Notice

DESCRIPTION CN109721105A

Molybdenum disulfide nanoflower materials and their preparation methods, molybdenum disulfide nanoflower anode materials and their preparation methods, and batteries.

二硫化钼纳米花材料及其制备方法、二硫化钼纳米花负极材 料及其制备方法以及电池

[0001]

Technical Field

技术领域

[0002]

This invention relates to the field of battery technology, and particularly to molybdenum disulfide nanoflower materials and their preparation methods, molybdenum disulfide nanoflower anode materials and their preparation methods, and batteries.

本发明涉及电池技术领域，且特别涉及二硫化钼纳米花材料及其制备方法、二硫化钼纳米花负极材料及其制备方法以及电池。

[0003]

Background Technology

背景技术

[0004]

The depletion of resources and air pollution caused by the extraction and use of fossil fuels have become a global concern, creating an urgent need for the development of green energy storage systems.

化石燃料开采使用带来的资源枯竭和空气污染成为全球关注的焦点，对绿色能源存储系统的发展提出了迫切的要求。

Lithium-ion batteries, which were invented in the early 1990s, have the advantages of high energy density and long cycle life.

锂离子电池作为九十年代初诞生的储能设备，具有能量密度高、循环寿命长的优点。

However, lithium resources are limited and unevenly distributed globally, and organic electrolytes are flammable, posing safety hazards. These problems have forced people to look for new, cheaper, and safer energy storage devices to meet the needs of large-scale energy storage for electric vehicles, smart grids, and other applications.

然而,锂资源储量有限且在全球分布不均，有机电解液易燃形成安全隐患，这些问题都迫使人们寻找更加廉价、安全的新型储能设备，以满足电动汽车、智能电网等大型能源存储的需求。

[0005]

Non-flammable aqueous electrolytes have a higher safety factor, and aqueous electrolyte batteries have better application prospects.

不可燃的水系电解液具有更高的安全系数，水系电解液电池具有较佳的应用前景。

[0006]

Summary of the Invention

发明内容

[0007]

The first objective of this invention is to provide a method for preparing molybdenum disulfide nanoflower materials, which can prepare molybdenum disulfide nanoflowers with graphene-like layered structures and theoretical capacity, and the method is simple and easy to implement.

本发明的第一个目的在于提供一种二硫化钼纳米花材料的制备方法，该方法能够制备出具有类石墨烯层状结构和理论容量的二硫化钼纳米花，且该方法简便易行。

[0008]

The second objective of this invention is to provide a molybdenum disulfide nanoflower material, which has a graphene-like layered structure and theoretical capacity, and the structure of the molybdenum disulfide nanoflower has a large specific surface area, thus showing good application prospects.

本发明的第二个目的在于提供一种二硫化钼纳米花材料，其具有类石墨烯层状结构和理论容量，且该二硫化钼纳米花的机构具有较大的比表面积，具有较佳的应用前景。

[0009]

The third objective of this invention is to provide a method for preparing molybdenum disulfide nanoflower anode material. This method is simple and easy to implement, and the molybdenum disulfide nanoflower anode material prepared by this method can improve the capacity recovery capability of the battery made from it.

本发明的第三个目的在于提供一种二硫化钼纳米花负极材料的制备方法，该方法简单易行，且该方法制备的二硫化钼纳米花负极材料能够提升由其制得的电池的电容量恢复能力等。

[0010]

The fourth objective of this invention is to provide a disulfide nanoflower anode material that can be used to prepare batteries to improve the battery's capacity recovery capability, etc.

本发明的第四个目的在于提供一种二硫化纳米花负极材料，其能够用于制备电池，以改善电池的电容量恢复能力等。

[0011]

The fifth object of the present invention is to provide a battery with better capacity and better capacity recovery capability.

本发明的第五个目的在于提供一种电池，该电池电容量较佳，且具有较佳的电容量恢复能力。

[0012]

The present invention is achieved by the following technical solution.

本发明是采用以下技术方案来实现的。

[0013]

This invention proposes a method for preparing molybdenum disulfide nanoflower materials, which includes dissolving molybdate and sulfur source in a solvent to obtain a pre-mixed mixture; reacting the pre-mixed mixture at high temperature to obtain a suspension; centrifuging the suspension and washing the precipitate to obtain molybdenum disulfide nanoflower materials.

本发明提出一种二硫化钼纳米花材料的制备方法，其包括将钼酸盐和硫源溶解于溶剂中，得到预制混合物；将预制混合物高温反应后，得到悬浮液；将悬浮液离心后对沉淀物进行清洗，得到二硫化钼纳米花材料。

[0014]

This invention proposes a molybdenum disulfide nanoflower material, which is prepared by the above-mentioned method for preparing molybdenum disulfide nanoflower materials.

本发明提出一种二硫化钼纳米花材料，其是由上述的二硫化钼纳米花材料的制备方法制备的。

[0015]

This invention proposes a method for preparing molybdenum disulfide nanoflower anode material, which includes: mixing dried molybdenum disulfide nanoflower material, a conductive agent, and a binder to form a slurry; coating the slurry onto a current collector; and drying it to form a negative electrode sheet.

本发明提出一种二硫化钼纳米花负极材料的制备方法，其包括：将干燥的、由上述的二硫化钼纳米花材料以及导电剂、粘结剂混合制成浆液；将浆液涂覆于集流体，干燥后制成负极极片。

[0016]

This invention proposes a molybdenum disulfide nanoflower anode material, which is prepared by the above-mentioned preparation method of molybdenum disulfide nanoflower anode material.

本发明提出一种二硫化钼纳米花负极材料，其是由上述的二硫化钼纳米花负极材料的制备方法制备的。

[0017]

This invention proposes a battery in which the negative electrode material includes the above-mentioned molybdenum disulfide nanoflower negative electrode material.

本发明提出一种电池，该电池的负极材料包括上述的二硫化钼纳米花负极材料。

[0018]

The present invention also proposes a battery in which the negative electrode material comprises molybdenum disulfide nanomaterials and the electrolyte comprises an aluminum ion-containing aqueous electrolyte; preferably, the concentration of the electrolyte is 0.2-2 mol/L.

本发明还提出一种电池，该电池的负极材料包括二硫化钼纳米材料，电池的电解液包括含铝离子水系电解液；优选地，电解液的浓度为0.2-2mol/L。

[0019]

The beneficial effects of the preparation method of molybdenum disulfide nanoflower material in this invention are as follows: The preparation method of molybdenum disulfide nanoflower material provided by this invention involves dissolving and mixing molybdate and sulfur source, then reacting at high temperature to obtain a suspension. After centrifuging the suspension, the precipitate is washed to obtain molybdenum disulfide nanoflower material. The above method is simple and easy to operate, and the obtained molybdenum disulfide nanoflower material has a graphene-like layered structure and theoretical capacity.

本发明实施例的二硫化钼纳米花材料的制备方法的有益效果是：本发明提供的二硫化钼纳米花材料的制备方法通过价格钼酸盐和硫源溶解、混合，再高温反应制得悬浮液，然后对悬浮液离心后对沉淀物进行清洗，以得到二硫化钼纳米花材料，上述方法简答易操作，且制得的二硫化钼纳米花材料具有类石墨烯层状结构和理论容量。

[0020]

The beneficial effects of the molybdenum disulfide nanoflower material in this invention are as follows: the molybdenum disulfide nanoflower material is prepared by the above method, and it has a graphene-like layered structure and theoretical capacity. Moreover, the structure of the molybdenum disulfide nanoflower has a large specific surface area and has good application prospects.

本发明实施例的二硫化钼纳米花材料的有益效果是：该二硫化钼纳米花材料由上述的方法制得，其具有类石墨烯层状结构和理论容量，且该二硫化钼纳米花的机构具有较大的比表面积，具有较佳的应用前景。

[0021]

The beneficial effect of the preparation method of molybdenum disulfide nanoflower anode material in this invention is that the anode raw material used in the preparation method is the above-mentioned molybdenum disulfide nanoflower material, which can improve the capacitance recovery ability of the anode material.

本发明实施例的二硫化钼纳米花负极材料的制备方法的有益效果是：该制备方法中采用的负极原料为上述的二硫化钼纳米花材料，能够改善负极材料的电容量恢复能力。

[0022]

The beneficial effects of the molybdenum disulfide nanoflower anode material in this invention are: the molybdenum disulfide nanoflower anode material is prepared by the above method and has better capacity recovery capability.

本发明实施例的二硫化钼纳米花负极材料的有益效果是：该二硫化钼纳米花负极材料是由上述的方法制备的，具有较佳的电容量恢复能力。

[0023]

The beneficial effect of the battery in this embodiment of the invention is that the negative electrode material of the battery is the above-mentioned molybdenum disulfide nanoflower negative electrode material, which has better capacity recovery capability, thereby improving the capacity recovery capability of the battery.

本发明实施例的电池的有益效果是：该电池的负极材料为上述的二硫化钼纳米花负极材料，二硫化钼纳米花负极材料的电容量恢复能力较佳，以改善电池的电容量恢复能力。

[0024]

The beneficial effects of the battery in this embodiment of the invention are as follows: the negative electrode material of the battery is molybdenum disulfide nanoflower material, and the electrolyte is an aluminum ion-containing aqueous electrolyte, which improves the battery's capacity recovery capability on the one hand, and improves the battery's safety performance on the other hand.

本发明实施例的电池的有益效果是：该电池的负极材料为二硫化钼纳米花材料，电解液为含铝离子水系电解液，一方面改善了该电池的电容量恢复能力，另一方面改善了电池的安全性能。

[0025]

Attached Figure Description

附图说明

[0026]

To more clearly illustrate the technical solutions of the embodiments of the present invention, the accompanying drawings used in the embodiments will be briefly introduced below. It should be understood that the following drawings only show some embodiments of the present invention and should not be regarded as a limitation on the scope. For those skilled in the art, other related drawings can be obtained based on these drawings without creative effort.

为了更清楚地说明本发明实施例的技术方案，下面将对实施例中所需要使用的附图作简单地介绍，应当理解，以下附图仅示出了本发明的某些实施例，因此不应被看作是对范围的限定，对于本领域普通技术人员来讲，在不付出创造性劳动的前提下，还可以根据这些附图获得其他相关的附图。

[0027]

Figure 1 shows the XRD (X-ray diffraction) pattern of the molybdenum disulfide nanoflowers prepared in Example 8 of this invention;

图1为本发明实施例8中制备的二硫化钼纳米花的XRD(X射线衍射)图谱；

[0028]

Figure 2 is a rate performance curve of the molybdenum disulfide nanoflowers prepared in Example 8 of the present invention in a 1 mol/L aluminum chloride solution.

图2为本发明实施例8中制备的二硫化钼纳米花在1mol/L氯化铝溶液中的倍率性能曲线图；

[0029]

Figure 3 is a cycle curve of the molybdenum disulfide nanoflowers prepared in Example 8 of the present invention in a 1 mol/L aluminum chloride solution.

图3为本发明实施例8中制备的二硫化钼纳米花1mol/L氯化铝溶液中的循环曲线图。

[0030]

Detailed Implementation

具体实施方式

[0031]

To make the objectives, technical solutions, and advantages of the embodiments of the present invention clearer, the technical solutions in the embodiments of the present invention will be clearly and completely described below.

为使本发明实施例的目的、技术方案和优点更加清楚，下面将对本发明实施例中的技术方案进行清楚、完整地描述。

Unless otherwise specified in the examples, the conditions shall be performed according to the standard conditions or the conditions recommended by the manufacturer.

实施例中未注明具体条件者，按照常规条件或制造商建议的条件进行。

If the manufacturers of the reagents or instruments used are not specified, they are all conventional products that can be purchased commercially.

所用试剂或仪器未注明生产厂商者，均为可以通过市售购买获得的常规产品。

[0032]

The following provides a detailed description of the molybdenum disulfide nanoflower material and its preparation method, the molybdenum disulfide nanoflower anode material and its preparation method, and the battery according to embodiments of the present invention.

下面对本发明实施例的二硫化钼纳米花材料及其制备方法、二硫化钼纳米花负极材料及其制备方法以及电池进行具体说明。

[0033]

The preparation method of the molybdenum disulfide nanoflower material of the present invention includes: dissolving molybdate and sulfur source in a solvent to obtain a pre-mixed mixture; reacting the pre-mixed mixture at high temperature to obtain a suspension; centrifuging the suspension and washing the precipitate to obtain the molybdenum disulfide nanoflower material.

本发明的二硫化钼纳米花材料的制备方法包括：将钼酸盐和硫源溶解于溶剂中，得到预制混合物；将预制混合物高温反应，得到悬浮液；将悬浮液离心后对沉淀物进行清洗，得到二硫化钼纳米花材料。

[0034]

Specifically, the solvent mentioned above includes water. After adding molybdate and sulfur source to the solvent and stirring for no less than 30 minutes, a pre-mixed mixture is obtained.

详细地，上述溶剂包括水，将钼酸盐和硫源添加于溶剂中搅拌不少于30min后，得打预制混合物。

[0035]

The aforementioned molybdates include at least one of the following: ammonium molybdate ((NH₄)₆Mo₇O₂₄・4H₂O), sodium molybdate, etc.

上述钼酸盐包括钼酸铵((NH₄)₆Mo₇O₂₄・4H₂O)、钼酸钠等钼酸盐中的至少一种。

[0036]

The sulfur source mentioned above includes at least one of the sulfur sources such as thiourea (N₂H₄CS) and thioacetamide.

上述硫源包括硫脲(N₂H₄CS)、硫代乙酰胺等硫源中的至少一种。

[0037]

Preferably, the molar ratio of the above molybdate to the sulfur source is less than or equal to 1:7.

优选地，上述钼酸盐与硫源的摩尔比小于等于1:7。

[0038]

The above high-temperature reaction can be carried out in a reactor. Specifically, the obtained pre-mixed material is poured into the reactor and reacted at a temperature greater than or equal to 180°C for 6-48 hours.

上述高温反应可以在反应釜中进行，详细地，将得到的预制混合物倒入反应釜中，在温度大于等于180°C条件下反应6h-48h。

[0039]

The centrifugation rate for the above suspension was 6000-8000 r/min.

上述悬浮液离心的离心速率为6000-8000r/min。

[0040]

The precipitate obtained after centrifugation should be washed repeatedly with deionized water and ethanol at least three times.

对于离心后得到的沉淀物清洗包括用去离子水和乙醇重复清洗不少于3次。

[0041]

Furthermore, after the precipitate is washed, the washed precipitate is dried to obtain molybdenum disulfide nanoflower material; in detail, the precipitate can be dried by forced air drying at a temperature of 70-90°C for about 12 hours to obtain molybdenum disulfide nanoflower material.

进一步地，在将沉淀物清洗完成后，将清洗后的沉淀物干燥后可得到二硫化钼纳米花材料；详细地，可以对沉淀物进行鼓风干燥，干燥的温度为70-90°C，干燥时间在12h左右，即可得到二硫化钼纳米花材料。

[0042]

The preparation method of the molybdenum disulfide nanoflower anode material of the present invention includes: mixing the molybdenum disulfide nanoflower material prepared according to the above method with a conductive agent and a binder to form a slurry; coating the slurry onto a current collector, and drying it to form a negative electrode sheet.

本发明的二硫化钼纳米花负极材料的制备方法包括：将按照上述方法制备的额二硫化钼纳米花材料以及导电剂、粘结剂混合制成浆液；将浆液涂覆于集流体，干燥后制成负极极片。

[0043]

In detail, the mass ratio between molybdenum disulfide nanoflower material, conductive agent, and binder can be 80-90:10-20:1-10.

详细地，二硫化钼纳米花材料、导电剂、粘结剂之间的质量比可以是80-90:10-20:1-10。

[0044]

The aforementioned conductive agent includes at least one of acetylene black, conductive carbon black (Super-P), Ketjen black, or graphene.

上述导电剂包括乙炔黑、导电炭黑(Super-P)、科琴黑或石墨烯中的至少一种。

[0045]

The aforementioned adhesive includes at least one of polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), sodium carboxymethyl cellulose (CMC), or styrene-butadiene rubber (SBR).

上述粘结剂包括聚四氟乙烯(PTFE)、聚偏氟乙烯(PVDF)、羧甲基纤维素钠(CMC)或丁苯橡胶(SBR)中的至少一种。

[0046]

The aforementioned current collector includes one of the following: carbon paper, stainless steel, titanium sheet, tantalum sheet, etc., which are stable in the electrolyte.

上述集流体包括在电解液中稳定的碳纸、不锈钢、钛片、钽片等中的一种。

[0047]

Furthermore, after coating the slurry onto the current collector, it is placed in a vacuum drying oven and dried at 60-120°C to produce molybdenum disulfide nanoflower anode material.

进一步地，将浆液涂覆于集流体后，放入真空干燥箱中以60-120°C进行烘干，以制成二硫化钼纳米花负极材料。

[0048]

The negative electrode material of the battery in this invention is the above-mentioned molybdenum disulfide nanoflower negative electrode material.

本发明中的电池的负极材料采用上述的二硫化钼纳米花负极材料。

[0049]

Furthermore, the electrolyte in the battery includes an aluminum-containing aqueous electrolyte; preferably, the concentration of the electrolyte is 0.2-2 mol/L.

进一步地该电池中的电解液包括含铝离子水系电解液；优选地，电解液的浓度为0.2-2mol/L。

[0050]

In detail, the above-mentioned aluminum ion-containing aqueous electrode solution is a solution prepared from at least one raw material including aluminum chloride, aluminum sulfate, aluminum nitrate, and aluminum acetate.

详细地，上述含铝离子水系电极液由包括氯化铝、硫酸铝、硝酸铝、乙酸铝等至少一种原料制备的溶液。

[0051]

It should be noted that the positive electrode material of this battery can be any of the positive electrode materials in related technologies, such as lithium manganese oxide, nickel-cobalt-aluminum ternary materials, lithium iron phosphate, etc., and no specific limitation is made here.

需要说明的是，该电池的正极材料可以选用相关技术中的各种正极材料，例如：锰酸锂、镍钴铝三元材料、磷酸铁锂等，在此不作具体限定。

[0052]

The present invention also provides a battery, wherein the negative electrode material of the battery comprises molybdenum disulfide nanoflower material, and the electrolyte comprises an aluminum ion-containing aqueous electrolyte, preferably, the concentration of the electrolyte is 0.2-2 mol/L.

本发明还提供一种电池，该电池的负极材料包括二硫化钼纳米花材料，电解液包括含铝离子水系电解液，优选地，电解液的浓度为0.2-2mol/L。

It should be noted that the negative electrode material in this battery can be prepared using molybdenum disulfide nanoflower materials prepared by the methods provided in the prior art.

需要说明的是，该电池中的负极材料可以有现有技术中盖提供的方法制备的二硫化钼纳米花材料制备。

[0053]

It should be noted that the positive electrode material of this battery can be any of the positive electrode materials in related technologies, such as graphite, lithium manganese oxide, nickel-cobalt-aluminum ternary materials, lithium iron phosphate, etc., without specific limitations.

需要说明的是，该电池的正极材料可以选用相关技术中的各种正极材料，例如：石墨、锰酸锂、镍钴铝三元材料、磷酸铁锂等，在此不作具体限定。

[0054]

The following detailed description, in conjunction with embodiments, provides the molybdenum disulfide nanoflower material and its preparation method, the molybdenum disulfide nanoflower anode material and its preparation method, and the battery of the present invention.

以下结合实施例对本发明的二硫化钼纳米花材料及其制备方法、二硫化钼纳米花负极材料及其制备方法以及电池作进一步的详细描述。

[0055]

Example 1

实施例1

[0056]

1.412 g of (NH₄)₆Mo₇O₂₄・4H₂O and 0.7 g of N₂H₄CS were dissolved sequentially in 60 ml of water and stirred for at least 30 min to prepare a homogeneous aqueous solution. This solution was then poured into a 50 ml reaction vessel and reacted at 180 °C for 6 h. After the reaction was completed, the resulting suspension was centrifuged at 7000 r/min and washed repeatedly with deionized water and anhydrous ethanol at least three times. The precipitate was dried in a blower dryer at 80 °C for 12 h to obtain MoS₂ (molybdenum disulfide nanoflower material).

将1.412g的(NH₄)₆Mo₇O₂₄·4H₂O和0.7g的N₂H₄CS依次溶解于60ml的水中，搅拌至少30min，配成均匀的混合水溶液，倒入到50ml的反应釜中，180°C反应6h；反应结束后，将所得悬浮液以7000r/min的转速离心分离，并用去离子水和无水乙醇反复清洗3次以上；将沉淀物在鼓风干燥机80°C干燥12h，得到MoS₂(二硫化钼纳米花材料)。

[0057]

MoS₂: acetylene black: PVDF = 80:15:5 (mass ratio) was slurried, uniformly coated on graphite paper, and then dried in a vacuum drying oven at 60-120°C to prepare molybdenum disulfide nanoflower anode material.

将MoS₂：乙炔黑：PVDF＝80:15:5(质量比)进行制浆，均匀涂覆在石墨纸上，然后在60～120°C真空干燥箱中烘干，制成二硫化钼纳米花负极材料。

[0058]

Battery preparation: Aluminum chloride hexahydrate was dissolved in 250 ml of deionized water to prepare a 0.2 mol/L aluminum chloride solution; the above molybdenum disulfide nanoflower anode material was used as the anode, graphite rod electrode was used as the counter electrode, and silver-silver chloride was used as the reference electrode.

制备电池：将六水氯化铝溶解到250ml去离子水中配置0.2mol/L氯化铝溶液；并以上述二硫化钼纳米花负极材料为负极，石墨棒电极 为对电极，以银-氯化银为参比电极。

[0059]

Example 2

实施例2

[0060]

1.412 g of (NH₄)₆Mo₇O₂₄・4H<sub>2< /sub>O and 1.46 g of N₂H₄CS were dissolved sequentially in 60 ml of water and stirred for at least 30 minutes to prepare a homogeneous aqueous solution. This solution was then poured into a 50 ml reaction vessel and reacted at 220 °C for 48 h. After the reaction was completed, the resulting suspension was centrifuged at 7000 r/min and washed repeatedly with deionized water and anhydrous ethanol at least three times. The precipitate was dried in a blower dryer at 80 °C for 12 h to obtain MoS₂ (molybdenum disulfide nanoflower material).

将1.412g的(NH₄)₆Mo₇O₂₄・4H₂O和1.46g的N₂H₄CS依次溶解于60ml水中，搅拌至少30分钟，配成均匀的混合水溶液，倒入到50ml的反应釜中，220°C反应48h；反应结束后，将所得悬浮液以7000r/min的转速离心分离，并用去离子水和无水乙醇反复清洗3次以上；将沉淀物在鼓风干燥机80°C干燥12h，得到MoS₂(二硫化钼纳米花材料)。

[0061]

MoS₂:Super-P:PTFE = 80:15:5 (mass ratio) was slurried, uniformly coated on stainless steel, and then dried in a vacuum drying oven at 60-120°C to prepare molybdenum disulfide nanoflower anode material.

将MoS₂：Super-P：PTFE＝80:15:5(质量比)进行制浆，均匀涂覆在不锈钢上，然后在60～120°C真空干燥箱中烘干，制成二硫化钼纳米花负极材料。

[0062]

Battery preparation: Dissolve aluminum sulfate octadeca in 250 ml of deionized water to prepare a 2 mol/L aluminum sulfate solution. Use the above molybdenum disulfide nanoflower anode material as the anode, graphite rod electrode as the counter electrode, and silver-silver chloride as the reference electrode.

制备电池：将十八水硫酸铝溶解到250ml去离子水中配置2mol/L硫酸铝溶液，并以上述二硫化钼纳米花负极材料为负极，石墨棒电极 为对电极，以银-氯化银为参比电极。

[0063]

Example 3

实施例3

[0064]

A pre-mixture was prepared by mixing (NH₄)₆Mo<sub>7< /sub>O₂₄・4H₂O and N₂H₄CS in a molar ratio of 1:7 with water and stirring for 35 min. The pre-mixture was then poured into a reactor and reacted at 200°C for 30 h. After the reaction was completed, the suspension was centrifuged at 6000 r/min to obtain the precipitate, which was repeatedly washed four times with deionized water and anhydrous ethanol. The precipitate was then dried in a blower at 70°C for 18 h to obtain molybdenum disulfide nanoflower materials.

将摩尔比为1:7的(NH₄)₆Mo₇O₂₄・4H₂O和N₂H₄CS加水混合，搅拌35min，制得预制混合物；将预制混合物倒入反应釜中，在200°C条件下高温反应30h，反应完成后将悬浮液在6000r/min离心得到沉淀物，用去离子水和无水乙醇重复冲洗4次，在鼓风干燥机中以70°C，干燥18h，得到二硫化钼纳米花材料。

[0065]

A slurry was prepared by mixing molybdenum disulfide nanoflower material, conductive agent, and binder in a weight ratio of 90:8:2. The slurry was coated onto stainless steel and dried in a vacuum drying oven at 100°C to produce molybdenum disulfide nanoflower anode material.

将重量比为90:8:2的二硫化钼纳米花材料、导电剂和粘结剂制成浆液，将浆液涂覆于不锈钢，在100°C真空干燥箱中烘干，制成二硫化钼纳米花负极材料。

The conductive agent is a mixture of Ketjen black and graphene, and the binder is a mixture of sodium carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR).

导电剂为科琴黑和石墨烯的混合物，粘结剂为羧甲基纤维素钠(CMC)和丁苯橡胶(SBR)的混合物。

[0066]

Battery preparation: Aluminum nitrate was prepared into an aqueous electrode solution containing aluminum ions with a concentration of 0.2 mol/L. The above-mentioned molybdenum disulfide nanoflower anode material was used as the anode, graphite rod electrode was used as the counter electrode (positive electrode), and silver-silver chloride was used as the reference electrode.

制备电池：将硝酸铝制成浓度为0.2mol/L的含铝离子水系电极液，以上述二硫化钼纳米花负极材料为负极，石墨棒电极 为对电极(正极)，以银-氯化银为参比电极。

[0067]

Example 4

实施例4

[0068]

A pre-mixture was prepared by mixing (NH₄)₆Mo<sub>7<
/sub>O₂₄・4H₂O and N₂H₄CS in a molar ratio of 1:8 with water and stirring for 40 min. The pre-mixture was then poured into a reactor and reacted at 240°C for 10 h. After the reaction was completed, the suspension was centrifuged at 8000 r/min to obtain the precipitate, which was repeatedly washed four times with deionized water and anhydrous ethanol. The precipitate was then dried in a blower at 90°C for 11 h to obtain molybdenum disulfide nanoflower materials.

将摩尔比为1:8的(NH₄)₆Mo₇O<sub>24<
/sub>・4H₂O和N₂H₄CS加水混合，搅拌40min，制得预制混合物；将预制混合物倒入反应釜中，在240°C条件下高温反应10h，反应完成后将悬浮液在8000r
/min离心得到沉淀物，用去离子水和无水乙醇重复冲洗4次，在鼓风干燥机中以90°C，干燥11h，得到二硫化钼纳米花材料。

[0069]

A slurry was prepared by mixing molybdenum disulfide nanoflower material, conductive agent, and binder in a weight ratio of 80:14:6. The slurry was coated onto stainless steel and dried in a vacuum drying oven at 60°C to produce molybdenum disulfide nanoflower anode material.

将重量比为80:14:6的二硫化钼纳米花材料、导电剂和粘结剂制成浆液，将浆液涂覆于不锈钢，在60°C真空干燥箱中烘干，制成二硫化钼纳米花负极材料。

The conductive agent is a mixture of acetylene black, Super-P (conductive carbon black) and Ketjen black, and the binder is a mixture of polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and sodium carboxymethyl cellulose (CMC).

导电剂为乙炔黑、Super-P(导电炭黑)和科琴黑的混合物，粘结剂为聚四氟乙烯(PTFE)、聚偏氟乙烯(PVDF)和羧甲基纤维素钠(CMC)的混合物。

[0070]

Battery preparation: Aluminum acetate was prepared into an aqueous electrode solution containing aluminum ions with a concentration of 1.6 mol/L. The above-mentioned molybdenum disulfide nanoflower anode material was used as the anode, graphite rod electrode was used as the counter electrode (positive electrode), and silver-silver chloride was used as the reference electrode.

制备电池：将乙酸铝制成浓度为1.6mol/L的含铝离子水系电极液，以上述二硫化钼纳米花负极材料为负极，石墨棒电极 为对电极(正极)，以银-氯化银为参比电极。

[0071]

Example 5

实施例5

[0072]

Sodium molybdate and thioacetate in a molar ratio of 1:7.5 were mixed with water and stirred for 32 min to obtain a pre-mixture. The pre-mixture was poured into a reaction vessel and reacted at 236°C for 24 h. After the reaction was completed, the suspension was centrifuged at

7500 r/min to obtain the precipitate, which was repeatedly washed 5 times with deionized water and anhydrous ethanol. The precipitate was then dried in a blower at 86°C for 13 h to obtain molybdenum disulfide nanoflower materials.

将摩尔比为1:7.5的钼酸钠和硫代乙酰加水混合，搅拌32min，制得预制混合物；将预制混合物倒入反应釜中，在236°C条件下高温反应24h，反应完成后将悬浮液在7500r/min离心得到沉淀物，用去离子水和无水乙醇重复冲洗5次，在鼓风干燥机中以86°C，干燥13h，得到二硫化钼纳米花材料。

[0073]

A slurry was prepared by mixing molybdenum disulfide nanoflower material, conductive agent, and binder in a weight ratio of 80:18:2. The slurry was coated onto tantalum sheets and dried in a vacuum drying oven at 100°C to prepare molybdenum disulfide nanoflower anode material.

将重量比为80:18:2的二硫化钼纳米花材料、导电剂和粘结剂制成浆液，将浆液涂覆于钽片，在100°C真空干燥箱中烘干，制成二硫化钼纳米花负极材料。

The conductive agent is conductive carbon black, and the binder is styrene-butadiene rubber (SBR).

导电剂为导电炭黑，粘结剂为丁苯橡胶(SBR)。

[0074]

Battery preparation: Aluminum chloride and aluminum sulfate were mixed to prepare an aluminum ion-containing aqueous electrode solution with a concentration of 1.2 mol/L. The above-mentioned molybdenum disulfide nanoflower anode material was used as the anode, graphite rod electrode was used as the counter electrode (positive electrode), and silver-silver chloride was used as the reference electrode.

制备电池：将氯化铝和硫酸铝混合制成浓度为1.2mol/L的含铝离子水系电极液，以上述二硫化钼纳米花负极材料为负极，石墨棒电极 为对电极(正极)，以银-氯化银为参比电极。

[0075]

Example 6

实施例6

[0076]

A pre-mixture was prepared by mixing (NH₄)₆Mo₇O₂₄・4H₂O, sodium molybdate, N₂H₄CS, and thioacetamide in a molar ratio of 1:7 with water and stirring for 45 min. The pre-mixture was then poured into a reaction vessel and reacted at 260°C for 24 h. After the reaction was completed, the suspension was centrifuged at 6500 r/min to obtain the precipitate, which was repeatedly washed three times with deionized water and anhydrous ethanol, and then dried at 85°C in a blower dryer to obtain molybdenum disulfide nanoflower materials.

将摩尔比为1:7的(NH₄)₆Mo₇O₂₄・4H₂O、钼酸钠和N₂H₄CS和硫代乙酰胺加水混合，搅拌45min，制得预制混合物；将预制混合物倒入反应釜中，在260°C条件下高温反应24h，反应完成后将悬浮液在6500r/min离心得到沉淀物，用去离子水和无水乙醇重复冲洗3次，在鼓风干燥机中以85°C，干燥，得到二硫化钼纳米花材料。

[0077]

A slurry was prepared by mixing molybdenum disulfide nanoflower material, conductive agent, and binder in a weight ratio of 80:10:10. The slurry was coated onto a titanium sheet and dried in a vacuum drying oven at 100°C to produce a molybdenum disulfide nanoflower anode material.

将重量比为80:10:10的二硫化钼纳米花材料、导电剂和粘结剂制成浆液，将浆液涂覆于钛片，在100°C真空干燥箱中烘干，制成二硫化钼纳米花负极材料。

The conductive agent is acetylene black, and the binder is polytetrafluoroethylene (PTFE).

导电剂为乙炔黑，粘结剂为聚四氟乙烯(PTFE)。

[0078]

Battery preparation: Aluminum chloride was prepared into an aqueous electrode solution containing aluminum ions with a concentration of 1.5 mol/L. The above-mentioned molybdenum disulfide nanoflower anode material was used as the anode, lithium iron phosphate electrode was used as the counter electrode (positive electrode), and silver-silver chloride was used as the reference electrode.

制备电池：将氯化铝制成浓度为1.5mol/L的含铝离子水系电极液，以上述二硫化钼纳米花负极材料为负极，磷酸铁锂电极 为对电极(正极)，以银-氯化银为参比电极。

[0079]

Example 7

实施例7

[0080]

Commercially available molybdenum disulfide nanoflower material was mixed with conductive agent and binder to form a slurry with a weight ratio of 80:15:5. The slurry was coated onto titanium sheets and dried in a vacuum drying oven at 100°C to produce molybdenum disulfide nanoflower anode material.

选用市售的二硫化钼纳米花材料与导电剂、粘结剂混合制成浆液，重量比为80:15:5，将浆液涂覆于钛片，在100°C真空干燥箱中烘干，制成二硫化钼纳米花负极材料。

The conductive agent is acetylene black, and the binder is polytetrafluoroethylene (PTFE).

导电剂为乙炔黑，粘结剂为聚四氟乙烯(PTFE)。

[0081]

Battery preparation: Aluminum chloride was prepared into an aqueous electrode solution containing aluminum ions with a concentration of 1.5 mol/L. The above-mentioned molybdenum disulfide nanoflower anode material was used as the anode, lithium iron phosphate electrode was used as the counter electrode (positive electrode), and silver-silver chloride was used as the reference electrode.

制备电池：将氯化铝制成浓度为1.5mol/L的含铝离子水系电极液，以上述二硫化钼纳米花负极材料为负极，磷酸铁锂电极 为对电极(正极)，以银-氯化银为参比电极。

[0082]

Example 8

实施例8

[0083]

1.412 g of (NH₄)₆Mo₇O₂₄・4H₂O and 1.46 g of N₂H₄CS were dissolved sequentially in 60 ml of water and stirred for at least 30 minutes to prepare a homogeneous aqueous solution. This solution was then poured into a 50 ml reaction vessel and reacted at 220 °C for 48 h. After the reaction was completed, the resulting suspension was centrifuged at 7000 r/min and washed repeatedly with deionized water and anhydrous ethanol at least three times. The precipitate was dried in a blower dryer at 80 °C for 12 h to obtain MoS₂ (molybdenum disulfide nanoflower material).

将1.412g的(NH₄)₆Mo₇O₂₄・4H₂O和1.46g的N₂H₄CS依次溶解于60ml水中，搅拌至少30分钟，配成均匀的混合水溶液，倒入到50ml的反应釜中，220°C反应48h；反应结束后，将所得悬浮液以7000r/min的转速离心分离，并用去离子水和无水乙醇反复清洗3次以上；将沉淀物在鼓风干燥机80°C干燥12h，得到MoS₂(二硫化钼纳米花材料)。

[0084]

MoS₂:Super-P:PTFE = 80:15:5 (mass ratio) was slurried, uniformly coated on stainless steel, and then dried in a vacuum drying oven at 60-120°C to produce molybdenum disulfide nanoflower anode material.

将MoS₂：Super-P：PTFE＝80:15:5(质量比)进行制浆，均匀涂覆在不锈钢上，然后在60～120°C真空干燥箱中烘干，制成二硫化钼纳米花负极材料。

[0085]

Battery preparation: Aluminum chloride octadecahydrate was dissolved in 250 ml of deionized water to prepare a 1 mol/L aluminum chloride solution. The above molybdenum disulfide nanoflower anode material was used as the anode, graphite rod electrode was used as the counter electrode, and silver-silver chloride was used as the reference electrode.

制备电池：将十八水氯化铝溶解到250ml去离子水中配置1mol/L氯化铝溶液，并以上述二硫化钼纳米花负极材料为负极，石墨棒电极 为对电极，以银-氯化银为参比电极。

[0086]

Comparative Example 1

对比例1

[0087]

Comparative Example 1 prepared molybdenum disulfide nanoflower materials, anode materials, and batteries using a method similar to that in Example 3. In the preparation of molybdenum disulfide nanoflower materials, the molar ratio of (NH₄)₆Mo₇O₂₄・4H₂O and N₂H₄CS was 1:4, and other method steps were the same as in Example 3.

对比例1采用与实施例3相似的方法制备二硫化钼纳米花材料、负极材料和电池，其中，制备二硫化钼纳米花材料时，(NH₄)₆Mo₇O₂₄・4H₂O和N₂H₄CS的摩尔比为1:4，其他方法步骤参照实施例3。

[0088]

Comparative Example 2

对比例2

[0089]

Comparative Example 2 prepared molybdenum disulfide nanoflower materials, anode materials, and batteries using a method similar to that in Example 3. The weight ratio of molybdenum disulfide nanoflower materials, conductive agents, and binders was 55:28:17, and other method steps were the same as in Example 3.

对比例2采用与实施例3相似的方法制备二硫化钼纳米花材料、负极材料和电池，其中，二硫化钼纳米花材料、导电剂和粘结剂的重量比为55:28:17，其他方法步骤参照实施例3。

[0090]

Comparative Example 3

对比例3

[0091]

Comparative Example 3 uses a similar method to Example 3 to prepare molybdenum disulfide nanoflower materials, negative electrode materials, and batteries. In this case, PC (propylene carbonate) is used as the electrolyte when preparing the battery, and other methods and steps are the same as in Example 3.

对比例3采用与实施例3相似的方法制备二硫化钼纳米花材料、负极材料和电池，其中，制备电池时选用PC(碳酸丙烯酯)为电解液，其他方法步骤参照实施例3。

[0092]

Comparative Example 4

对比例4

[0093]

Comparative Example 4 prepared molybdenum disulfide nanoflower materials, anode materials, and batteries using a method similar to that of Example 3. Specifically, when preparing the molybdenum disulfide nanoflower materials, the molar ratio of (NH<sub>4< /sub>)₆Mo₇O₂₄・4H₂O and N<sub>2< /sub>H₄CS was 1:4, and the weight ratio of the molybdenum disulfide nanoflower materials, conductive agent, and binder was 55:28:17. When preparing the batteries, PC (propylene carbonate) was used as the electrolyte. Other method steps were the same as in Example 3.

对比例4采用与实施例3相似的方法制备二硫化钼纳米花材料、负极材料和电池，其中，制备二硫化钼纳米花材料时，(NH₄)₆Mo₇O₂₄・4H₂O和N₂H₄CS的摩尔比为1:4，二硫化钼纳米花材料、导电剂和粘结剂的重量比为55:28:17，制备电池时选用PC(碳酸丙烯酯)为电解液，其他方法步骤参照实施例3。

[0094]

The specific capacity retention rate of the batteries prepared in Examples 1-8 and Comparative Examples 1-4 was tested for cyclic discharge: Test method: The discharge capacity was measured under the conditions of 0.5C/0.5C and 2.75-4.4V charge and discharge. The capacity retention rate was measured after 100 cycles at this rate. The results are shown in Table 1.

对实施例1-8和的对比例1-4制备的电池进行循环放电比容保持率的测试：测试方法：在0.5C/0.5C，2.75-4.4V充放的条件下，测放电容量，该倍率下，100次循环后测容量保持率，结果见表1。

[0095]

Table 1. Volume retention rate after 100 cycles

表1 100次循环后测容量保持率

[0098]

As can be seen from the results in Table 1, the methods for preparing molybdenum disulfide nanoflowers, preparing negative electrode materials, and preparing batteries of the present invention can enable batteries to have better capacity retention.

由表1的结果可知，本发明的制备二硫化钼纳米花的方法、制备负极材料的方法，制备电池的方法能够使电池具有较佳的容量保持率。

[0099]

As shown in Figure 2, molybdenum disulfide nanoflowers have a high specific capacity at a current density of 1 A/g, but the specific capacity decreases rapidly with increasing current density.

由图2可知，二硫化钼纳米花在1A/g的电流密度下具有较高的比容量，随着电流密度的增大，比容量迅速降低。

When the current density recovered to 1 A/g, the capacity did not decrease significantly, indicating that molybdenum disulfide nanoflowers have good capacity recovery ability.

当电流密度恢复到1A/g时，容量没有明显的下降，说明二硫化钼纳米花具有较好的容量恢复能力。

[0100]

As shown in Figure 3, the specific capacity of molybdenum disulfide nanoflowers gradually decreases with the increase of the number of cycles, but the cycle can still continue. This indicates that molybdenum disulfide nanoflowers can be used as electrode materials for aqueous aluminum-ion batteries.

由图3可知，随着循环次数的提升，二硫化钼纳米花的比容量逐渐降低，但是仍能保证循环继续，这说明二硫化钼纳米花可作为水系铝离子电池电极材料。

[0101]

In summary, the beneficial effects of the preparation method of molybdenum disulfide nanoflower material in the embodiments of the present invention are as follows: The preparation method of molybdenum disulfide nanoflower material provided by the present invention involves dissolving and mixing molybdate and sulfur source, then reacting at high temperature to obtain a suspension, followed by centrifugation of the suspension and washing of the precipitate to obtain molybdenum disulfide nanoflower material. The above method is simple and easy to operate, and the obtained molybdenum disulfide nanoflower material has a graphene-like layered structure and theoretical capacity.

综上所述，本发明实施例的二硫化钼纳米花材料的制备方法的有益效果是：本发明提供的二硫化钼纳米花材料的制备方法通过价格钼酸盐和硫源溶解、混合，再高温反应制得悬浮液，然后对悬浮液离心后对沉淀物进行清洗，以得到二硫化钼纳米花材料，上述方法简答易操作，且制得的二硫化钼纳米花材料具有类石墨烯层状结构和理论容量。

[0102]

The beneficial effects of the molybdenum disulfide nanoflower material in this invention are as follows: the molybdenum disulfide nanoflower material is prepared by the above method, and it has a graphene-like layered structure and theoretical capacity. Moreover, the structure of the molybdenum disulfide nanoflower has a large specific surface area and has good application prospects.

本发明实施例的二硫化钼纳米花材料的有益效果是：该二硫化钼纳米花材料由上述的方法制得，其具有类石墨烯层状结构和理论容量，且该二硫化钼纳米花的机构具有较大的比表面积，具有较佳的应用前景。

[0103]

The beneficial effect of the preparation method of molybdenum disulfide nanoflower anode material in this invention is that the anode raw material used in the preparation method is the above-mentioned molybdenum disulfide nanoflower material, which can improve the capacitance recovery ability of the anode material.

本发明实施例的二硫化钼纳米花负极材料的制备方法的有益效果是：该制备方法中采用的负极原料为上述的二硫化钼纳米花材料，能够改善负极材料的电容量恢复能力。

[0104]

The beneficial effects of the molybdenum disulfide nanoflower anode material in this invention are: the molybdenum disulfide nanoflower anode material is prepared by the above method and has better capacity recovery capability.

本发明实施例的二硫化钼纳米花负极材料的有益效果是：该二硫化钼纳米花负极材料是由上述的方法制备的，具有较佳的电容量恢复能力。

[0105]

The beneficial effect of the battery in this embodiment of the invention is that the negative electrode material of the battery is the above-mentioned molybdenum disulfide nanoflower negative electrode material, which has better capacity recovery capability, thereby improving the capacity recovery capability of the battery.

本发明实施例的电池的有益效果是：该电池的负极材料为上述的二硫化钼纳米花负极材料，二硫化钼纳米花负极材料的电容量恢复能力较佳，以改善电池的电容量恢复能力。

[0106]

The beneficial effects of the battery in this embodiment of the invention are as follows: the negative electrode material of the battery is molybdenum disulfide nanoflower material, and the electrolyte is an aluminum ion-containing aqueous electrolyte, which improves the battery's capacity recovery capability on the one hand, and improves the battery's safety performance on the other hand.

本发明实施例的电池的有益效果是：该电池的负极材料为二硫化钼纳米花材料，电解液为含铝离子水系电解液，一方面改善了该电池的电容量恢复能力，另一方面改善了电池的安全性能。

[0107]

The embodiments described above are some, but not all, of the embodiments of the present invention.

以上所描述的实施例是本发明一部分实施例，而不是全部的实施例。

The detailed description of the embodiments of the present invention is not intended to limit the scope of the claimed invention, but merely to illustrate selected embodiments of the invention.

本发明的实施例的详细描述并非旨在限制要求保护的本发明的范围，而是仅仅表示本发明的选定实施例。

Based on the embodiments of this invention, all other embodiments obtained by those skilled in the art without inventive effort are within the scope of protection of this invention.

基于本发明中的实施例，本领域普通技术人员在没有作出创造性劳动前提下所获得的所有其他实施例，都属于本发明保护的范围。