图（SEM），从图中可以看出三维二硫化钼花是由超薄的并且垂直于石墨烯基基底上的超薄二硫化钼纳米片自组装而成，从图1中可以看出二硫化钼纳米横向尺寸大小为100-200nm。

Figure 2 is a high-resolution transmission electron microscope (HRTEM) image of the three-dimensional molybdenum disulfide nanoflower-graphene composite prepared in this invention.

图2为本发明制备的三维二硫化钼纳米花-石墨烯复合物的高分辨透射电子显微镜图（HRTEM）。

As can be seen from the figure, the molybdenum disulfide nanosheets have a relatively small number of layers, with an interlayer spacing of 0.85 nm on the 002 surface.

从图中可以看出二硫化钼纳米片有较少的层数组成，其002面上的层间距为0.85nm。

Molybdenum disulfide, as an electrocatalytic hydrogen evolution catalyst, has its catalytic active center located at the edge of the 002 facet.

二硫化钼作为一种电催化析氢催化剂，其催化活性中心位于002面上的边缘。

This invention synthesizes a three-dimensional molybdenum disulfide nanoflower-graphene composite material, in which molybdenum disulfide nanoflowers are vertically grown on graphene. This not only provides more active centers that facilitate hydrogen ion contact, but also reduces the electron transport resistance between layers on the 002 surface.

本发明通过合成一种三维二硫化钼纳米花-石墨烯符合材料，得到了二硫化钼纳米花垂直生长在石墨烯上，不仅得到了有利于氢离子接触的更多的活性中心，而且降低了电子在002面上层与层之间的传输电阻。

The formation of three-dimensional molybdenum disulfide nanoflowers creates a three-dimensional network structure between ultrathin molybdenum disulfide sheets, enhancing the stability of the catalyst.

三维二硫化钼纳米花形成，使超薄二硫化钼片之间形成了三维网状结构增强了催化剂的稳定性。

Furthermore, the enlarged interlayer spacing (0.85 nm) of the 002 facet not only facilitates the aggregation of more hydrogen ions at the edge of the active center, but also effectively reduces the impact of volume changes during catalyst use.

另外扩大的002面的层间距（0.85nm）不仅便于更多的氢离子聚集在活性中心的边缘，而且有效的降低了催化剂在使用过程中体积改变所造成的影响。

This also improves the stability of the catalyst.

因此也提高了催化剂的稳定性。

[0030]

Example 2: In this example, a glassy carbon electrode was prepared using the three-dimensional molybdenum disulfide nanoflower-graphene composite material prepared in Example 1. Specifically, 3 mg of dried three-dimensional molybdenum disulfide nanoflower-graphene composite material was added to 1.5 mL of a deionized water-ethanol mixture with a volume ratio of (3:1), and 120 μL of a 5 wt% Nafion solution was added. After sonication for half an hour, a suspension was obtained.

实施例2，本实施例采用实施例1制备的三维二硫化钼纳米花-石墨烯复合材料制备玻碳电极，具体为：将3mg干燥后的三维二硫化钼纳米花-石墨烯复合材料加入到1.5mL体积比为（3：1）的去离子水—乙醇混合液中，并加入120uL质量分数为5wt%Nafion溶液中，超声半个小时后得到悬浮液。

Then, 5 μL of the suspension was measured with a pipette and dropped onto the glassy carbon electrode. After natural drying, a molybdenum disulfide-graphene modified glassy carbon electrode was obtained.

然后用移液枪量取悬浮液5uL的悬浮液滴涂在玻碳电极上，自然干燥后得到二硫化钼-石墨烯修饰的玻碳电极。

[0031]

Example 3: The electrode prepared in Example 2 was applied to the electrochemical hydrogen evolution process, specifically as follows:

实施例3：将实施例2制备的电极应用于电化学析氢，具体为：

[0032]

A three-electrode system was constructed using a glassy carbon electrode (GCE) modified with a three-dimensional molybdenum disulfide nanoflower-graphene composite as the working electrode (WE), a saturated calomel electrode as the reference electrode (RE), and a platinum wire as the counter electrode (CE), with 0.5M sulfuric acid as the electrolyte.

将三维二硫化钼纳米花-石墨烯复合物修饰的玻碳电极（GCE）为工作电极（WE）、饱和甘汞电极为参比电极（RE）、铂丝为对电极（CE）组成三电极体系，以0.5M硫酸为电解液。

Before conducting electrochemical tests, saturated nitrogen gas is introduced to remove oxygen from the solution.

在进行电化学测试前，通入饱和氮气，除去溶液中的氧气。

The electrodes were then calibrated using the formula: SCE = RHE + 0.267V.

并对电极进行校准正 SCE=RHE+0.267V。

Figure 3 shows the polarization curves of the three-dimensional molybdenum disulfide nanoflower-graphene composite prepared for this invention. As can be seen from the figure, when the overpotential is 250mV, the current density reaches 43mA/cm ² , which is converted to a mass current density of 304A/g.

图3为为本发明制备的三维二硫化钼纳米花-石墨烯复合物的极化曲线（Polarization curves），从图中可以看出当过电位为250mV时，电流密度达到了43mA/cm ² ，换算成质量电流密度为304A/g。

Figure 4 shows the stability test curve of the three-dimensional molybdenum disulfide nanoflower-graphene composite prepared in this invention. As can be seen from the figure, after 2000 cycles, the current density at an overpotential of 250mV hardly changes.

图4为本发明制备的三维二硫化钼纳米花-石墨烯复合物的稳定性测试曲线（Durability test），从图中可以看出循环2000次后，其在过电位为250mV的电流密度几乎没有改变。

It exhibited high stability.

表现出了较高的稳定性。

[0033]

The method of the present invention for preparing the three-dimensional molybdenum disulfide-graphene composite is simple, highly reproducible, and easy to operate.

本发明方法制备的三维二硫化钼-石墨烯复合物制备方法简单，重复性高，可操作性强。

As a novel electrochemical hydrogen evolution catalyst, it exhibits extremely high mass current density and catalytic stability.

作为一种新型的电化学析氢催化剂，表现出了极高的质量电流密度，催化稳定性。

Compared to traditional molybdenum disulfide/graphene composites.

相对于传统的二硫化钼/石墨烯复合物。

Its bias potential is only 103mV.

其偏置电位为仅103mV。