Notice

DESCRIPTION CN120646820A

An adsorption-enhanced preparation method for biomass tar-modified flash-evaporated graphene

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一种生物质焦油改性闪蒸石墨烯的吸附增强制备方法

[0001]

Technical Field

技术领域

[n0001]

This invention relates to the field of graphene technology, specifically to an adsorption-enhanced preparation method for biomass tar-modified flash-evaporated graphene.

本发明涉及石墨烯技术领域，具体为一种生物质焦油改性闪蒸石墨烯的吸附增强制备方法。

[0003]

Background Technology

背景技术

[n0002]

With the acceleration of global industrialization, heavy metal pollution has become one of the major challenges in the environmental field.

随着全球工业化进程的加速，重金属污染已成为环境领域的重大挑战之一。

Heavy metal ions such as lead, cadmium, and mercury are widely present in industrial wastewater. They are highly toxic, easily accumulate, and are difficult to degrade naturally. Once they enter water bodies, they can be transferred through the food chain, ultimately causing serious harm to human health.

重金属离子如铅、镉、汞等在工业废水中广泛存在，它们具有高毒性、易积累且难以自然降解的特点，一旦进入水体，会通过食物链传递，最终对人体健康造成严重危害。

Traditional methods for treating heavy metal wastewater mainly include chemical precipitation, ion exchange, membrane separation, and adsorption.

传统的重金属废水处理方法主要包括化学沉淀法、离子交换法、膜分离法和吸附法等。

Among them, adsorption method has attracted widespread attention due to its simple operation, low cost, high efficiency and ability to achieve deep removal of heavy metal ions.

其中，吸附法因其操作简便、成本低廉、效率较高且可实现重金属离子的深度去除而受到广泛关注。

[n0003]

Graphene, as a novel two-dimensional nanomaterial, possesses high specific surface area, excellent mechanical properties, good thermal and chemical stability, and abundant surface functional groups, making it a promising candidate for adsorption applications.

石墨烯作为一种新型的二维纳米材料，具有高比表面积、优异的力学性能、良好的热稳定性和化学稳定性，以及丰富的表面官能团，使其在吸附领域展现出巨大的潜力。

However, most current methods for preparing graphene suffer from problems such as high cost, complex processes, and serious environmental pollution. Common preparation methods include chemical vapor deposition, redox method, and mechanical exfoliation. Chemical vapor deposition requires harsh conditions such as high temperature and high vacuum, and has high equipment requirements and high cost; although the redox method is relatively simple to operate, the strong oxidants and reducing agents used can cause environmental pollution; mechanical stripping has extremely low yield and is difficult to apply on a large scale.

然而，目前石墨烯的制备方法大多存在成本高、工艺复杂、环境污染严重等问题。 常见的制备方法包括化学气相沉积、氧化还原法、机械剥离法等。 化学气相沉积法需要高温、高真空等苛刻条件，设备要求高，成本昂贵；氧化还原法虽然操作相对简单，但使用的强氧化剂和还原剂会对环境造成污染；机械剥离法的产率极低，难以大规模应用。

[n0004]

Biomass tar is a byproduct of the thermochemical conversion of biomass. It is mainly composed of various organic compounds, including aromatic hydrocarbons such as benzene, toluene, and naphthalene, as well as oxygen-containing organic compounds such as phenols, alcohols, and aldehydes.

生物质焦油是生物质热化学转化过程中产生的副产物，主要由各种有机化合物组成，包括苯、甲苯、萘等芳烃以及酚类、醇类、醛类等含氧有机物。

Traditional methods for treating biomass tar mainly involve physical separation or simple chemical conversion to separate it into products such as light oil and heavy oil. However, these methods often fail to fully utilize the high carbon resources in the tar and are prone to generating secondary pollution during the treatment process. Biomass tar has the characteristics of high carbon content, high oxygen content, high calorific value, high coating properties, high foaming properties and low impurities, making it a good carbon source that can be used to prepare high value-added carbon materials.

传统的生物质焦油处理方法主要是通过物理分离或简单的化学转化，将其分离成轻油、重油等产品，但这些方法往往无法充分利用焦油中的高碳资源，且处理过程中容易产生二次污染。 生物质焦油具有高碳含量、高含氧量、高热值、高包裹性、高发泡性能和杂质少等特性，是一种良好的碳源，可用于制备高附加值的碳材料。

[n0005]

Existing technologies for utilizing biomass tar to prepare high-value-added materials have the following shortcomings:

现有技术在利用生物质焦油制备高附加值材料方面存在以下不足：

[n0006]

Firstly, although existing research has recognized that biomass tar contains abundant carbon resources, the utilization of tar is mostly limited to simple physical separation or low-value-added chemical product production due to traditional processing technology. This has failed to fully leverage its high carbon characteristics and renewable advantages, making it difficult to achieve high-value utilization of biomass tar and meet the current requirements for resource recycling and sustainable development.

其一，尽管已有研究认识到生物质焦油中蕴含丰富的碳资源，但受限于传统工艺技术，对焦油的利用大多停留在简单的物理分离或低附加值的化工产品生产上，未能充分发挥其高碳特性和可再生优势，难以实现生物质焦油的高值化利用，无法满足当前对资源循环利用和可持续发展的要求。

[n0007]

Secondly, traditional methods for preparing graphene have many limitations.

其二，对于石墨烯的制备，传统方法存在诸多局限性。

Chemical vapor deposition relies on high temperature and high pressure conditions, resulting in high costs; redox methods use a large number of chemical reagents, causing environmental pollution; mechanical stripping methods have extremely low yields and are difficult to mass-produce.

化学气相沉积法依赖高温高压条件，导致成本高昂；氧化还原法使用大量化学试剂，造成环境污染；机械剥离法产率极低，难以规模生产。

These limitations restrict the large-scale application of graphene, especially in cost-sensitive environmental remediation fields.

这些局限性使得石墨烯的大规模应用受到限制，尤其是在对成本敏感的环境治理领域。

[n0008]

Thirdly, in the development of adsorption materials, existing graphene-based adsorbents have problems such as insufficient surface active sites, poor selectivity for heavy metal ion adsorption, and difficulty in recycling and reuse.

其三，在吸附材料的开发上，现有石墨烯基吸附剂存在表面活性位点不足、对重金属离子吸附选择性差、难以回收再利用等问题。

This limits its adsorption efficiency and lifespan in practical applications, making it difficult to meet the demand for efficient, economical, and environmentally friendly removal of heavy metal wastewater.

这导致其在实际应用中的吸附效率和使用寿命受限，难以满足高效、经济、环保去除重金属废水的需求。

[n0009]

Given the shortcomings of the existing technologies, there is an urgent need for a method that can efficiently utilize biomass tar resources, is environmentally friendly, and can produce high-

quality graphene adsorbent materials on a large scale, so as to realize the high-value utilization of biomass tar and the efficient treatment of heavy metal wastewater, thereby promoting technological progress and sustainable development in related fields.

鉴于以上现有技术的不足，迫切需要一种能够高效利用生物质焦油资源、绿色环保且可规模化生产高质量石墨烯吸附材料的方法，以实现生物质焦油的高值化利用和重金属废水的高效治理，推动相关领域的技术进步和可持续发展。

[0012]

Summary of the Invention

发明内容

[n0010]

To address the shortcomings of existing technologies, this invention provides an adsorption-enhanced preparation method for biomass tar-modified flash-evaporated graphene, which solves the problems mentioned in the background section.

针对现有技术的不足，本发明提供了一种生物质焦油改性闪蒸石墨烯的吸附增强制备方法，解决了上述背景技术中所提出的问题。

[n0011]

To achieve the above objectives, the present invention provides the following technical solution: a method for preparing adsorption-enhanced graphene modified from biomass tar, comprising the following steps:

为实现以上目的，本发明通过以下技术方案予以实现：一种生物质焦油改性闪蒸石墨烯的吸附增强制备方法，包括以下步骤：

[n0012]

Biomass tar is mixed with nitrogen and iron sources and pretreated to obtain a mixed slurry;

将生物质焦油与氮源和铁源混合，进行预处理，得到混合浆料；

[n0013]

The mixed slurry was freeze-dried to obtain a dried sample;

对所述混合浆料进行冷冻干燥，得到干燥样品；

[n0014]

The dried sample was subjected to sequential heating treatment in an inert gas atmosphere, heated to a set carbonization temperature at a specific heating rate and held at that temperature for a predetermined time to obtain a tar carbon precursor.

将所述干燥样品在惰性气体氛围下，依次进行升温处理，以特定升温速率升温至设定碳化温度并保温预定时间，得到焦油碳前驱体；

[n0015]

The tar carbon precursor is subjected to flash Joule heat treatment. By adjusting the discharge voltage and discharge time, the tar carbon precursor is instantly converted into modified flash graphene.

将所述焦油碳前驱体进行闪蒸焦耳热处理，通过调节放电电压和放电时间，使焦油碳前驱体瞬间转化为改性闪蒸石墨烯。

[n0016]

Preferably, the biomass tar is a byproduct generated during the thermochemical conversion of biomass, including tar generated during biomass gasification or pyrolysis.

优选的，所述生物质焦油为生物质热化学转化过程中产生的副产物，包括生物质气化或热解过程中产生的焦油。

[n0017]

Preferably, the nitrogen source is one or more of urea or disodium ethylenediaminetetraacetate, and the iron source is ferric chloride.

优选的，所述氮源为尿素或乙二胺四乙酸二钠中的一种或多种，所述铁源为氯化铁。

[n0018]

Preferably, the pretreatment includes ultrasonically dispersing biomass tar with a nitrogen source and an iron source at room temperature for 10-60 minutes, followed by stirring for 1-6 hours.

优选的，所述预处理包括将生物质焦油与氮源和铁源在常温下进行超声分散，超声时间为10-60min，然后继续搅拌1-6h。

[n0019]

Preferably, the freeze-drying temperature is -40°C to -80°C, and the drying time is 12-48 hours.

优选的，所述冷冻干燥的温度为-40°C至-80°C，干燥时间12-48h。

[n0020]

Preferably, the heating rate is 5-10°C/min, the carbonization temperature is 700-900°C, and the holding time is 1-3h.

优选的，所述升温速率为5-10°C/min，碳化温度为700-900°C，保温预定时间为1-3h。

[n0021]

Preferably, the flash joule heat treatment specifically involves: placing the tar carbon precursor in a quartz tube, sealing both ends with graphite plugs, evacuating to a negative pressure state, connecting a DC power supply, charging through a capacitor bank to a set discharge voltage, and then discharging instantaneously. The discharge voltage is 130-170V, and the discharge time is 0.1-1s.

优选的，所述闪蒸焦耳热处理具体为：将焦油碳前驱体置于石英管中，用石墨堵头封堵两端，抽真空至负压状态，接通直流电源，通过电容器组充电至设定放电电压后瞬间放电，放电电压130-170V，放电时间为0.1-1s。

[n0022]

Preferably, the method further includes a step of testing the adsorption performance of the modified flash graphene, specifically: mixing the prepared modified flash graphene with a solution containing heavy metal ions to carry out an adsorption reaction, and calculating the adsorption capacity and removal rate by measuring the concentration of heavy metal ions in the solution before and after adsorption.

优选的，还包括对所述改性闪蒸石墨烯进行吸附性能测试的步骤，具体为：将制备得到的改性闪蒸石墨烯与含重金属离子的溶液混合进行吸附反应，通过测定吸附前后溶液中重金属离子浓度，计算吸附容量和去除率。

[n0023]

Preferably, the heavy metal ion is one or more of lead ions, cadmium ions, copper ions, or mercury ions.

优选的，所述重金属离子为铅离子、镉离子、铜离子或汞离子中的一种或多种。

[n0024]

This invention provides an adsorption-enhanced preparation method for biomass tar-modified flash-evaporated graphene.

本发明提供了一种生物质焦油改性闪蒸石墨烯的吸附增强制备方法。

It has the following beneficial effects:

具备以下有益效果：

[n0025]

1. This invention prepares modified flash graphene from biomass tar, realizing the high-value utilization of biomass tar.

1、本发明通过生物质焦油为原料制备改性闪蒸石墨烯，实现了生物质焦油的高值化利用。

Transforming it into high-value-added modified flash graphene materials not only solves the problem of biomass tar treatment, but also avoids environmental pollution problems such as soil and water pollution caused by direct discharge or simple treatment of tar, resulting in significant environmental benefits.

将其转化为高附加值的改性闪蒸石墨烯材料，不仅解决了生物质焦油的处理难题，还避免了因焦油直接排放或简单处理带来的土壤、水体等环境污染问题，具有显著的环境效益。

Meanwhile, compared with traditional methods of preparing graphene using fossil fuels, this method utilizes renewable biomass resources, reduces dependence on non-renewable energy sources, conforms to the concept of sustainable development, and helps promote the development of biomass energy resource utilization technology and the construction of a low-carbon economy.

同时，相比传统以化石能源为原料制备石墨烯的方法，本方法利用可再生的生物质资源，降低了对不可再生能源的依赖，符合可持续发展的理念，有助于推动生物质能资源化技术的发展以及低碳经济的建设。

[n0026]

2. The present invention modifies biomass tar by introducing nitrogen and iron sources during the preparation process and combining it with flash evaporation Joule heat treatment, resulting in modified flash graphene with excellent adsorption properties.

2、本发明通过在制备过程中引入氮源和铁源对生物质焦油进行改性，并结合闪蒸焦耳热处理，所制得的改性闪蒸石墨烯具有优异的吸附性能。

Nitrogen doping introduces abundant nitrogen-containing functional groups to the surface of graphene. These functional groups can interact strongly with heavy metal ions, greatly enhancing the adsorption capacity of graphene for heavy metal ions.

氮元素的掺杂为石墨烯表面引入了丰富的含氮官能团，这些官能团能够与重金属离子发生强烈的配位作用，大大增强了石墨烯对重金属离子的吸附能力。

The addition of an iron source promotes the generation of magnetic nanoparticles, giving the resulting graphene a magnetic quality. This facilitates solid-liquid separation after adsorption by applying an external magnetic field, thereby improving the recyclability and reusability of the adsorbent.

而铁源的加入则促进了磁性纳米颗粒的生成，使制得的石墨烯具备磁性，便于吸附完成后通过外加磁场实现固液分离，提高了吸附剂的可回收性和重复利用率。

[0030]

Attached Figure Description

附图说明

[n0027]

Figure 1 is a flowchart of the present invention;

图1为本发明的流程图；

[n0028]

Figure 2 is a graph of isothermal adsorption curves of Pb²⁺ on carbon tar in an embodiment of the present invention.

图2为本发明实施例中焦油碳对Pb²⁺等温吸附曲线图；

[n0029]

Figure 3 is a kinetic curve of tar carbon to Pb_NER2 in an embodiment of the present invention;

图3为本发明实施例中焦油碳对Pb²⁺动力学曲线图；

[n0030]

Figure 4 shows the Raman characterization of flash graphene from different samples at different discharge times in the embodiments of the present invention.

图4为本发明实施例中不同样品在不同放电时间下的闪蒸石墨烯的拉曼表征图；

[n0031]

Figure 5 is a hysteresis loop diagram of the NFe10-800-0.2 sample in an embodiment of the present invention.

图5为本发明实施例中NFe10-800-0.2样品的磁滞回线图。

[0036]

Detailed Implementation

具体实施方式

[n0032]

The technical solutions in the embodiments of the present invention will be clearly and completely described below with reference to the accompanying drawings. Obviously, the

described embodiments are only some embodiments of the present invention, and not all embodiments.

下面将结合本发明说明书附图，对本发明实施例中的技术方案进行清楚、完整地描述，显然，所描述的实施例仅仅是本发明一部分实施例，而不是全部的实施例。

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

基于本发明中的实施例，本领域普通技术人员在没有做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。

[n0033]

This invention provides a method for preparing adsorption-enhanced graphene modified from biomass tar using flash evaporation, comprising the following steps:

本发明实施例提供一种生物质焦油改性闪蒸石墨烯的吸附增强制备方法，包括以下步骤：

[n0034]

Biomass tar is mixed with nitrogen and iron sources and pretreated to obtain a mixed slurry. Biomass tar is a byproduct of biomass thermochemical conversion, including tar produced during biomass gasification or pyrolysis.

将生物质焦油与氮源和铁源混合，进行预处理，得到混合浆料；生物质焦油为生物质热化学转化过程中产生的副产物，包括生物质气化或热解过程中产生的焦油。

The nitrogen source is urea.

氮源为尿素。

[n0035]

Specifically, biomass tar is a complex mixture produced during the thermochemical transformation of biomass (such as gasification or pyrolysis), containing a variety of organic compounds.

具体地，生物质焦油是生物质在热化学转化(如气化或热解)过程中产生的复杂混合物，含有多种有机化合物。

By mixing biomass tar with a nitrogen source (urea in this example) and an iron source, and through pretreatment (such as ultrasonic dispersion and stirring), the various components can be fully contacted and uniformly dispersed to form a mixed slurry.

将生物质焦油与氮源(本例中为尿素)和铁源混合，通过预处理(如超声分散和搅拌)，可以使各种成分充分接触并均匀分散，形成混合浆料。

This mixing process facilitates subsequent reaction and processing steps, preparing the biomass tar for further conversion and modification.

这一混合过程有助于后续的反应和处理步骤，为生物质焦油的进一步转化和改性做准备。

[n0036]

The mixed slurry was freeze-dried to obtain a dried sample.

对混合浆料进行冷冻干燥，得到干燥样品。

[n0037]

The dried sample was subjected to sequential heating treatment in an inert gas atmosphere, heated to the set carbonization temperature at a specific heating rate and held at the temperature for a predetermined time to obtain tar carbon precursor.

将干燥样品在惰性气体氛围下，依次进行升温处理，以特定升温速率升温至设定碳化温度并保温预定时间，得到焦油碳前驱体；

[n0038]

Specifically, an inert gas atmosphere (such as argon or nitrogen) can prevent the dried sample from undergoing oxidation with oxygen during high-temperature processing.

具体地，在惰性气体(如氩气或氮气)氛围下，可以防止干燥样品在高温处理过程中与氧气发生氧化反应。

By heating the dried sample to a set carbonization temperature at a specific heating rate and holding it at that temperature for a certain period of time, the dried sample can undergo a carbonization reaction to form a tar carbon precursor.

通过以特定的升温速率将干燥样品升温至设定的碳化温度，并保温一定时间，可以使干燥样品发生碳化反应，形成焦油碳前驱体。

This carbonization process is a key step in converting biomass tar into carbon materials with specific structures and properties, preparing for subsequent flash joule heat treatment.

这一碳化过程是将生物质焦油转化为具有特定结构和性质的碳材料的关键步骤，为后续的闪蒸焦耳热处理做准备。

[n0039]

The tar carbon precursor is subjected to flash Joule heat treatment. By adjusting the discharge voltage and discharge time, the tar carbon precursor is instantly converted into modified flash graphene.

将焦油碳前驱体进行闪蒸焦耳热处理，通过调节放电电压和放电时间，使焦油碳前驱体瞬间转化为改性闪蒸石墨烯。

[n0040]

Specifically, flash Joule heat treatment is a technique that uses the high temperature and high pressure conditions generated by an electric pulse to cause an instantaneous structural transformation in a material.

具体地，闪蒸焦耳热处理是一种利用电脉冲产生的高温和高压条件使材料瞬间发生结构转变的技术。

The tar carbon precursor is placed in a specific device (such as a quartz tube), both ends are sealed with graphite plugs, and a vacuum is drawn to a negative pressure state. Then, a DC power supply is connected, and the precursor is charged through a capacitor bank to a set discharge voltage and then discharged instantaneously. The tar carbon precursor is subjected to high temperature and high pressure.

将焦油碳前驱体置于特定的装置(如石英管)中，用石墨堵头封堵两端，并抽真空至负压状态，然后接通直流电源，通过电容器组充电至设定放电电压后瞬间放电，焦油碳前驱体在高温和高压。

By adjusting the discharge voltage and discharge time, the structure and properties of graphene can be controlled, thereby achieving the modification and optimization of graphene.

通过调节放电电压和放电时间，可以控制石墨烯的结构和性质，从而实现对石墨烯的改性和优化。

[n0041]

The pretreatment process involves ultrasonically dispersing biomass tar with nitrogen and iron sources at room temperature for 30 minutes, followed by stirring for 4 hours.

预处理包括将生物质焦油与氮源和铁源在常温下进行超声分散，超声时间为30min，然后继续搅拌4h。

The freeze-drying temperature was -60°C, and the drying time was 24 hours.

冷冻干燥的温度为-60°C，干燥时间24h。

The heating rate is 10°C/min, the carbonization temperature is 800°C, and the holding time is 3h.

升温速率为10°C/min，碳化温度为800°C，保温预定时间为3h。

[n0042]

Specifically, the purpose of ultrasonic dispersion and stirring is to fully mix biomass tar with nitrogen (urea) and iron sources to ensure uniform dispersion of each component and provide good contact conditions for subsequent reactions.

具体地，超声分散和搅拌的目的是将生物质焦油与氮源(尿素)和铁源充分混合，确保各组分均匀分散，为后续的反应提供良好的接触条件。

Ultrasonic dispersion utilizes the cavitation effect of ultrasound to refine particles in a mixture, improve mixing uniformity, and create a more uniform reaction environment for subsequent chemical reactions.

超声分散能够利用超声波的空化作用，使混合物中的颗粒细化，提高混合均匀度，为后续的化学反应创造更均匀的反应环境。

[n0043]

The purpose of freeze drying is to remove moisture from the mixed slurry and obtain a dried sample.

冷冻干燥的目的是去除混合浆料中的水分，得到干燥样品。

Choosing -60°C low-temperature freeze drying can prevent the organic components in biomass tar from oxidizing or decomposing at high temperatures, while also avoiding adverse reactions between nitrogen and iron sources at high temperatures, thus ensuring the stability and activity of the precursor.

选择-60°C的低温冷冻干燥，可以防止生物质焦油中的有机成分在高温下发生氧化或分解，同时也能避免氮源和铁源在高温下发生不良反应，保证前驱体的稳定性和活性。

[n0044]

The flash joule heat treatment is as follows: the tar carbon precursor is placed in a quartz tube, both ends are sealed with graphite plugs, a vacuum is drawn to a negative pressure state, a DC power supply is connected, and the capacitor bank is charged to the set discharge voltage and then discharged instantaneously. The discharge voltage is 160V and the discharge time is 0.2s.

闪蒸焦耳热处理具体为：将焦油碳前驱体置于石英管中，用石墨堵头封堵两端，抽真空至负压状态，接通直流电源，通过电容器组充电至设定放电电压后瞬间放电，放电电压160V，放电时间为0.2s。

[n0045]

Specifically, flash Joule heat treatment utilizes the high temperature and high pressure conditions generated by an electric pulse to instantly convert tar carbon precursors into modified flash graphene.

具体地，闪蒸焦耳热处理是利用电脉冲产生的高温和高压条件，将焦油碳前驱体瞬间转化为改性闪蒸石墨烯。

This method can cause the precursor to undergo structural reorganization in a very short time, forming graphene with a two-dimensional layered structure.

这种方法能够在极短的时间内使前驱体发生结构重组，形成具有二维层状结构的石墨烯。

[n0046]

Parameter selection: Quartz tube and graphite plug are selected to provide a closed and high-temperature stable reaction environment. At the same time, the graphite plug can also be used as an electrode to facilitate energization.

参数选择：选择石英管和石墨堵头是为了提供一个密闭且高温稳定的反应环境，同时石墨堵头还可以作为电极，便于通电。

Vacuuming to a negative pressure state can prevent oxygen and nitrogen in the air from interfering with the reaction process, ensuring the stability and safety of the reaction.

抽真空至负压状态可以避免空气中的氧气和氮气等对反应过程的干扰，保证反应的稳定性和安全性。

The discharge voltage of 160V and the discharge time of 0.2 seconds were chosen to provide sufficient energy in a short time to rapidly heat the tar carbon precursor to a high temperature state, thereby achieving structural transformation, while avoiding excessive discharge that could lead to excessive growth or structural damage of graphene.

放电电压选择160V，放电时间选择0.2秒，是为了在短时间内提供足够的能量，使焦油碳前驱体迅速升温至高温状态，实现结构转变，同时避免过度放电导致石墨烯的过度生长或结构破坏。

[n0047]

It also includes a step of testing the adsorption performance of modified flash graphene, specifically: the prepared modified flash graphene is mixed with a solution containing heavy metal ions to carry out an adsorption reaction, and the adsorption capacity and removal rate are calculated by measuring the concentration of heavy metal ions in the solution before and after adsorption.

还包括对改性闪蒸石墨烯进行吸附性能测试的步骤，具体为：将制备得到的改性闪蒸石墨烯与含重金属离子的溶液混合进行吸附反应，通过测定吸附前后溶液中重金属离子浓度，计算吸附容量和去除率。

The heavy metal ion is lead ion.

重金属离子为铅离子。

[n0048]

Specifically, modified flash graphene with excellent adsorption properties is prepared by mixing biomass tar with nitrogen and iron sources and then performing pretreatment, freeze drying, carbonization, and flash Joule heat treatment.

具体地，通过将生物质焦油与氮源和铁源混合，经预处理、冷冻干燥、碳化和闪蒸焦耳热处理等步骤，制备出具有优异吸附性能的改性闪蒸石墨烯。

This method not only enables the high-value utilization of biomass tar but also reduces environmental pollution.

该方法不仅实现了生物质焦油的高值化利用，减少了环境污染。

[n0049]

Graphene adsorbent Pb_NER3 adsorption experiment

石墨烯吸附剂Pb²⁺吸附实验

[n0050]

The effects of initial lead concentration, adsorption contact time, adsorption temperature, initial pH, adsorbent dosage, and Na+ on adsorption capacity and lead removal efficiency were mainly investigated.

主要探讨了初始铅浓度、吸附接触时间、吸附温度、初始pH、吸附剂用量和Na+对吸附容量和铅去除效率的影响。

The initial lead concentration ranged from 10 mg/L to 5000 mg/L, the adsorption contact time ranged from 1 min to 60 min, the adsorption ambient temperature ranged from 25°C to 45°C, the initial solution pH ranged from 2 to 7, and the adsorbent dosage ranged from 0.33 g/L to 1.67 g/L.

其中初始铅浓度变化范围为10mg/L-5000mg/L，吸附接触时间变化范围为1min-60min，吸附环境温度变化范围为25°C-45°C,初始溶液pH值为2-7和吸附剂投加量变化范围为0.33g/L-1.67g/L。

[n0051]

All experiments were repeated three times, and the average of the three repeated measurements was used for data analysis.

所有实验均重复三次，取重复测定三次的平均值进行数据分析。

The measured concentration is calculated using the following formulas to obtain the lead adsorption capacity (q_e, mg/g) and removal rate (η, %):

通过以下公式计算测得的浓度，以获得铅吸附量(q_e，mg/g)和去除率(η,%)：

[n0052]

q_e=V(C₀-C_e)/m

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q_e＝V(C₀-C_e)/m

[n0053]

η=(C₀-C_e)/C₀

η＝(C₀-C_e)/C₀

[n0054]

Where: q_e is the equilibrium adsorption capacity of lead, mg/g; η is the removal efficiency of lead, %; V is the initial solution volume, mL; C₀ is the initial concentration of lead solution, mg/L; C_e is the equilibrium concentration of lead solution, mg/L; m is the mass of dried adsorbent, g.

其中：q_e为铅的平衡吸附容量，mg/g；η为铅的去除效率，%；V为初始溶液的体积，mL；C₀为铅溶液的初始浓度，mg/L；C_e为铅溶液的平衡浓度，mg/L；m为干燥的吸附剂的质量，g。

[n0055]

Isothermal adsorption experiment:

等温吸附实验：

[n0056]

Weigh 50 mg of adsorbent into centrifuge tubes, and add 50 mL of lead solutions with concentrations of 10 mg/L, 40 mg/L, 70 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 300 mg/L, 500 mg/L, 750 mg/L, 1000 mg/L, 2000 mg/L, 3000 mg/L, 4000 mg/L, and 5000 mg/L, respectively. Cap the centrifuge tubes and label them. Place the centrifuge tubes in a constant temperature shaker set to 25°C, rotate at 150 rad/min, and react for 60 min. Take the filtrate after filtration

through a 0.22 μm pore size membrane and measure the lead content in the filtrate using an ICP-OES analyzer.

分别称取吸附剂50mg于离心管内，分别加入10mg/L、40mg/L、70mg/L、100mg/L、150mg/L、200mg/L、300mg/L、500mg/L、750mg/L、1000mg/L、2000mg/L、3000mg/L、4000mg/L、5000mg/L的铅溶液50mL，盖好离心管盖并标记好，将离心管置于温度设置为25°C的恒温振荡器中，转速为150rad/min，反应60min，取经0.22μm孔径膜过滤后的滤液，使用ICP-OES测试仪测量滤液中的铅含量。

[n0057]

The Langmuir isothermal adsorption model is as follows:

其中Langmuir等温吸附模型如下：

[n0059]

The Freundlich isothermal adsorption model is as follows:

其中Freundlich等温吸附模型如下：

[n0060]

q_e＝k_fC_e

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q_e＝k_fC_e

1/

n

---

n

[n0061]

Where: q_e is the equilibrium adsorption capacity of lead, mg/g; q_m is the maximum adsorption capacity, mg/g; C_e is the equilibrium concentration, mg/L; k_l is the Langmuir adsorption constant, L/mg; k_f is the Freundlich adsorption constant in units of mg¹⁻ⁿ・Lⁿ/g; and n is the Freundlich exponent.

其中：q_e为铅的平衡吸附容量，mg/g；q_m为最大吸附量，mg/g；C_e为平衡浓度，mg/L；k_l为Langmuir吸附常数，L/mg；k_f为Freundlich吸附常数单位，mg¹⁻ⁿ·Lⁿ/g；n为Freundlich指数。

[n0062]

Adsorption kinetics experiment

吸附动力学实验

[n0063]

Weigh 80 mg of adsorbent into centrifuge tubes, add 80 mL of 2000 mg/L lead solution, cap the centrifuge tubes and label them. Place the centrifuge tubes in a constant temperature shaker set to 25 °C and shake at 150 rad/min. Take samples at 2 min, 5 min, 10 min, 20 min, 40 min, 80 min, 120 min, 180 min, 280 min, 400 min, 580 min, 720 min and 1440 min respectively. Filter the filtrate through a 0.22 μm pore size membrane and measure the lead content in the filtrate using an ICP-OES analyzer.

分别称取吸附剂80mg于离心管内，加入2000mg/L的铅溶液80mL，盖好离心管盖并标记好，将离心管置于温度设置为25°C的恒温振荡器中，转速为150rad/min振荡反应，于2min、5min、10min、

20min、40min、80min、120min、180min、280min、400min、580min、720min、1440min分别取样，经0.22μm孔径膜过滤后的滤液，使用ICP-OES测试仪测量滤液中的铅含量。

The most common quasi-first-order and quasi-second-order kinetic models among many kinetic models were selected to fit the adsorption data.

选取了诸多动力学模型中最为常见的准一级动力学模型和准二级动力学模型对吸附数据进行拟合。

[n0064]

Quasi-first-order dynamic model:

准一级动力学模型：

[n0065]

Internal diffusion model of adsorbent: q_t＝k_{id}t^{1/2}+C

吸附剂内扩散模型：q_t＝k_{id}t^{1/2}+C

[n0066]

Quasi-second-order dynamic model:

准二级动力学模型：

[n0067]

Where: q_t is the amount of lead adsorbed per unit at contact time t (min), μg/g; q_e is the equilibrium amount of lead adsorbed per unit, μg/g; k₁ is the rate constant of the pseudo-first-order kinetic model, min⁻¹; k_{id} is the diffusion rate constant within the adsorbent, g・μg⁻¹・min⁻¹; C is a constant, related to the thickness at the boundary, μg/g; k₂ is the rate constant of the pseudo-second-order kinetic model, g・μg⁻¹・min⁻¹; h₀ is the initial adsorption rate, μg・g⁻¹・min⁻¹.

其中：q_t为在接触时间t(min)时的单位铅吸附量，μg/g；q_e为平衡单位铅吸附量，μg/g；k₁为准一级动力学模型的速率常数，min⁻¹；k_{id}为吸附剂内扩散速率常数，g・μg⁻¹・min⁻¹；C为常数，与边界处厚度有关，μg/g；k₂为准二级动力学模型的速率常数，g・μg⁻¹・min⁻¹；h₀为初始吸附率，μg・g⁻¹・min⁻¹。

[n0068]

Adsorption thermodynamics experiment

吸附热力学实验

[n0069]

Weigh 80 mg of adsorbent into centrifuge tubes, add 80 mL of 2000 mg/L lead solution, cap the centrifuge tubes and label them. Place the centrifuge tubes in constant temperature shakers set to 25°C, 35°C and 45°C respectively, and shake at 150 rad/min. After 60 min, take samples, filter the filtrate through a 0.22 μm pore size membrane, and measure the lead content in the filtrate using an ICP-OES analyzer.

分别称取吸附剂80mg于离心管内，加入2000mg/L的铅溶液80mL，盖好离心管盖并标记好，将离心管分别置于温度设置为25°C、35°C和45°C的恒温振荡器中，转速为150rad/min振荡反应，于60min后分别取样，经0.22μm孔径膜过滤后的滤液，使用ICP-OES测试仪测量滤液中的铅含量。

[n0070]

Arrhenius equation: lnk₂＝lnA-E_a/(RT)

阿伦尼乌斯方程：lnk₂＝lnA-E_a/(RT)

[n0071]

Gibbs free energy change formula: ΔG⁰＝-RTlnK_D

吉布斯自由能变化公式:ΔG⁰＝-RTlnK_D

[n0072]

Adsorption equilibrium constant formula: K_D＝q_e/C_e

吸附平衡常数公式：K_D＝q_e/C_e

[n0073]

Van der Hoff equation: lnK_D＝-ΔH⁰/(RT)+ΔS⁰/R

范特霍夫方程：lnK_D＝-ΔH⁰/(RT)+ΔS⁰/R

[n0074]

Wherein, k₂ is the rate constant of the pseudo-second-order kinetic model, g・μg⁻¹・min⁻¹; A is the pre-exponential factor of the Arrhenius formula; R is the universal gas constant, 8.314 J・mol⁻¹・K⁻¹; T is the reaction temperature, K; E_a is the activation energy of the adsorption reaction, kJ・mol⁻¹; K_D is the partition coefficient of the adsorbent; C_e is the outlet concentration of the reactor at adsorption equilibrium, μg /m³; ΔH⁰ is the enthalpy change, kJ・mol⁻¹; ΔS⁰ is the entropy change, J・mol⁻¹K⁻¹.

其中，k₂为准二级动力学模型的速率常数，g・μg⁻¹・min⁻¹；A为Arrhenius公式指前因子；R为通用气体常数，8.314J・mol⁻¹・K⁻¹；T为反应温度，K；E_a吸附反应活化能，kJ・mol⁻¹；K_D为吸附剂的分配系数；C_e为吸附平衡时反应器的出口浓度，μg /m³；ΔH⁰为焓变，kJ・mol⁻¹；ΔS⁰为熵变，J・mol⁻¹K⁻¹。

[n0075]

Raman scattering is an effect in which light is scattered by molecules within a transparent medium, causing a change in its frequency. Raman spectroscopy uses the change in reflected light energy to represent the rotational and vibrational modes of the lattice or molecules within the medium.

拉曼散射效应是当光透过透明的介质时，其被介质内分子散射而导致频率改变的一种效应，拉曼光谱利用分析反射光能量的变化量来表示介质内的晶格或分子的旋转模式以及振动模式。

When photons in a material interact with electrons and incident photons, an inelastic scattering phenomenon, known as Raman spectroscopy, occurs.

当材料中的生子与电子和入射的光子发生相互作用时，会产生一种非弹性散射现象，即拉曼光谱。

[n0076]

Transmission electron microscopy analysis.

透射电子显微镜分析。

Transmission electron microscopy projects an accelerated and focused electron beam onto a very thin sample. The electrons collide with atoms in the sample and change direction, thus producing solid angle scattering.

透射电镜是把经加速和聚集的电子束投射到非常薄的样品上，电子与样品中的原子碰撞而改变方向，从而产生立体角散射。

The size of the scattering angle is related to the density and thickness of the sample, thus it can form images with different brightness.

散射角的大小与样品的密度、厚度相关，因此可以形成明暗不同的影像。

[n0077]

Scanning electron microscopy analysis.

扫描电子显微镜分析。

Scanning electron microscopy (SEM) uses a scanning beam of electrons to scan and image a sample, allowing for further observation of the sample's surface morphology. It is based on

the interaction between electrons and matter to obtain various physical information about the sample. The observation method for testing the surface morphology of a sample can be simply described as receiving, magnifying, and displaying the information.

扫描电镜是使用电子的扫描束，对样品进行扫描成像，进一步观察样品的表面形态，其依据是电子与物质之间的作用来获取样品的各种物理信息，测试试样表面形貌的观察方式可以简述为对信息的接收，放大和显示成像。

[n0078]

X-ray photoelectron spectroscopy analysis.

X射线光电子能谱分析。

X-ray photoelectron spectroscopy analysis uses X-rays to irradiate a sample, causing the inner-shell electrons or valence electrons of atoms or molecules to be excited and emitted.

X射线光电子能谱分析是用X射线去辐射样品，使原子或分子的内层电子或价电子受激发射出来。

Electrons excited by photons are called photoelectrons.

被光子激发出来的电子称为光电子。

The energy of photoelectrons can be measured, and a photoelectron energy spectrum can be plotted with the kinetic energy/binding energy of the photoelectrons (E_b＝h_vlight energy-E_kkinetic energy-w work function) as the abscissa and the relative intensity (pulse/s) as the ordinate.

可以测量光电子的能量，以光电子的动能/束缚能(E_b＝h_v光能量-E_k动能-w功函数)为横坐标，相对强度(脉冲/s)为纵坐标可做出光电子能谱图。

This allows us to obtain information about the sample.

从而获得试样有关信息。

[n0079]

X-ray diffraction analysis.

X射线衍射分析。

X-ray diffraction is a process in which X-rays of wavelength on the same order of magnitude as the interatomic distance are emitted into the sample to be tested. The diffraction phenomenon is produced by the X-rays irradiating the sample, and the distribution and intensity of the diffraction in space reflect the cellular structure of the sample.

X射线衍射是通过向待测样品发出与原子间距数量级相同波长的X射线，射线照射样品产生衍射现象，衍射在空间的分布及强弱反应出样品的晶胞结构。

[n0080]

Fourier transform infrared spectroscopy analysis.

傅立叶红外光谱分析。

FTIR is an instrument used to analyze the structure and composition of substances. It uses Fourier transform to convert the infrared radiation absorbed by a substance into a visible light signal for analysis. Different functional groups correspond to different infrared radiation absorption.

FTIR是一种用于分析物质结构和成分的仪器，而它利用傅里叶变换将物质吸收的红外辐射转换为可见光信号进行分析，不同的官能团对应于不同的红外辐射吸收。

Fourier transform infrared spectroscopy can be used to determine the types and distribution of functional groups on the surface of different samples.

采用傅立叶红外光谱仪器可测定不同样品表面官能团种类及分布。

[n0081]

Nitrogen adsorption-desorption test.

氮气吸附-脱附测试。

The pore structure of the prepared graphene was characterized using a nitrogen adsorption /desorption apparatus.

采用氮气吸附/脱附仪对所制备石墨烯孔隙结构进行表征。

Based on the measured isothermal adsorption/desorption results, the specific surface area, total pore volume, and average pore diameter were obtained using the BET method.

根据测得的等温吸/脱附结果，通过BET方法获得比表面积、总孔容积以及平均孔径。

[n0082]

Magnetometer analysis of vibrating samples.

振动样品磁强计分析。

VSM can be used to test the magnetic properties of modified graphene.

VSM可测试改性石墨烯的磁性。

When the sample particle size is reduced to the nanometer scale, it exhibits superparamagnetism.

当样品粒径减小到纳米级时，表现为超顺磁性。

Superparamagnetism can be identified by temperature dependence and magnetization-temperature curves.

超顺磁性可以通过温度依赖性、磁化-温度曲线来识别。

[n0083]

Adsorption experiments of Pb²⁺ on carbon tar were conducted, and adsorption kinetics and isothermal adsorption analyses were performed. The results are shown in Figures 2 and 3. The adsorption capacity of Pb²⁺ by NFe10-800 and NFe20-800 was significantly improved compared with that of NFe0-800, indicating that the introduction of Fe element has a positive effect on the adsorption performance of Pb²⁺ of the adsorbent.

对焦油碳进行Pb²⁺吸附实验，同时进行吸附动力学分析和等温吸附分析，结果如图2和图3所示，NFe10-800和NFe20-800对比于NFe0-800的Pb²⁺吸附容量有显著提高，表明Fe元素的引入，对吸附剂的Pb²⁺吸附性能有正向影响。

This is because ferric chloride acts as a pore-forming agent in the carbonization of biomass tar, giving the tar carbon a porous structure that is beneficial for adsorption.

这是由于氯化铁可生物质焦油碳化中的成孔剂，使焦油碳具有益于吸附的孔隙结构。

[n0084]

Flash-electrode graphene samples were prepared at different discharge times (0.1s, 0.2s, 0.3s, 0.4s, 0.5s) and Raman characterized them. The results are shown in Figure 4.

制备不同样品在不同放电时间(0.1s、0.2s、0.3s、0.4s、0.5s)下的闪蒸石墨烯，对其进行拉曼表征，结果见图4。

[n0085]

As shown in Figure 4, as the discharge time decreases, graphene obtains a larger 2D peak intensity, which is beneficial to the increase of I_{2D}/I_G and obtaining graphene with fewer layers.

由图4可知，随着放电时间的减小，石墨烯获得更大的2D峰强度，有利于I_{2D}/I_G的增大，获得层数更少的石墨烯。

Meanwhile, compared to Tar-800 and NFe0-800, NFe10-800 and NFe20-800 have lower D peak intensities, which is beneficial for reducing I_D/I_G and obtaining graphene with smaller defects.

同时，相比于Tar-800和NFe0-800，NFe10-800和NFe20-800拥有更低的D峰强度，有利于I_D/I_G的减小，获得缺陷更小的石墨烯。

[n0086]

As shown in Figure 5, the hysteresis loop of NFe10-800-0.2 exhibits a typical S-shaped curve and shows superparamagnetism, indicating good recycling performance.

由图5可知，NFe10-800-0.2的磁滞回线呈现典型的S型曲线，且表现为超顺磁性，具有良好的回收性能。

The saturation magnetization is approximately 90 emu/g.

饱和磁化强度约为90emu/g。

[n0087]

In summary, the preparation of modified flash graphene using biomass tar as a raw material achieves the high-value utilization of biomass tar.

综上所述：通过生物质焦油为原料制备改性闪蒸石墨烯，实现了生物质焦油的高值化利用。

Transforming it into high-value-added modified flash graphene materials not only solves the problem of biomass tar treatment, but also avoids environmental pollution problems such as soil and water pollution caused by direct discharge or simple treatment of tar, resulting in significant environmental benefits.

将其转化为高附加值的改性闪蒸石墨烯材料，不仅解决了生物质焦油的处理难题，还避免了因焦油直接排放或简单处理带来的土壤、水体等环境污染问题，具有显著的环境效益。

Meanwhile, compared with traditional methods of preparing graphene using fossil fuels, this method utilizes renewable biomass resources, reduces dependence on non-renewable energy sources, conforms to the concept of sustainable development, and helps promote the development of biomass energy resource utilization technology and the construction of a low-carbon economy.

同时，相比传统以化石能源为原料制备石墨烯的方法，本方法利用可再生的生物质资源，降低了对不可再生能源的依赖，符合可持续发展的理念，有助于推动生物质能资源化技术的发展以及低碳经济的建设。

[n0088]

Although embodiments of the invention have been shown and described, it will be understood by those skilled in the art that various changes, modifications, substitutions and alterations can be made to these embodiments without departing from the principles and spirit of the invention, the scope of which is defined by the appended claims and their equivalents.

尽管已经示出和描述了本发明的实施例，对于本领域的普通技术人员而言，可以理解在不脱离本发明的原理和精神的情况下可以对这些实施例进行多种变化、修改、替换和变型，本发明的范围由所附权利要求及其等同物限定。