Notice

DESCRIPTION CN109019616A

Preparation and application of a three-dimensional hybrid material of silica/molybdenum disulfide

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一种二氧化硅/二硫化钼三维杂化材料的制备及应用

[0001]

Technical Field

技术领域

[0002]

This invention relates to the preparation and application of a three-dimensional hybrid material of silicon dioxide/molybdenum disulfide, belonging to the field of inorganic nano-hybrid material preparation.

本发明涉及一种二氧化硅/二硫化钼三维杂化材料的制备及应用，属于无机纳米杂化材料制备领域。

[0003]

Background Technology

背景技术

[0004]

In recent years, the application fields of various civil, decorative and industrial fibers and nonwoven fabrics have expanded rapidly, becoming an indispensable part of daily life and industrial production.

近年来，各类民用、装饰用和产业用纤维及非织造布的应用领域快速扩大，成为日常生活和工业生产不可或缺的部分。

However, these materials are inherently flammable and easily ignited by external heat sources. During combustion, they release large amounts of heat, smoke, and toxic gases, seriously endangering life and property. According to statistics, fires of all sizes in my country cause more than 500 million yuan in losses to society every year, and serious fires caused by the flammability of fiber products account for more than half of these.

然而，这些材料本身具有易燃特性，易被外部热源引燃，并在燃烧过程中释放大量的热量、烟气及有毒气，严重危及生命财产安全，据统计，我国平均每年的大小火灾都会给社会造成5亿元以上的损失，而由纤维制品的易燃而引发的严重火灾就占了一半以上。

Developing high-performance, low-dosage flame retardants is an effective way to improve the added value and safety of fiber products, making them less prone to ignition or slowing down the burning rate.

开发高性能、低用量的阻燃剂，是提高纤维制品的附加值与安全性，使其不易着火燃烧或能够减慢燃烧速度的一种有效方法。

[0005]

Flame retardants can be classified into organic flame retardants and inorganic flame retardants according to their chemical structure.

阻燃剂按化学结构可分为有机阻燃剂和无机阻燃剂。

Organic flame retardants include organophosphorus, nitrogen, and boron-based flame retardants. When added to the material matrix, these flame retardants have problems such as high dosage (>20%), poor compatibility, environmental unfriendliness, and poor thermal stability. When they react with fiber materials, they can easily reduce their mechanical properties and water resistance.

有机类阻燃剂包括有机磷、氮、硼系阻燃剂，当添加到材料基体中时，该类阻燃剂存在用量大(>20%)、相容性较差、不环保、热稳定性较差等问题；当与纤维材料反应时，易造成其力学性能、耐水洗性能等的降低。

Inorganic flame retardants mainly include metal hydrates, red phosphorus, boron compounds, and antimony compounds. In particular, silica nanoparticles have advantages over organic flame retardants, such as good thermal stability, non-volatility, long-lasting effect, and low price. However, metal hydroxides have high polarity and poor compatibility with polymer materials. Furthermore, the large amount added during use can greatly deteriorate the physical properties of the material.

无机类阻燃剂主要有金属水合物、红磷、硼类化合物、锑类化合物等，特别是二氧化硅纳米粒子，相比于有机阻燃剂，其具有热稳定性好、不挥发、效果持久、价格便宜等特点，然而金属氢氧化物由于极性大,与高分子材料相容性差,并且在使用过程中添加量大，会极大地恶化材料的物理性能。

[0006]

Inorganic nanomaterials have become a new favorite in the flame retardant field due to their excellent gas barrier properties, good thermal stability, low addition amount, green and environmentally friendly properties, and minimal negative impact on the mechanical properties and thermal stability of the matrix, and can even play a reinforcing role.

无机纳米材料由于其具有优异的气体阻隔性能、优良热稳定性、添加量少、绿色环保，而且对基体的力学性能及热稳定性的负面影响较小,甚至还可以发挥增强效应，已成为阻燃领域的新宠。

Molybdenum disulfide, as a new type of flame retardant material, has relatively low thermal conductivity and a high melting point (1185°C). It can effectively inhibit the penetration of external heat and oxygen and the release of toxic substances. Molybdenum atoms can also catalyze the formation of a large number of carbon layers in the matrix to reduce heat exchange. However, the flame retardant efficiency of molybdenum disulfide alone is limited, as it often exhibits severe aggregation in the polymer matrix, weakening the interfacial interaction between molybdenum disulfide and the matrix.

二硫化钼作为一种新兴的阻燃材料，具有相对较低的热导率和高熔点(1185℃)，能有效抑制外部热量及氧气的渗透和有毒物质的释放，钼原子还能催化基体形成大量碳层以减少热交换。 但是，单靠二硫化钼的阻燃效率是有限的，它往往在聚合物基体中表现出严重的聚集，削弱了二硫化钼与基体的界面相互作用。

[0007]

To improve the flame retardant efficiency and interfacial interaction of molybdenum disulfide, scholars at home and abroad have conducted research on the synergistic flame retardancy of molybdenum disulfide inorganic hybrids. For example, in 2014, Xiaming Feng et al. published in the Journal of Materials Chemistry A, Volume 2, pp. 13299-13308, that they prepared molybdenum disulfide/cobalt hydroxyoxide (MoS2/CoOOH) hybrid materials by in-situ synthesis, which can significantly improve the thermal stability of epoxy resin and reduce CO release.

为了提高二硫化钼的阻燃效率及界面相互作用，国内外学者对二硫化钼无机杂化协同阻燃进行研究，如：2014年XiamingFeng等在《Journal of Materials Chemistry A》第2卷13299-13308页发表通过原位合成法制备二硫化钼/羟基氧化钴(MoS2/CoOOH)杂化材料，能明显提高环氧树脂的热稳定性并减少CO的释放。

In 2016, Dong Wang et al. published in ACS Applied Materials & Interfaces, Vol. 8, pp. 34735-34743, on the use of molybdenum disulfide nanosheets/graphene hybrid materials for flame retardancy of unsaturated polyesters, achieving a good synergistic flame retardant effect. In 2017, Hélio Ribeiro et al. published in ACS Applied Materials & Interfaces that molybdenum disulfide/hexagonal boron nitride nanocomposites were used for flame retardancy of epoxy resins, which effectively improved their thermal stability. Silica, as an inorganic nano flame retardant, has the advantages of being environmentally friendly and non-toxic, and can improve the thermal stability of materials and the stability of the carbon layer. Currently, Keqing Zhou reported on the research of molybdenum disulfide nanosheets/silica hybrid materials for flame-retardant epoxy resins in the Journal of Hazardous Materials, Volume 344, pp. 1078-1089 (2018). However, the molybdenum disulfide nanosheets in this hybrid material contain fewer active sites, and the silica particles are large and non-uniform (150nm), resulting in low silica loading, difficult morphology control, and insignificant flame-retardant effect.

2016年Dong Wang等在《ACS AppliedMaterials&Interfaces》第8卷34735-34743页发表二硫化钼纳米片/石墨烯杂化材料用于不饱和聚酯的阻燃，达到了较好的协同阻燃效果。 2017年HélioRibeiro等在《ACS AppliedMaterials &Interfaces》发表二硫化钼/六方氮化硼纳米杂化物用于环氧树脂阻燃，有效提高了其热稳定性。 二氧化硅作为一种无机纳米阻燃剂，具有环保、无毒的优点，能提高材料的热稳定性及碳层的稳定性。 目前，Keqing Zhou在《Journal of Hazardous Materials》第

344卷1078-1089页(2018年)报道了二硫化钼纳米片/二氧化硅杂化材料用于阻燃环氧树脂的研究，但该杂化材料中二硫化钼纳米片所含活性位点较少，二氧化硅粒径大且不均匀(150nm)，使得二氧化硅负载量低，形貌难以控制，阻燃效果不显著。

[0008]

The aforementioned literature all uses molybdenum disulfide nanosheets as a substrate to prepare nano-hybrid materials. Sheet materials are prone to stacking and have poor dispersibility. They have fewer active reaction sites (sulfur defects, vacancies, and edge sites), smaller specific surface area and loadable area, making it difficult to effectively prepare molybdenum disulfide hybrid flame retardants with multiple defects, high loading capacity and controllable morphology, and thus it is difficult to maximize the flame retardant efficiency.

上述文献都是以二硫化钼纳米片为基底制备纳米杂化材料，片层材料容易堆叠，分散性不好，其活性反应位点(硫缺陷、空位、边缘位点)较少，比表面积及可负载区域较小，难以达到多缺陷、高负载量及形貌可控二硫化钼杂化阻燃剂的有效制备，阻燃效率难以达到最大化。

[0009]

Summary of the Invention

发明内容

[0010]

To address the aforementioned issues and maximize flame retardant efficiency, this invention designs a method for in-situ loading ultra-small functionalized silica nanoparticles onto a layered structure resembling a sandwich, using molybdenum disulfide as a carrier. This constructs a three-dimensional hybrid flame retardant of silica/molybdenum disulfide. The flame retardant consists of silica nanoparticles uniformly loaded onto molybdenum disulfide nanoflowers. The preparation process is simple, green, and efficient. The sandwich-like layered structure of molybdenum disulfide is a nanoflower structure that replaces the traditional nanosheet structure. Its three-dimensional structure and large space effectively increase the loading of silica nanoparticles and improve the flame retardant efficiency, matrix compatibility, and mechanical reinforcement effect of the hybrid flame retardant.

为了解决上述问题，是阻燃效率实现最大化，本发明设计了一种三层原子形成类似三明治的层状结构的二硫化钼作为载体，原位负载超小功能化二氧化硅纳米粒子的方法，构建了一种二氧化硅/二硫化钼三维杂化材料阻燃剂，该阻燃剂由二氧化硅纳米颗粒均匀负载到二硫化钼纳米花构成，制备过程简单，绿色高效，其中类似三明治层状结构的二硫化钼是一种纳米花结构，取代了传统的纳米片结构，立体结构，空间大，能有效增加纳米二氧化硅纳米粒子的负载量，并提高杂化阻燃剂的阻燃效率、基体的相容性及力学增强效应。

[0011]

The first objective of this invention is to provide a method for preparing a three-dimensional hybrid material of silica/molybdenum disulfide, the method comprising: synthesizing molybdenum disulfide nanoflowers from a molybdenum source and a sulfur source using a hydrothermal method; then using the obtained molybdenum disulfide nanoflowers as a substrate, chemically bonding them with a silicon source and a thiol-containing silane coupling agent to synthesize ultra-small silica nanoparticles in situ and uniformly loading them onto the molybdenum disulfide nanoflowers to obtain a three-dimensional hybrid material of silica/molybdenum disulfide.

本发明的第一个目的是提供一种二氧化硅/二硫化钼三维杂化材料的制备方法，所述方法包括：将钼源和硫源利用水热法合成二硫化钼纳米花，然后将所得到的二硫化钼纳米花作为基底，与硅源、含巯基的硅烷偶联剂通过化学键键接，原位合成超小二氧化硅纳米粒子并均匀负载到二硫化钼纳米花上，得到二氧化硅/二硫化钼三维杂化材料。

[0012]

In one embodiment of the present invention, the molybdenum source includes one of ammonium molybdate tetrahydrate, sodium molybdate, and molybdenum oxide.

本发明的一种实施方式中，所述钼源包括四水合钼酸铵、钼酸钠、氧化钼中的一种。

[0013]

In one embodiment of the present invention, the sulfur source includes one of thiourea, thioacetamide, and sodium thiocyanate.

本发明的一种实施方式中，所述硫源包括硫脲、硫代乙酰胺、硫氰酸钠中的一种。

[0014]

In one embodiment of the present invention, the mass fraction ratio of the added molybdenum source and sulfur source is (1-1.5):(2-3).

本发明的一种实施方式中，所述钼源和硫源的添加量质量分数比例为(1～1.5)：(2～3)。

[0015]

In one embodiment of the present invention, the silicon source includes one of tetraethyl orthosilicate and sodium silicate.

本发明的一种实施方式中，所述硅源包括正硅酸四乙酯、硅酸钠中的一种。

[0016]

In one embodiment of the present invention, the mercapto-containing silane coupling agent includes one of γ-mercaptopropyltriethoxysilane (KH580) and (3-mercaptopropyl) trimethoxysilane (KH590).

本发明的一种实施方式中，所述含巯基的硅烷偶联剂包括γ-巯丙基三乙氧基硅烷(KH580)，(3-巯基丙基)三甲氧基硅烷(KH590)中的一种。

[0017]

In one embodiment of the present invention, the volume ratio of the silicon source and the mercapto-containing silane coupling agent is (2-4):(0.5-1.5).

本发明的一种实施方式中，所述硅源、含巯基的硅烷偶联剂的添加量体积比为(2～4)：(0.5～1.5)。

[0018]

In one embodiment of the present invention, the mass-to-volume ratio of the molybdenum disulfide nanoflowers to the silicon source is (0.1-0.2):(2-4).

本发明的一种实施方式中，所述二硫化钼纳米花与硅源的质量体积比为(0.1～0.2)：(2～4)。

[0019]

In one embodiment of the present invention, the particle size of the molybdenum disulfide nanoflowers is 100-200 nm.

本发明的一种实施方式中，所述二硫化钼纳米花的粒径为100-200nm。

[0020]

In one embodiment of the present invention, the particle size of the ultra-small silica nanoparticles is 10-15 nm.

本发明的一种实施方式中，所述超小二氧化硅纳米粒子的粒径为10-15nm。

[0021]

In one embodiment of the present invention, the method specifically includes the following steps:

本发明的一种实施方式中，所述方法具体包括如下步骤：

[0022]

(1) Add molybdenum source and sulfur source to deionized water to dissolve, stir to prepare a solution, mix evenly by ultrasonication, transfer to a hydrothermal reactor, react at 160-240°C for 8-24h, wash by centrifugation with deionized water, and dry at 60°C to obtain molybdenum disulfide nanoflowers.

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(1)将钼源、硫源加入去离子水中溶解，搅拌配成溶液，超声混合均匀后转入水热釜中，160～240°C反应8～24h，去离子水离心清洗，60°C烘干，得到二硫化钼纳米花。

[0023]

(2) Take a small amount of molybdenum disulfide nanoflowers obtained in step (1), disperse them in deionized water by ultrasonication, add a silicon source, adjust the pH to 8-10.5, react at 40-65°C and 400-600rpm for 12-24h, then add a silane coupling agent containing mercapto groups and continue the reaction for 8-12h.

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(2)取少量步骤(1)中得到的二硫化钼纳米花，超声分散在去离子水中，加入硅源，调节pH＝8-10.5，40～65°C，400～600rpm，反应12～24h，再加入含巯基的硅烷偶联剂，继续反应8～12h。
The molybdenum disulfide nanoflowers were washed alternately by centrifugation with deionized water and dried under vacuum at 60°C to obtain a three-dimensional hybrid material of molybdenum disulfide nanoflowers supported on ultra-small functionalized silica.

乙醇与去离子水交替离心清洗，60°C真空干燥，得到二硫化钼纳米花原位负载超小功能化二氧化硅的二硫化钼三维杂化材料。

[0024]

The second objective of this invention is to provide a three-dimensional hybrid material of silicon dioxide/molybdenum disulfide prepared by the above method.

本发明的第二个目的是提供一种利用上述方法制备得到的二氧化硅/二硫化钼三维杂化材料。

[0025]

The third objective of this invention is to provide a flame-retardant polyacrylonitrile fiber, which is obtained by adding the above-mentioned silica/molybdenum disulfide three-dimensional hybrid material to a polyacrylonitrile spinning solution and then wet spinning.

本发明的第三个目的是提供一种阻燃聚丙烯腈纤维，所述阻燃聚丙烯腈纤维是将上述二氧化硅/二硫化钼三维杂化材料添加到聚丙烯腈纺丝液中，湿法纺丝即可得到。

[0026]

The fourth objective of this invention is to apply the above-mentioned silicon dioxide /molybdenum disulfide three-dimensional hybrid material to the field of flame retardancy.

本发明的第四个目的是将上述二氧化硅/二硫化钼三维杂化材料应用于阻燃领域中。

[0027]

Beneficial effects of this invention:

本发明有益效果：

[0028]

This invention utilizes inexpensive and readily available raw materials to prepare molybdenum disulfide nanoflowers loaded with ultra-small silica nanoparticles through in-situ reaction. The process is low-cost, simple, and highly controllable in morphology. The molybdenum disulfide nanoflowers have numerous reactive sites and a large specific surface area, while the loaded silica particles are small and uniform in size, have a high loading capacity, and have no other functional groups on their surface.

本发明利用廉价易得的原料，通过原位反应制备二硫化钼纳米花负载超小二氧化硅纳米粒子，成本低廉，反应过程简单、形貌可控性强,二硫化钼纳米花反应活性位点多、比表面积大，负载的二氧化硅粒径小而均匀、负载量多、表面无其它基团。

This material has a uniform structure, excellent morphology, and superior performance. It exhibits a good synergistic flame-retardant effect and high flame-retardant efficiency when used in the flame-retardant field. At the same time, it improves the compatibility of nano flame retardants, which greatly enhances the compatibility and mechanical reinforcement effect of the matrix.

该材料结构均一，形貌优良、性能优异，用于阻燃领域具有很好的协同阻燃效应，阻燃效率高；同时提高了纳米阻燃剂相容性，使基体的相容性及力学增强效应得到大大改善。

[0029]

Attached Figure Description

附图说明

[0030]

Figure 1 shows the SEM image of molybdenum disulfide nanoflowers;

图1为二硫化钼纳米花的SEM图；

[0031]

Figure 2 shows a TEM image of silica nanoparticles;

图2为二氧化硅纳米粒子的TEM图；

[0032]

Figure 3 shows a TEM image of the three-dimensional hybrid material of silicon dioxide /molybdenum disulfide;

图3为二氧化硅/二硫化钼三维杂化材料的TEM图；

[0033]

Figure 4 shows the SEM image of the three-dimensional hybrid material of silica/molybdenum disulfide;

图4为二氧化硅/二硫化钼三维杂化材料的SEM图；

[0034]

Figure 5 shows the XRD pattern of the three-dimensional hybrid material of silica /molybdenum disulfide;

图5为二氧化硅/二硫化钼三维杂化材料的XRD图；

[0035]

Figure 6 shows the XPS plot of the three-dimensional hybrid material of silica/molybdenum disulfide;

图6为二氧化硅/二硫化钼三维杂化材料的XPS图；

[0036]

Figure 7 shows the SEM image of flame-retardant polyacrylonitrile fiber;

图7为阻燃聚丙烯腈纤维的SEM图；

[0037]

Figure 8 shows the TGA diagram of flame-retardant polyacrylonitrile fiber;

图8为阻燃聚丙烯腈纤维的TGA图；

[0038]

Figure 9 shows the heat release rate of flame-retardant polyacrylonitrile fiber.

图9为阻燃聚丙烯腈纤维的热释放速率图；

[0039]

Figure 10 shows the heat release rate of flame-retardant polyacrylonitrile fiber.

图10为阻燃聚丙烯腈纤维的热释放速率图。

[0040]

Detailed Implementation

具体实施方式

[0041]

The specific content of the present invention will be described in detail below with reference to specific embodiments:

下面结合具体实施例对本发明的具体内容具体说明如下:

[0042]

Example 1

实施例1

[0043]

Preparation of silica/molybdenum disulfide three-dimensional hybrid material: Weigh 1.28g ammonium molybdate tetrahydrate and 2.3g sodium thiocyanate, dissolve them in 40mL deionized water, and then transfer them to a 100mL hydrothermal reactor. React at 220°C for 10h in a muffle furnace.

二氧化硅/二硫化钼三维杂化材料的制备：称取1.28g四水合钼酸铵，2.3g硫氰酸钠，溶于40mL去离子水中，然后转移至100mL水热釜中，马弗炉中220°C反应10h。

The molybdenum disulfide nanoflowers were obtained by centrifugation and washing three times with deionized water and drying at 60°C.

用去离子水离心清洗三次，60°C烘干得到二硫化钼纳米花。

Weigh 0.2g of molybdenum disulfide nanoflowers and ultrasonically disperse them in 100mL of deionized water. Then add 4mL of tetraethyl orthosilicate, adjust the pH to 9.7 with ammonia, and react at 60°C and 550rpm for 24h. Then add 1.5mL of (3-mercaptopropyl) trimethoxysilane and continue the reaction for 12h.

称取0.2g二硫化钼纳米花，超声分散在100mL去离子水中，然后加入4mL正硅酸四乙酯，用氨水调节pH＝9.7，60°C，550rpm反应24h，再加入1.5mL(3-巯基丙基)三甲氧基硅烷，继续反应12h。

The solution after the reaction was washed three times with alternating ethanol and deionized water and dried under vacuum at 60°C to obtain a hybrid material of molybdenum disulfide nanoflowers supported on ultra-small functionalized silica nanoparticles.

反应后的溶液用乙醇和去离子水交替清洗三次，60°C真空干燥，得到二硫化钼纳米花原位负载超小功能化二氧化硅纳米粒子杂化材料。

[0044]

The morphology of the obtained molybdenum disulfide nanoflowers is shown in Figure 1, with a diameter of 100-200 nm. The silica nanospheres are shown in Figure 2, with a diameter of 10-15 nm, exhibiting uniform size and no obvious agglomeration. As shown in Figure 3, a large amount of silica was successfully loaded in the middle of the molybdenum disulfide nanoflower layers, increasing the interlayer spacing. Silica particles of approximately 10-15 nm in size were uniformly modified onto the molybdenum disulfide nanoflowers, presenting a three-dimensional hierarchical structure. The structure exhibits excellent structural stability (Figure 4). As can be seen from Figure 5, in addition to the characteristic diffraction peaks of molybdenum disulfide nanoflowers, a new strong characteristic peak of silica appears at 23° in the hybrid material, indicating the successful loading of silica. Compared with pure molybdenum disulfide nanoflowers, the hybrid material has lower contents of sulfur (14.27%) and molybdenum (6.74%), and higher contents of silicon (25.24%) and oxygen (53.75%) (see Table 1 for elemental contents), indicating a large loading of silica (Figure 6).

所得到的二硫化钼纳米花的形貌如图1所示，其直径大小为100-200nm；二氧化硅纳米微球如图2所示，二氧化硅纳米微球的直径大小为10～15nm，大小均匀，无明显团聚；二氧化硅/二硫化钼三维杂化材料从图3可知大量二氧化硅成功负载在二硫化钼纳米花片层中间，增大了其层间距；大小为10-15nm左右的二氧化硅被均匀修饰在二硫化钼纳米花上，呈现三维层级结构，显示出优良的结构稳定性(图4)，从图5可看出，除了二硫化钼纳米花的特征衍射峰，杂化材料在23°出现一个新的二氧化硅的强特征峰，表明二氧化硅的成功负载；相比于纯二硫化钼纳米花，杂化材料中硫(14.27%)、

钼元素(6.74%)含量较低，硅(25.24%)、氧元素(53.75%)呈现较高含量(元素含量见表1)，表明二氧化硅的大量负载(图6)。

The specific elemental contents of molybdenum disulfide nanoflowers and hybrid materials are shown in Table 1:

二硫化钼纳米花及杂化材料中具体的元素含量如表1所示：

[0045]

Table 1. Elemental content of molybdenum disulfide nanoflowers and hybrid materials

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表1二硫化钼纳米花及杂化材料的元素含量

[0047]

Preparation of flame-retardant polyacrylonitrile fiber: Weigh 0.06g of molybdenum disulfide nanoflowers in situ loaded with ultra-small functionalized silica nanoparticle hybrid material, ultrasonically disperse it in 15g of N,N-dimethylformamide (DMF), then add 3g of polyacrylonitrile powder, dissolve at 80°C for 8h, and place the resulting spinning solution in a vacuum oven at 60°C for 2h for degassing treatment.

阻燃聚丙烯腈纤维的制备：称取0.06g二硫化钼纳米花原位负载超小功能化二氧化硅纳米粒子杂化材料，超声分散在15g N,N-二甲基甲酰胺(DMF)中，再加入3g聚丙烯腈粉末，80°C溶解8h，得到的纺丝液置于60°C真空烘箱中2h，进行脱泡处理。

Spinning was performed using a TYD01 spinning injection pump with the following parameters: speed 10 μL min, needle inner diameter 0.3 mm, and coagulation bath containing an aqueous solution of DMF (60% DMF content).

用TYD01纺丝注射泵进行纺丝，纺丝参数为：速度10μL min⁻¹，针头内径0.3mm，凝固浴DMF的水溶液(DMF含量60%)。

The obtained polyacrylonitrile fibers were dried at 60°C for 24 hours to obtain flame-retardant polyacrylonitrile fibers.

得到的聚丙烯腈纤维60°C干燥24h，得到阻燃聚丙烯腈纤维。

[0048]

As shown in Figure 7, the obtained flame-retardant polyacrylonitrile fiber has fewer pores in its cross-section, shorter groove-like cracks, and uniform distribution of hybrid materials in the fiber matrix. According to the TGA diagram of the flame-retardant polyacrylonitrile fiber (Figure 8), the temperature at which the mass loss of the flame-retardant polyacrylonitrile fiber is 10% (311.8°C) and the residual carbon content (58.7%) are significantly improved

compared with pure polyacrylonitrile fiber (300.5℃ and 50.5%, respectively). The maximum heat release rate of the flame-retardant polyacrylonitrile fiber (98.27W/g) is reduced by 46.1% compared with pure polyacrylonitrile fiber (182.4W/g) (Figure 9). The total heat release of the flame-retardant polyacrylonitrile fiber (19.9kJ/g) is reduced by 25.2% compared with pure polyacrylonitrile fiber (26.6kJ/g) (Figure 10).

由图7可以看出，所得到的阻燃聚丙烯腈纤维的纤维截面孔洞较少，沟壑状裂纹较短，杂化材料在纤维基体分布均匀，根据阻燃聚丙烯腈纤维的TGA图(图8)可知，阻燃聚丙烯腈纤维质量损失10%的温度(311.8°C)和残碳量(58.7%)相比于纯聚丙烯腈纤维(分别为300.5°C和50.5%)有极大提高；阻燃聚丙烯腈纤维最大热释放速率(98.27W/g)相比于纯聚丙烯腈纤维(182.4W/g)降低了46.1%(图9)；阻燃聚丙烯腈纤维总热释放量(19.9kJ/g)相比于纯聚丙烯腈纤维(26.6kJ/g)降低了25.2%(图10)。

[0049]

Example 2

实施例2

[0050]

Weigh 1.28g ammonium molybdate tetrahydrate and 2.3g sodium thiocyanate, dissolve them in 40mL of deionized water, then transfer them to a 100mL hydrothermal reactor and react them in a muffle furnace at 220℃ for 10h.

称取1.28g四水合钼酸铵，2.3g硫氰酸钠，溶于40mL去离子水中，然后转移至100mL水热釜中，马弗炉中220℃反应10h。

The molybdenum disulfide nanoflowers were obtained by centrifugation and washing three times with deionized water and drying at 60°C.

用去离子水离心清洗三次，60℃烘干得到二硫化钼纳米花。

Weigh 0.8g of molybdenum disulfide nanoflowers and ultrasonically disperse them in 100mL of deionized water. Then add 2mL of tetraethyl orthosilicate, adjust the pH to 9.7 with ammonia, and react at 60℃ and 550rpm for 24h. Then add 0.5mL of (3-mercaptopropyl) trimethoxysilane and continue the reaction for 12h.

称取0.8g二硫化钼纳米花，超声分散在100mL去离子水中，然后加入2mL正硅酸四乙酯，用氨水调节pH＝9.7，60℃，550rpm反应24h，再加入0.5mL(3-巯基丙基)三甲氧基硅烷，续反应12h。

The solution after the reaction was washed three times alternately with ethanol and deionized water and dried under vacuum at 60°C to obtain a hybrid material of molybdenum disulfide nanoflowers supported on ultra-small functionalized silica nanoparticles.

反应后的溶液用乙醇和去离子水交替清洗三次，60°C真空干燥，得到二硫化钼纳米花原位负载超小功能化二氧化硅纳米粒子杂化材料。

[0051]

The obtained silica/molybdenum disulfide three-dimensional hybrid material contains sulfur (35.3%), molybdenum (16.7.7%), silicon (16.1%), and oxygen (31.9%), with a good loading, but slightly worse than that in Example 1, indicating that the amount of silicon source and coupling agent has a certain influence on the silica loading.

所得到的二氧化硅/二硫化钼三维杂化材料中含硫(35.3%)、钼元素(16.7.7%)，而硅(16.1%)、氧元素(31.9%)，负载量较好，但相比实施例1中的稍差，表明硅源及偶联剂的用量对二氧化硅负载量有一定的影响。

[0052]

The flame-retardant polyacrylonitrile fiber prepared using the method in Example 1 has a residual carbon content of 58.8%, a maximum heat release rate of 102.3 W/g, and a total heat

release of 20.2 kJ/g. The flame-retardant effect meets the requirements, but is slightly worse than that in Example 1, indicating that the silica loading has a certain impact on the flame-retardant performance of the fiber.

利用实施例1中的方法制备得到的阻燃聚丙烯腈纤维：残碳量58.8%，最大热释放速率102.3W/g，总热释放量20.2kJ/g，阻燃效果满足要求，但比实施例1中稍差，说明二氧化硅负载量对纤维的阻燃性能有一定影响。

[0053]

Example 3

实施例3

[0054]

Weigh 1.28g ammonium molybdate tetrahydrate and 2.3g sodium thiocyanate, dissolve them in 40mL of deionized water, then transfer them to a 100mL hydrothermal reactor and react them in a muffle furnace at 220°C for 10h.

称取1.28g四水合钼酸铵，2.3g硫氰酸钠，溶于40mL去离子水中，然后转移至100mL水热釜中，马弗炉中220°C反应10h。

The molybdenum disulfide nanoflowers were obtained by centrifugation and washing three times with deionized water and drying at 60°C.

用去离子水离心清洗三次，60°C烘干得到二硫化钼纳米花。

Weigh 0.8g of molybdenum disulfide nanoflowers and ultrasonically disperse them in 100mL of deionized water. Then add 4mL of tetraethyl orthosilicate, adjust the pH to 9.7 with ammonia, and react at 40°C and 550rpm for 24h. Then add 1.5mL of (3-mercaptopropyl) trimethoxysilane and continue the reaction for 12h.

称取0.8g二硫化钼纳米花，超声分散在100mL去离子水中，然后加入4mL正硅酸四乙酯，用氨水调节pH＝9.7，40°C，550rpm反应24h，再加入1.5mL(3-巯基丙基)三甲氧基硅烷，续反应12h。

The solution after the reaction was washed three times alternately with ethanol and deionized water and dried under vacuum at 60°C to obtain a hybrid material of molybdenum disulfide nanoflowers supported on ultra-small functionalized silica nanoparticles.

反应后的溶液用乙醇和去离子水交替清洗三次，60°C真空干燥，得到二硫化钼纳米花原位负载超小功能化二氧化硅纳米粒子杂化材料。

[0055]

The obtained silica/molybdenum disulfide three-dimensional hybrid material contains sulfur (28.2%), molybdenum (14.3%), silicon (18.7%), and oxygen (38.8%), indicating that temperature has a certain influence on the formation and loading of silica.

所得到的二氧化硅/二硫化钼三维杂化材料中含硫(28.2%)、钼元素(14.3%)，而硅(18.7%)、氧元素(38.8%)，说明温度对二氧化硅的形成及负载量有一定的影响。

[0056]

The flame-retardant polyacrylonitrile fiber prepared using the method in Example 1 has the following characteristics: residual carbon content 59.1%, maximum heat release rate 100.1 W/g, and total heat release 20.7 kJ/g.

利用实施例1中的方法制备得到的阻燃聚丙烯腈纤维：残碳量59.1%，最大热释放速率100.1W/g，总热释放量20.7kJ/g。

[0057]

Table 2. Material element content of the hybrid materials obtained in Examples 1-3

表2实施例1-3所得杂化材料中的材料元素含量

[0059]

Table 3 Flame retardant properties of the flame retardant materials obtained in Examples 1-3

表3实施例1-3所得阻燃材料中的阻燃性能

[0061]

As shown in Table 2-3, the amount of silicon source, coupling agent, and temperature during the loading process have a significant impact on the material's performance.

由表2-3可知，负载过程中的硅源、偶联剂用量及温度都对材料的性能有较大影响。

[0062]

Comparative Example 1

对比例1

[0063]

Preparation of flame-retardant polyacrylonitrile fibers using silica nanoflowers:

二氧化硅纳米花制备阻燃聚丙烯腈纤维：

[0064]

Weigh 0.06g of molybdenum disulfide nanoflowers from Example 1, ultrasonically disperse them in 15g of N,N-dimethylformamide (DMF), then add 3g of polyacrylonitrile powder, dissolve at 80°C for 8h, and place the resulting spinning solution in a vacuum oven at 60°C for 2h for degassing treatment.

称取0.06g实施1中的二硫化钼纳米花，超声分散在15g N,N-二甲基甲酰胺(DMF)中，再加入3g聚丙烯腈粉末，80°C溶解8h，得到的纺丝液置于60°C真空烘箱中2h，进行脱泡处理。

Spinning was performed using a TYD01 spinning injection pump with the following parameters: speed 10 μL min⁻¹, needle inner diameter 0.3 mm, and coagulation bath containing an aqueous solution of DMF (60% DMF content).

用TYD01纺丝注射泵进行纺丝，纺丝参数为：速度10μL min⁻¹，针头内径0.3mm，凝固浴DMF的水溶液(DMF含量60%)。

The obtained polyacrylonitrile fibers were dried at 60°C for 24 hours to obtain flame-retardant polyacrylonitrile fibers.

得到的聚丙烯腈纤维60℃干燥24h，得到阻燃聚丙烯腈纤维。

[0065]

The relevant performance parameters of the obtained flame-retardant polyacrylonitrile fiber are shown in Tables 4 and 5: residual carbon content 54.4%, maximum heat release rate 126.4 W/g, total heat release 21.8 kJ/g, which is inferior to that of hybrid flame-retardant fiber.

所得到的阻燃聚丙烯腈纤维相关性能参数如表4、5所示：残碳量54.4%，最大热释放速率126.4W/g，总热释放量21.8kJ/g，劣于杂化阻燃纤维。

[0066]

Comparative Example 2

对比例2

[0067]

Preparation of flame-retardant polyacrylonitrile fibers using silica nanospheres:

二氧化硅纳米微球制备阻燃聚丙烯腈纤维：

[0068]

Weigh 0.06g of silica nanospheres and ultrasonically disperse them in 15g of N,N-dimethylformamide (DMF). Then add 3g of polyacrylonitrile powder and dissolve at 80°C for 8h. Place the resulting spinning solution in a vacuum oven at 60°C for 2h to degas.

称取0.06g二氧化硅纳米微球，超声分散在15g N,N-二甲基甲酰胺(DMF)中，再加入3g聚丙烯腈粉末，80°C溶解8h，得到的纺丝液置于60°C真空烘箱中2h，进行脱泡处理。

Spinning was performed using a TYD01 spinning injection pump with the following parameters: speed 10 μL min⁻¹, needle inner diameter 0.3 mm, and coagulation bath consisting of an aqueous solution of DMF (DMF content 60%).

用TYD01纺丝注射泵进行纺丝，纺丝参数为：速度10μL min⁻¹，针头内径0.3mm，凝固浴DMF的水溶液(DMF含量60%)。

The obtained polyacrylonitrile fibers were dried at 60°C for 24 hours to obtain flame-retardant polyacrylonitrile fibers.

得到的聚丙烯腈纤维60°C干燥24h，得到阻燃聚丙烯腈纤维。

[0069]

The relevant performance parameters of the flame-retardant polyacrylonitrile fiber obtained by the method in Example 1 are shown in Tables 4 and 5: residual carbon content 51.3%, maximum heat release rate 171.1 W/g, total heat release 22.5 kJ/g, which are slightly better than pure polyacrylonitrile fiber, but worse than hybrid flame-retardant fiber.

利用实施例1中的方法所得到的阻燃聚丙烯腈纤维相关性能参数如表4、5所示：残碳量51.3%，最大热释放速率171.1W/g，总热释放量22.5kJ/g，稍优于纯聚丙烯腈纤维，劣于杂化阻燃纤维。

[0070]

Comparative Example 3

对比例3

[0071]

Preparation of flame-retardant polyacrylonitrile fibers from silica nanosheets:

二氧化硅纳米片制备阻燃聚丙烯腈纤维：

[0072]

Weigh 0.1g of molybdenum disulfide nanosheets and ultrasonically disperse them in 100mL of deionized water. Then add 3.8mL of tetraethyl orthosilicate, adjust the pH to 9.7 with ammonia, and react at 60°C and 550rpm for 24h. Then add 1.5mL of (3-mercaptopropyl) trimethoxysilane and continue the reaction for 12h.

称取0.1g二硫化钼纳米片，超声分散在100mL去离子水中，然后加入3.8mL正硅酸四乙酯，用氨水调节pH＝9.7，60°C，550rpm反应24h，再加入1.5mL(3-巯基丙基)三甲氧基硅烷，继续反应12h。The solution after the reaction was washed three times alternately with ethanol and deionized water, and then dried under vacuum at 60°C to obtain a molybdenum disulfide nanosheet-supported silica nanoparticle hybrid material.

反应后的溶液用乙醇和去离子水交替清洗三次，60°C真空干燥，得到二硫化钼纳米片负载二氧化硅纳米粒子杂化材料。

[0073]

The obtained silica/molybdenum disulfide hybrid material contains sulfur (54.3%) and molybdenum (25.7%), while the contents of silicon (6.1%) and oxygen (13.9%) are low, indicating that there is very little silica loaded on the molybdenum disulfide nanosheets.

所得到的二氧化硅/二硫化钼杂化材料：含硫(54.3%)、钼元素(25.7%)，而硅(6.1%)、氧元素(13.9%)含量较低，表明二硫化钼纳米片上负载的二氧化硅极少。

[0074]

The relevant performance parameters of the flame-retardant polyacrylonitrile fiber prepared by the method in Example 1 are shown in Tables 4 and 5: residual carbon content 53.1%, maximum heat release rate 134.8 W/g, total heat release 23.5 kJ/g, which is inferior to the three-dimensional nanoflower/silica hybrid flame-retardant fiber.

利用实施例1中的方法制备得到的阻燃聚丙烯腈纤维相关性能参数如表4、5所示：残碳量53.1%，最大热释放速率134.8W/g，总热释放量23.5kJ/g，劣于三维纳米花/二氧化硅杂化阻燃纤维。

[0075]

Table 4 shows the elemental contents of the materials obtained in Comparative Examples 1-3.

表4对比例1-3所得材料的元素含量

[0077]

Table 5 shows the flame retardant properties of the flame retardant materials obtained in Comparative Examples 1-3.

表5对比例1-3所得阻燃材料中的阻燃性能

[0079]

Although the present invention has been disclosed above with reference to preferred embodiments, it is not intended to limit the present invention. Anyone skilled in the art can make various modifications and alterations without departing from the spirit and scope of the present invention. Therefore, the scope of protection of the present invention should be determined by the claims.

虽然本发明已以较佳实施例公开如上，但其并非用以限定本发明，任何熟悉此技术的人，在不脱离本发明的精神和范围内，都可做各种的改动与修饰，因此本发明的保护范围应该以权利要求书所界定的为准。