DESCRIPTION CN110079785A

Preparation methods of copper-based graphene composite materials and copper-based graphene composite materials

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铜基石墨烯复合材料的制备方法和铜基石墨烯复合材料

[0001]

Technical Field

技术领域

[0002]

This application relates to the field of composite material technology, and in particular to a method for preparing a copper-based graphene composite material and the copper-based graphene composite material itself.

本申请涉及复合材料技术领域，尤其涉及一种铜基石墨烯复合材料的制备方法和铜基石墨烯复合材料。

[0003]

Background Technology

背景技术

[0004]

In recent years, with the rapid development of modern technology, the performance requirements of copper-based composite materials have become increasingly demanding, for example, requiring their electrical conductivity to be higher than that of pure silver.

近年来，随着现代科技的快速发展，铜基复合材料的性能需求越来越高，例如，要求其电导率高于纯银。

The extremely high electrical conductivity and electron mobility of graphene make it possible for copper-based composite materials to achieve electrical conductivity comparable to pure silver.

而石墨烯所具有的极高电导率和电子迁移率为铜基复合材料的电导率达到纯银提供了可能。

[0005]

Currently, the common method is to disperse a solid carbon source on the surface of spherical copper powder, then use chemical vapor deposition to convert the solid carbon source into graphene that grows along the surface of the spherical copper powder, thus obtaining graphene-copper composite powder. Then, the graphene-copper composite powder is densified by hot pressing sintering process to obtain copper-based graphene composite material.

目前，常通过将固体碳源分散在球形铜粉表面，之后利用化学气相沉积技术将固体碳源转换为沿球形铜粉表面生长的石墨烯，得到石墨烯-铜复合粉末，然后再通过热压烧结工艺将石墨烯-铜复合粉末致密化，得到铜基石墨烯复合材料。

[0006]

However, the electrical conductivity of the copper-based graphene composite material prepared by the above method is still low and cannot meet the requirements.

但是，通过上述方法制备的铜基石墨烯复合材料，其电导率仍然较低，不能满足要求。

[0007]

Summary of the Invention

发明内容

[0008]

In view of this, this application provides a method for preparing a copper-based graphene composite material and a copper-based graphene composite material, in order to solve the problem that the electrical conductivity of copper-based graphene composite materials prepared by existing methods is low and cannot meet the requirements.

有鉴于此，本申请提供一种铜基石墨烯复合材料的制备方法和铜基石墨烯复合材料，以解决采用现有的方法制备出的铜基石墨烯复合材料的电导率较低，不能满足要求的问题。

[0009]

The first aspect of this application provides a method for preparing a copper-based graphene composite material, comprising:

本申请第一方面提供一种铜基石墨烯复合材料的制备方法，包括：

[0010]

An electrochemical polishing process was used to pretreat the original plate-shaped copper substrate to obtain a pretreated copper substrate, wherein the thickness of the original plate-shaped copper substrate was 5 μm to 25 μm.

采用电化学抛光工艺对原始板状铜基底进行预处理，得到预处理后的铜基底，其中，所述原始板状铜基底的厚度为5μm～25μm；

[0011]

Graphene was grown on the upper and lower surfaces of the pretreated copper substrate using a chemical vapor deposition process to obtain a graphene-coated copper substrate.

采用化学气相沉积工艺在所述预处理后的铜基底的上下表面生长石墨烯，得到石墨烯包覆铜基底；

[0012]

At least one of the graphene-coated copper substrates is subjected to hot pressing and sintering to obtain a copper-based graphene composite material; wherein the copper-based graphene composite material is a layered composite material formed by alternating composites of graphene and copper substrate, and the copper substrate is in a single crystal state in the thickness direction of the layered composite material and is preferably oriented with (111) crystal plane.

对至少一片所述石墨烯包覆铜基底进行热压烧结处理，得到铜基石墨烯复合材料；其中，上述铜基石墨烯复合材料为由石墨烯和铜基底交替复合形成的层状复合材料，铜基底在所述层状复合材料的厚度方向上呈单晶态，且呈(111)晶面择优取向。

[0013]

Furthermore, the original plate-shaped copper substrate has a thickness of 9 µm.

进一步地，所述原始板状铜基底的厚度为9µm。

[0014]

Furthermore, the hot-pressing and sintering process of at least one graphene-coated copper substrate specifically includes:

进一步地，所述对至少一片所述石墨烯包覆铜基底进行热压烧结处理，具体包括：

[0015]

At least one graphene-coated copper substrate is subjected to hot-press sintering treatment under the conditions of sintering temperature of 800°C～950°C, sintering pressure of 30MPa～150MPa and sintering time of 10min～30min.

在烧结温度为800°C～950°C、烧结压强为30MPa～150MPa和烧结时间为10min～30min的条件下，对至少一片所述石墨烯包覆铜基底进行热压烧结处理。

[0016]

Further, the hot-pressing sintering treatment of at least one graphene-coated copper substrate under the conditions of a sintering temperature of 800°C～950°C, a sintering pressure of 30MPa～150MPa, and a sintering time of 10min～30min specifically includes:

进一步地，所述在烧结温度为800°C～950°C、烧结压强为30MPa～150MPa和烧结时间为10min～30min的条件下，对至少一片所述石墨烯包覆铜基底进行热压烧结处理，具体包括：

[0017]

At least one graphene-coated copper substrate was subjected to hot-press sintering at a sintering temperature of 900°C, a sintering pressure of 50MPa, and a sintering time of 20min.

在烧结温度为900°C、烧结压强为50MPa和烧结时间为20min的条件下，对至少一片所述石墨烯包覆铜基底进行热压烧结处理。

[0018]

Furthermore, the step of growing graphene on the upper and lower surfaces of the pretreated copper substrate using chemical vapor deposition to obtain a graphene-coated copper substrate specifically includes:

进一步地，所述采用化学气相沉积工艺在所述预处理后的铜基底的上下表面生长石墨烯，得到石墨烯包覆铜基底，具体包括：

[0019]

A single layer of graphene was grown on the upper and lower surfaces of the pretreated copper substrate using a chemical vapor deposition process to obtain a graphene-coated copper substrate.

采用化学气相沉积工艺在所述预处理后的铜基底的上下表面生长单层石墨烯，得到石墨烯包覆铜基底。

[0020]

Furthermore, the step of growing graphene on the upper and lower surfaces of the pretreated copper substrate using chemical vapor deposition to obtain a graphene-coated copper substrate specifically includes:

进一步地，所述采用化学气相沉积工艺在所述预处理后的铜基底的上下表面生长石墨烯，得到石墨烯包覆铜基底，具体包括：

[0021]

Single-crystal graphene was grown on the upper and lower surfaces of the pretreated copper substrate using a chemical vapor deposition process to obtain a graphene-coated copper substrate.

采用化学气相沉积工艺在所述预处理后的铜基底的上下表面生长单晶石墨烯，得到石墨烯包覆铜基底。

[0022]

Furthermore, the process of growing single-crystal graphene on the upper and lower surfaces of the pretreated copper substrate using chemical vapor deposition to obtain a graphene-coated copper substrate specifically includes:

进一步地，所述采用化学气相沉积工艺在所述预处理后的铜基底的上下表面生长单晶石墨烯，得到石墨烯包覆铜基底，具体包括：

[0023]

The pretreated copper substrate is placed in the reactor;

将所述预处理后的铜基底置于反应器中；

[0024]

Argon and hydrogen are introduced into the reactor to purge the air from the reactor.

向所述反应器中通入氩气和氢气，以排尽所述反应器中的空气；

[0025]

Under the protection of argon atmosphere, the temperature of the reactor is raised to the preset reaction temperature at a preset heating rate and held for 30 minutes;

在氩气气氛保护下，以预设的升温速率将所述反应器的温度升高至预设的反应温度，并保持30min；

[0026]

A gaseous carbon source and hydrogen are introduced into the reactor and reacted for 1 min to 10 min to grow single-crystal graphene on the upper surface of the pretreated copper substrate.

向所述反应器通入气体碳源和氢气，反应1min～10min，以在所述预处理后的铜基底的上表面生长单晶石墨烯；

[0027]

While keeping the gaseous carbon source and the flow rate of hydrogen constant, the temperature of the reactor is reduced until it drops below 100°C to obtain a graphene-coated copper substrate.

保持所述气体碳源和所述氢气的气流量不变，降低所述反应器的温度，直至温度降至100°C以下，得到石墨烯包覆铜基底。

[0028]

Furthermore, the preset heating rate is 20°C/min.

进一步地，所述预设的升温速率为20°C/min。

[0029]

Furthermore, the preset reaction temperature is 1000°C.

进一步地，所述预设的反应温度为1000°C。

[0030]

The second aspect of this application provides a copper-based graphene composite material prepared according to any method provided in the first aspect of this application. The composite material is a layered composite material formed by alternating composites of graphene and copper substrate. The copper substrate is in a single crystal state in the thickness direction of the layered composite material and is preferably oriented with a (111) crystal plane.

本申请第二方面提供一种根据本申请第一方面提供的任一方法制备的铜基石墨烯复合材料，所述复合材料为由石墨烯和铜基底交替复合形成的层状复合材料，所述铜基底在所述层状复合材料的厚度方向上呈单晶态，且呈(111)晶面择优取向。

[0031]

The method for preparing the copper-based graphene composite material provided in this application involves pretreating the original plate-shaped copper substrate using an electrochemical polishing process to obtain a pretreated copper substrate with a thickness of 2μm to 25μm. Then, graphene is grown on the upper and lower surfaces of the pretreated copper substrate using a chemical vapor deposition process to obtain a graphene-coated copper substrate. Finally, at least one graphene-coated copper substrate is subjected to hot pressing and sintering to obtain the copper-based graphene composite material.

本申请提供的铜基石墨烯复合材料的制备方法，采用电化学抛光工艺对原始板状铜基底进行预处理，得到预处理后的铜基底，且原始板状铜基底的厚度为2μm～25μm，进而采用化学气相沉积工艺在上述预处理后的铜基底的上下表面生长石墨烯，得到石墨烯包覆铜基底，并对至少一片石墨烯包覆铜基底进行热压烧结处理，得到铜基石墨烯复合材料。

Thus, due to the good matching relationship between the graphene honeycomb lattice and the copper (111) crystal plane lattice, after graphene deposition and growth, the grain size of the graphene-coated copper substrate surface increases significantly, and the crystal plane undergoes an orientation change. The graphene-coated copper substrate is preferentially oriented towards the (111) crystal plane, and the (111) crystal plane exhibits an arrangement similar to a single crystal long-range order within the material, effectively reducing the scattering effect of defects on electron transport parameters and improving the electrical conductivity of the material. In addition, hot pressing sintering significantly increases the bonding energy between the graphene and copper interface inside the graphene-coated copper substrate. The copper-graphene interface exhibits its intrinsic two-dimensional high conductivity, becoming a fast channel for charge carriers, which is beneficial to improving the electrical conductivity of the material. Therefore, the preparation method of the copper-based graphene composite material provided in this application can prepare copper-based graphene composite materials with high electrical conductivity.

这样，由于石墨烯蜂巢晶格与铜(111)晶面晶格具有良好的匹配关系，因此，在经过石墨烯沉积生长之后，石墨烯包覆铜基底表面的晶粒显著增大，并且晶面发生了取向转变，石墨烯包覆铜基底取向于(111)晶面择优取向，而(111)晶面在材料内部呈现出一种近似于单晶长程有序的排列方式，有效地降低缺陷对电子传输参数的散射作用，有利于提高材料的电导率；此外，热压烧结使得石墨烯包覆铜基底内部石墨烯与铜界面的结合能显著的提高，铜-石墨烯界面发挥了二维高导的本征特性，成为载流子的快速通道，有利于提高材料的电导率；因此，本申请提供的铜基石墨烯复合材料的制备方法能够制备出电导率较高的铜基石墨烯复合材料。

[0032]

Attached Figure Description

附图说明

[0033]

Figure 1 is a flowchart illustrating a method for preparing a copper-based graphene composite material according to an exemplary embodiment of this application;

图1为本申请一示例性实施例示出的铜基石墨烯复合材料的制备方法的流程图；

[0034]

Figure 2 is an SEM image of the original plate-shaped copper substrate and the pretreated copper substrate shown in an exemplary embodiment of this application;

图2为本申请一示例性实施例示出的原始板状铜基底和预处理后的铜基底的SEM图;

[0035]

Figure 3 is an X-ray diffraction pattern of a graphene-coated copper substrate obtained by the method provided in this application, as shown in an exemplary embodiment of this application.

图3为本申请一示例性实施例示出的采用本申请提供的方法得到的石墨烯包覆铜基底的X射线衍射图;

[0036]

Figure 4 is a Raman diagram of graphene grown using the method provided in this application, as illustrated in an exemplary embodiment of this application.

图4为本申请一示例性实施例示出的采用本申请提供的方法生长的石墨烯的Raman图;

[0037]

Figure 5 is an SEM image of a graphene-coated copper substrate obtained by the method provided in this application, as illustrated in an exemplary embodiment of this application.

图5为本申请一示例性实施例示出的采用本申请提供的方法得到的石墨烯包覆铜基底的SEM图。

[0038]

Detailed Implementation

具体实施方式

[0039]

Exemplary embodiments will now be described in detail, examples of which are illustrated in the accompanying drawings.

这里将详细地对示例性实施例进行说明，其示例表示在附图中。

When the following description refers to the accompanying drawings, unless otherwise indicated, the same numbers in different drawings represent the same or similar elements.

下面的描述涉及附图时，除非另有表示，不同附图中的相同数字表示相同或相似的要素。

The embodiments described in the following exemplary embodiments do not represent all embodiments consistent with this application.

以下示例性实施例中所描述的实施方式并不代表与本申请相一致的所有实施方式。

Rather, they are merely examples of apparatuses and methods consistent with some aspects of this application as detailed in the appended claims.

相反，它们仅是与如所附权利要求书中所详述的、本申请的一些方面相一致的装置和方法的例子。

[0040]

The terminology used in this application is for the purpose of describing particular embodiments only and is not intended to be limiting of this application.

在本申请使用的术语是仅仅出于描述特定实施例的目的，而非旨在限制本申请。

The singular forms “a,” “the,” and “the” used in this application and the appended claims are also intended to include the plural forms, unless the context clearly indicates otherwise.

在本申请和所附权利要求书中所使用的单数形式的“一种”、“所述”和“该”也旨在包括多数形式，除非上下文清楚地表示其他含义。

It should also be understood that the term “and/or” as used herein refers to and includes any or all possible combinations of one or more associated listed items.

还应当理解，本文中使用的术语“和/或”是指并包含一个或多个相关联的列出项目的任何或所有可能组合。

[0041]

It should be understood that although the terms first, second, third, etc. may be used in this application to describe various information, such information should not be limited to these terms.

应当理解，尽管在本申请可能采用术语第一、第二、第三等来描述各种信息，但这些信息不应限于这些术语。

These terms are only used to distinguish information of the same type from one another.

这些术语仅用来将同一类型的信息彼此区分开。

For example, without departing from the scope of this application, the first information may also be referred to as the second information, and similarly, the second information may also be referred to as the first information.

例如，在不脱离本申请范围的情况下，第一信息也可以被称为第二信息，类似地，第二信息也可以被称为第一信息。

Depending on the context, the word "if" as used here can be interpreted as "when," "when," or "in response to determination."

取决于语境，如在此所使用的词语“如果”可以被解释成为“在……时”或“当……时”或“响应于确定”。

[0042]

This application provides a method for preparing a copper-based graphene composite material and the copper-based graphene composite material itself, in order to solve the problem that the copper-based graphene composite material prepared by existing methods has low electrical conductivity and does not meet the requirements.

本申请提供一种铜基石墨烯复合材料的制备方法和铜基石墨烯复合材料，以解决采用现有的方法制备出的铜基石墨烯复合材料的电导率较低、不满足要求的问题。

[0043]

The technical solution of this application will be described in detail below with reference to specific embodiments.

下面以具体的实施例对本申请的技术方案进行详细说明。

The following specific embodiments can be combined with each other, and the same or similar concepts or processes may not be described again in some embodiments.

下面这几个具体的实施例可以相互结合，对于相同或相似的概念或过程可能在某些实施例不再赘述。

[0044]

Figure 1 is a flowchart illustrating a method for preparing a copper-based graphene composite material according to an exemplary embodiment of this application.

图1为本申请一示例性实施例示出的铜基石墨烯复合材料的制备方法的流程图。

Referring to Figure 1, the preparation method of the copper-based graphene composite material provided in this embodiment may include the following steps:

请参照图1，本实施例提供的铜基石墨烯复合材料的制备方法，可以包括以下步骤：

[0045]

S101. The original plate-shaped copper substrate is pretreated by electrochemical polishing process to obtain a pretreated copper substrate, wherein the thickness of the original plate-shaped copper substrate is 5μm to 25μm.

S101、采用电化学抛光工艺对原始板状铜基底进行预处理，得到预处理后的铜基底，其中，上述原始板状铜基底的厚度为5μm～25μm。

[0046]

Specifically, the purity of the original plate-shaped copper substrate is greater than 99.99%.

具体的，原始板状铜基底的纯度大于99.99%。

It should be noted that when growing graphene on a copper substrate, if the copper substrate is too thick, the resulting graphene will have more wrinkles, which is not conducive to improving the electrical conductivity of the material. Therefore, the method provided in this application controls the thickness of the original plate-shaped copper substrate to 5μm to 25μm, which can reduce the wrinkles of the resulting graphene and improve the conductivity of the composite material.

需要说明的是，在铜基底上生长石墨烯时，若铜基底太厚，则生成的石墨烯的褶皱较多，不利于提高材料的电导率，因此，本申请提供的方法，通过将原始板状铜基底的厚度控制在5μm～25μm，这样，可降低生成的石墨烯的褶皱，有利于提高复合材料的导电性。

[0047]

Optionally, in one possible implementation of this application, the thickness of the original plate-shaped copper substrate is 9 μm.

可选地，在本申请一可能的实现方式中，原始板状铜基底的厚度为9μm。

[0048]

It should be noted that extensive experimental verification has shown that the electrical conductivity of copper-based graphene composites prepared using a 9μm thick original plate-shaped copper substrate is superior to that prepared using original plate-shaped copper substrates of other thicknesses.

需要说明的是，通过大量试验验证表明，利用9μm厚的原始板状铜基底制得的铜基石墨烯复合材料的电导率优于利用其它厚度的原始板状铜基底制得的铜基石墨烯复合材料的电导率。

[0049]

Furthermore, the pretreatment of the original plate-shaped copper substrate is of great significance for the growth of high-quality graphene.

进一步地，原始板状铜基底的预处理对于生长高质量的石墨烯具有十分重要的意义。

This is because when the original plate-shaped copper substrate comes into contact with water during storage and use, an oxide layer will form on the surface of the copper substrate. The presence of the oxide will affect the catalytic effect of copper and greatly reduce the quality of the grown graphene.

这是因为原始板状铜基底在存储以及使用的过程中，只要接触到水，会在铜基底表面形成一层氧化物，氧化物的存在会影响铜的催化作用，大大降低所生长的石墨烯的质量。

In addition, due to the manufacturing process, the original plate-shaped copper substrate has many striped morphologies on its surface (such as steps, pits, protrusions, as well as polycrystalline phases and amorphous regions of the copper substrate itself, collectively referred to as defects), and the surface is quite rough. If these defects are not pretreated before graphene growth, they will inevitably affect the quality of the grown graphene.

另外，由于制作工艺原因，原始板状铜基底表面有很多的条纹状形貌(例如台阶、凹坑、凸起以及铜基底本身的多晶相和非晶区域，统称为缺陷)，表面相当粗糙，这些缺陷如若在石墨烯生长前不做预处理的话，必将对生长的石墨烯的质量产生影响。

Therefore, pretreatment of the original plate-shaped copper substrate is essential.

因此，对原始板状铜基底的预处理是十分必要的。

[0050]

The method for preparing copper-based graphene composite material provided in this embodiment involves pretreating the original plate-shaped copper substrate using an electrochemical polishing process to obtain a pretreated copper substrate.

本实施例提供的铜基石墨烯复合材料的制备方法，采用电化学抛光工艺对原始板状铜基底进行预处理，得到预处理后的铜基底。

Specifically, in one possible implementation of this application, the electrochemical polishing solution consists of: 100ml water, 50ml phosphoric acid, 50ml ethanol, 10ml isopropanol, and

1g urea; the anode is the original plate-shaped copper substrate, and the cathode is copper foil; after polishing for 1 minute at a voltage of 5V, the polished copper substrate is cleaned with deionized water and ethanol, and then dried to obtain the pretreated copper substrate.

具体的，在本申请一可能的实现方式中，电化学抛光溶液的成分为：100ml水、50ml磷酸、50ml乙醇、10ml异丙醇，1g尿素；阳极为原始板状铜基底，阴极为铜箔；在5V的电压下，抛光1min后，将抛光后的铜基底用去离子水和乙醇清洗干净，吹干，得到预处理后的铜基底。

It should be noted that before polishing, the original plate-shaped copper substrate can be ultrasonically cleaned for 10 minutes each with acetone, ethanol, and deionized water.

需要说明的是，在抛光之前，还可将原始板状铜基底依次用丙酮、乙醇、去离子水分别超声清洗10min。

[0051]

Furthermore, Figure 2 is an SEM image of the original plate-shaped copper substrate and the pre-treated copper substrate shown in an exemplary embodiment of this application.

进一步地，图2为本申请一示例性实施例示出的原始板状铜基底和预处理后的铜基底的SEM图。

In Figure 2a, the image is an SEM image of the original plate-shaped copper substrate, and in Figure 2b, the image is an SEM image of the pre-processed copper substrate.

其中，图2中a图为原始板状铜基底的SEM图，图2中的b图为预处理后的铜基底的SEM图。

Please refer to Figure 2. Compared to the original plate-shaped copper substrate, the surface of the pretreated copper substrate is basically without stripes and is very smooth, providing a good foundation for the growth of high-quality graphene.

请参照图2，相比于原始板状铜基底，预处理后的铜基底表面基本没有条纹，表面非常光滑，为生长高质量石墨烯提供了很好的基础。

[0052]

S102. Graphene is grown on the upper and lower surfaces of the pretreated copper substrate using chemical vapor deposition to obtain a graphene-coated copper substrate.

S102、采用化学气相沉积工艺在上述预处理后的铜基底的上下表面生长石墨烯，得到石墨烯包覆铜基底。

[0053]

The principle of growing graphene on a copper substrate using chemical vapor deposition is a surface catalysis mechanism, that is, the carbon content of the copper substrate is very low, and the carbon source is cracked and recombined under the catalysis of the copper substrate to generate graphene.

采用化学气相沉积法在铜基底上生长石墨烯的原理为表面催化机制，即铜基底的溶碳量很低，碳源在铜基底的催化下裂解重组而生成石墨烯。

[0054]

Specifically, the carbon source required for growing graphene can be a gaseous carbon source. For example, the carbon source required for growing graphene includes at least one of the following substances: carbon monoxide, methane, ethane, propane, butane, pentane, hexane, cyclohexane, ethylene, propylene, butadiene, pentene, cyclopentadiene, acetylene, methanol, ethanol, benzene, and toluene.

具体的，生长石墨烯所需的碳源可以为气态碳源，例如，生长石墨烯所需的碳源包括至少一种以下物质：一氧化碳、甲烷、乙烷、丙烷、丁烷、戊烷、己烷、环己烷、乙烯、丙烯、丁二烯、戊烯、环戊二烯、乙炔、甲醇、乙醇、苯和甲苯。

Of course, the carbon source required for the growth of graphene can also be a solid carbon source. For example, the carbon source required for the generation of graphene is polymethyl methacrylate (PMMA) or polystyrene.

当然，生长石墨烯所需的碳源也可以为固态碳源，例如，生成石墨烯所需的碳源为聚甲基丙烯酸甲酯(PMMA)或聚苯乙烯。

[0055]

The following example illustrates the specific process of growing graphene on the upper and lower surfaces of a pretreated copper substrate using chemical vapor deposition (CVD) with methane (purity greater than 99.9%) as the carbon source and hydrogen (purity greater than 99.999%) and argon (purity greater than 99.999%) as the carrier gases.

下面以碳源为甲烷(纯度大于99.9%)，载气为氢气(纯度大于99.999%)和氩气(纯度大于99.999%)为例，说明一下采用化学气相沉积工艺在预处理后的铜基底的上下表面生长石墨烯，得到石墨烯包覆铜基底的具体过程。

Specifically, it includes the following steps:

具体的，包括以下步骤：

[0056]

(1) Place the pretreated copper substrate into the reactor.

----

(1)将预处理后的铜基底放入反应器中。

[0057]

Specifically, the pretreated copper substrate can be placed in the reactor in a suspended manner so that both the upper and lower surfaces of the pretreated copper substrate can contact the carbon source, thereby growing graphene on the upper and lower surfaces of the pretreated copper substrate.

具体的，可将预处理后的铜基底以悬浮方式放入反应器中，以使预处理后的铜基底的上下表面均能接触碳源，以在预处理后的铜基底的上下表面生长石墨烯。

For example, four supports can be placed at the four corners of the pretreated copper substrate so that the upper and lower surfaces of the pretreated copper substrate can contact the carbon source.

例如，可采用四个支撑物支撑在预处理后的铜基底的四个角上，使预处理后的铜基底的上下表面均能接触碳源。

[0058]

(2) Introduce carrier gas (argon) into the reactor to purge the air from the reactor and prevent oxidation of the copper substrate during the heating process.

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(2)向反应器内通入载气(氩气)，以排空反应器内的空气，以免在升温过程中造成铜基底氧化。

[0059]

(3) Introduce carrier gas (a mixture of hydrogen and argon) into the reactor and raise the temperature of the reactor to the preset reaction temperature at a preset heating rate.

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(3)向反应器内通入载气(氢气和氩气的混合气)，以预设的升温速率将反应器的温度升高至预设的反应温度。

[0060]

For example, in one possible implementation, the preset heating rate is 20°C/min, and the preset reaction temperature is 900°C to 1050°C, for example, it could be 1000°C.

例如，在一可能的实现方式中，预设的升温速率为20°C/min，预设的反应温度为900°C～1050°C，例如，可以是1000°C。

[0061]

(4) After the reactor temperature reaches the preset reaction temperature, a gaseous carbon source is introduced into the reactor and the reaction is carried out for a period of time.

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(4)在反应器的温度达到预设的反应温度后，向反应器通入气体碳源，反应一段时间。

[0062]

(5) Keep the original gas flow rate of each gas unchanged, reduce the temperature of the reactor until the temperature drops below 100°C, and obtain the graphene-coated copper substrate.

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(5)保持各气体原有的气流量不变，降低反应器的温度，直至温度降至100°C以下，得到石墨烯包覆铜基底。

[0063]

It should be noted that, due to the good matching relationship between the graphene honeycomb lattice and the copper (111) crystal plane lattice, after graphene deposition and growth, the grains on the surface of the graphene-coated copper substrate are significantly increased, and the crystal planes undergo orientation transformation. The graphene-coated copper substrate exhibits a preferred orientation of the (111) crystal plane, and the (111) crystal planes in the material exhibit an arrangement that is close to a single crystal long-range order, which effectively reduces the scattering effect of defects on electron transport parameters and is beneficial to improving the electrical conductivity of the material.

需要说明的是，由于石墨烯蜂巢晶格与铜(111)晶面晶格具有良好的匹配关系，因此，在经过石墨烯沉积生长之后，石墨烯包覆铜基底表面的晶粒显著增大，并且晶面发生了取向转变，石墨烯包覆铜基底呈(111)晶面择优取向，而(111)晶面在材料内部呈现出一种近似于单晶长程有序的排列方式，有效地降低缺陷对电子传输参数的散射作用，有利于提高材料的电导率。

[0064]

Specifically, Figure 3 is an X-ray diffraction pattern of a graphene-coated copper substrate obtained by the method provided in this application, as shown in an exemplary embodiment of this application.

具体的，图3为本申请一示例性实施例示出的采用本申请提供的方法得到的石墨烯包覆铜基底的X射线衍射图。

In Figure 3a, the X-ray diffraction pattern of the original plate-shaped copper substrate is shown, and the X-ray diffraction pattern of the graphene-coated copper substrate is shown in Figure 3b.

其中，图3中a图为原始板状铜基底的X射线衍射图，图3中的b图为石墨烯包覆铜基底的X射线衍射图。

As can be seen from Figure 3, after graphene deposition and growth, the graphene-coated copper substrate exhibits a preferred orientation of the (111) crystal plane.

从图3可以看出，在经过石墨烯沉积生长之后，石墨烯包覆铜基底呈(111)晶面择优取向。

[0065]

Furthermore, Figure 4 is a Raman diagram of graphene grown using the method provided in this application, as illustrated in an exemplary embodiment of this application.

进一步地，图4为本申请一示例性实施例示出的采用本申请提供的方法生长的石墨烯的Raman图。

Figure 5 is an SEM image of a graphene-coated copper substrate obtained by the method provided in this application, as illustrated in an exemplary embodiment of this application.

图5为本申请一示例性实施例示出的采用本申请提供的方法得到的石墨烯包覆铜基底的SEM图。

First, as can be seen from Figure 4, the grown graphene does not have a D peak (defect peak), and the intensity of both the G peak and the 2D peak is relatively high. By comparing the intensity ratio of the 2D peak and the G peak, it can be seen that the number of graphene layers has been well controlled. The ratio of single-layer graphene is close to the theoretical value of 2.1, indicating that the quality of the grown graphene is high.

首先，从图4中可以看出，所生长的石墨烯不存在D峰(缺陷峰)，G峰和2D峰的强度均较高，通过比较2D峰和G峰强度比值可以看出，石墨烯的层数得到了较好的控制，其中单层石墨烯的比值接近理论值2.1，表明生长的石墨烯的质量较高。

Secondly, as can be seen from Figure 5, the grown graphene is relatively uniform and of high quality.

其次，从图5可以看出，生长的石墨烯较均匀，质量较高。

[0066]

Optionally, in one possible implementation of this application, step S102 specifically includes: growing a single layer of graphene on the upper and lower surfaces of the pretreated copper substrate using a chemical vapor deposition process to obtain a graphene-coated copper substrate.

可选地，在本申请一可能的实现方式中，步骤S102具体包括：采用化学气相沉积工艺在所述预处理后的铜基底的上下表面生长单层石墨烯，得到石墨烯包覆铜基底。

[0067]

Specifically, the process steps for growing monolayer graphene are similar to those described above, and will not be repeated here.

具体的，生长单层石墨烯的工艺步骤与前面所述的生长石墨烯的工艺步骤类似，此处不再赘述。

[0068]

It should be noted that by growing a single layer of graphene on a pretreated copper substrate, interlayer conduction and scattering can be reduced, which is beneficial to improving the electrical conductivity of the material.

需要说明的是，通过在预处理后的铜基底上生长单层石墨烯，这样，可降低层间传导和散射，有利于提高材料的电导率。

[0069]

Furthermore, in another possible implementation of this application, step S102 specifically includes: growing single-crystal graphene on the upper and lower surfaces of the pretreated copper substrate using a chemical vapor deposition process to obtain a graphene-coated copper substrate.

进一步地，在本申请另一可能的实现方式中，步骤S102具体包括：采用化学气相沉积工艺在所述预处理后的铜基底的上下表面生长单晶石墨烯，得到石墨烯包覆铜基底。

[0070]

Specifically, in one possible implementation of this application, the step of growing single-crystal graphene may include:

具体的，在本申请一可能的实现方式中，生长单晶石墨烯的步骤，可以包括：

[0071]

Step 1: Place the pretreated copper substrate in the reactor.

步骤一：将预处理后的铜基底置于反应器中。

[0072]

Specifically, the pretreated copper substrate can be placed in a reactor in a suspended manner so that both the upper and lower surfaces of the pretreated copper substrate can contact the carbon source, thereby growing graphene on the upper and lower surfaces of the pretreated copper substrate and generating graphene-coated copper substrate.

具体的，可以将预处理后的铜基底以悬浮方式置于反应器中，以使预处理后的铜基底的上下表面均能接触碳源，以在预处理后的铜基底的上下表面生长石墨烯，生成石墨烯包覆铜基底。

[0073]

Step 2: Introduce argon and hydrogen into the reactor to purge the air from the reactor.

步骤二：向反应器中通入氩气和氢气，以排尽反应器中的空气。

[0074]

Step 3: Under the protection of argon atmosphere, raise the temperature of the reactor to the preset reaction temperature at the preset heating rate and maintain it for 30 minutes.

步骤三：在氩气气氛保护下，以预设的升温速率将反应器的温度升高至预设的反应温度，并保持30min。

[0075]

Specifically, in one possible implementation of this application, the preset heating rate can be 20°C/min, and the preset reaction temperature can be 900°C～1050°C, for example, it can be 1000°C.

具体的，在本申请一可能的实现方式中，预设的升温速率可以为20°C/min，预设的反应温度可以为900°C～1050°C，例如，可以是1000°C。

[0076]

Step 4: Introduce gaseous carbon source and hydrogen into the reactor and react for 1 min to 10 min to grow single-crystal graphene on the upper and lower surfaces of the pretreated copper substrate.

步骤四：向反应器通入气体碳源和氢气，反应1min～10min，以在上述预处理后的铜基底的上下表面生长单晶石墨烯。

[0077]

Specifically, in one possible implementation of this application, the gaseous carbon source is a diluted carbon source, the diluent gas is argon, and the mass concentration of argon is 0.5%.

具体的，在本申请一可能的实现方式中，气体碳源为稀释碳源，稀释气体为氩气，且氩气的质量浓度为0.5%。

[0078]

Furthermore, the gas flow rates of the gaseous carbon source, hydrogen, and argon are 3 sccm (volume flow rate, per milliliter per minute under standard conditions), 10 sccm, and 100 sccm, respectively.

进一步地，气体碳源、氢气和氩气的气流量分别为3sccm(体积流量单位，标况下每毫升每分)、10sccm和100sccm。

[0079]

Step 5: Keep the gas flow rates of carbon source and hydrogen constant, and lower the temperature of the reactor until it drops below 100°C to obtain a graphene-coated copper substrate.

步骤五：保持气体碳源和氢气的气流量不变，降低反应器的温度，直至温度降至100°C以下，得到石墨烯包覆铜基底。

[0080]

S103. At least one of the above-mentioned graphene-coated copper substrates is subjected to hot pressing and sintering treatment to obtain a copper-based graphene composite material; wherein the above-mentioned copper-based graphene composite material is a layered composite material formed by alternating composite of graphene and copper substrate, and the copper substrate is in a single crystal state in the thickness direction of the above-mentioned layered composite material and is in a (111) crystal plane preferred orientation.

S103、对至少一片上述石墨烯包覆铜基底进行热压烧结处理，得到铜基石墨烯复合材料；其中，上述铜基石墨烯复合材料为由石墨烯和铜基底交替复合形成的层状复合材料，铜基底在上述层状复合材料的厚度方向上呈单晶态，且呈(111)晶面择优取向。

[0081]

In an optional embodiment of this application, the hot pressing sintering process described above is vacuum hot pressing sintering, hot pressing sintering under gas protection, discharge plasma sintering, or microwave sintering.

在本申请一可选的实施方式中，上述热压烧结处理为真空热压烧结处理、气体保护下热压烧结处理、放电等离子体烧结处理或微波烧结处理。

[0082]

Optionally, in one possible implementation of this application, in this step, at least one of the above-mentioned graphene-coated copper substrates can be subjected to hot pressing sintering treatment under the conditions of sintering temperature of 800°C～950°C, sintering pressure of 30MPa～150MPa and sintering time of 10min～30min.

可选地，在本申请一可能的实现方式中，本步骤中，可以在烧结温度为800°C～950°C、烧结压强为30MPa～150MPa和烧结时间为10min～30min的条件下，对至少一片上述石墨烯包覆铜基底进行热压烧结处理。

Preferably, at least one of the graphene-coated copper substrates is subjected to hot-press sintering treatment under the conditions of a sintering temperature of 900°C, a sintering pressure of 50 MPa, and a sintering time of 20 min.

优选地，在烧结温度为900°C、烧结压强为50MPa和烧结时间为20min的条件下，对至少一片所述石墨烯包覆铜基底进行热压烧结处理。

[0083]

It should be noted that, through repeated experimental studies, the method provided in this application has been proven that, under the conditions of a sintering temperature of 900°C, a sintering pressure of 50MPa, and a sintering time of 20min, the electrical conductivity of the copper-based graphene composite material obtained by hot pressing sintering is higher than that of the copper-based graphene composite material obtained under other experimental conditions.

需要说明的是，本申请提供的方法，经反复试验研究证明，在烧结温度为900°C、烧结压强为50MPa和烧结时间为20min的条件下，热压烧结得到的铜基石墨烯复合材料的电导率高于其他试验条件下得到的铜基石墨烯复合材料的电导率。

[0084]

The following sets of experimental data are provided to illustrate in detail the performance of the copper-based graphene composite material prepared by the preparation method of the copper-based graphene composite material provided in this application.

下面给出几组试验数据，用于详细说明本申请提供的铜基石墨烯复合材料的制备方法所制备的铜基石墨烯复合材料的性能。

[0085]

Experiment 1

试验一

[0086]

Using acetylene gas as a carbon source, monolayer graphene was grown on the upper and lower surfaces of a pretreated copper substrate with a thickness of 100 μm to obtain a graphene-coated copper substrate. Subsequently, five graphene-coated copper substrates were subjected to vacuum hot pressing sintering at a sintering temperature of 950℃, a sintering pressure of 10 MPa, and a sintering time of 30 min to obtain a copper-based graphene composite material.

以乙炔气体为碳源，在厚度为100μm的预处理后的铜基底的上下表面生长单层石墨烯，得到石墨烯包覆铜基底，之后，在烧结温度为950℃、烧结压强为10MPa和烧结时间为30min的条件下，将5片石墨烯包覆铜基底进行真空热压烧结处理，得到铜基石墨烯复合材料。

Testing showed that the electrical conductivity of this copper-based graphene composite material is higher than that of pure silver, meeting the requirements.

经检测，该铜基石墨烯复合材料的电导率高于纯银，满足要求。

[0087]

Experiment 2

试验二

[0088]

Using PMMA solid as a carbon source, 2 to 3 layers of graphene were grown on a pretreated copper substrate with a thickness of 7 μm to obtain a graphene-coated copper substrate. Then, under the conditions of sintering temperature of 800°C, sintering pressure of 30MPa and sintering time of 10min, the two graphene-coated copper substrates were hot-pressed and sintered under argon atmosphere protection to obtain a copper-based graphene composite material.

以PMMA固体为碳源，在厚度为7μm的预处理后的铜基底上生长2至3层石墨烯，得到石墨烯包覆铜基底，之后，在烧结温度为800°C、烧结压强为30MPa和烧结时间为10min的条件下，将2片石墨烯包覆铜基底在氩气气氛保护下进行热压烧结处理，得到铜基石墨烯复合材料。

Testing showed that the electrical conductivity of this copper-based graphene composite material is higher than that of pure silver, meeting the requirements.

经检测，该铜基石墨烯复合材料的电导率高于纯银，满足要求。

[0089]

Experiment 3

试验三

[0090]

Using methane gas as a carbon source, single-crystal graphene was grown on a pretreated copper substrate with a thickness of 9 μm to obtain a graphene-coated copper substrate. Then, a graphene-coated copper substrate was subjected to discharge plasma sintering treatment at a sintering temperature of 900°C, a sintering pressure of 50 MPa, and a sintering time of 20 min to obtain a copper-based graphene composite material.

以甲烷气体为碳源，在厚度为9μm的预处理后的铜基底上生长单晶石墨烯，得到石墨烯包覆铜基底，之后，在烧结温度为900°C、烧结压强为50MPa和烧结时间为20min的条件下，将1片石墨烯包覆铜基底进行放电等离子体烧结处理，得到铜基石墨烯复合材料。

Testing showed that the electrical conductivity of this copper-based graphene composite material is higher than that of pure silver, meeting the requirements.

经检测，该铜基石墨烯复合材料的电导率高于纯银，满足要求。

Furthermore, compared to Experiment 1 and Experiment 2, the electrical conductivity of the copper-based graphene composite material prepared using the method in this example is significantly improved.

此外，相比于试验一和试验二，采用本例方法制备出的铜基石墨烯复合材料的电导率明显提高。

[0091]

Therefore, the preparation method of the copper-based graphene composite material provided in this application uses chemical vapor deposition to grow graphene on a pretreated copper substrate, generating graphene to coat the copper substrate. The thickness of the copper substrate is 5μm to 25μm. In this way, the graphene generation process promotes significant growth of the copper substrate grains and changes the orientation of the crystal planes. The surface of the copper substrate has a (111) crystal plane distribution, and the grains grow into a single crystal state in the thickness direction of the copper substrate, which is beneficial to improving the electrical conductivity of the material.

由此可见，本申请提供的铜基石墨烯复合材料的制备方法，采用化学气相沉积法在预处理后的铜基底上生长石墨烯，生成石墨烯包覆铜基底，且铜基底的厚度为5μm～25μm，这样，石墨烯的生成过程促进铜基底晶粒显著长大，并且晶面发生取向转变，铜基底表面晶面取向(111)晶面分布，同时在铜基底的厚度方向晶粒生长为单晶状态，有利于提高材料的电导率。

In addition, hot pressing and sintering of graphene-coated copper substrates, with the simultaneous application of high temperature and high pressure, significantly reduces the internal defect density of the material, which is beneficial to improving the electrical conductivity of the material.

此外，对石墨烯包覆铜基底进行热压烧结处理，高温高压的同时施加使材料内部缺陷密度大幅降低，有利于提高材料的电导率。

Thus, because graphene promotes the transformation of the grain orientation of the copper substrate, the grains in the thickness direction of the copper substrate grow into a single crystal state, effectively reducing the scattering effect of defects on electron transport. In addition, hot pressing sintering significantly improves the bonding energy between the graphene inside the graphene-coated copper substrate and the copper interface, and the copper-graphene interface plays an intrinsic role of high two-dimensional conductivity, becoming a fast channel for charge carriers. Combining the above two aspects, the electrical conductivity of the prepared copper-based graphene composite material is significantly increased.

这样，由于石墨烯促进铜基底的晶粒取向的转变，铜基底的厚度方向晶粒生长为单晶状态，有效地降低缺陷对电子传输产生的散射作用，此外，热压烧结使得石墨烯包覆铜基底内部石墨烯与铜界面的结

合能得到显著的提高，铜-石墨烯界面发挥了二维高导的本征特性成为载流子的快速通道；综合上述两方面的影响，使制备出的铜基石墨烯复合材料的电导率明显增高。

[0092]

The second aspect of this application also provides a copper-based graphene composite material prepared according to the method provided in the first aspect of this application. The composite material is a layered composite material formed by alternating composites of graphene and copper substrate. The copper substrate is in a single crystal state in the thickness direction of the layered composite material and is preferably oriented with a (111) crystal plane.

本申请第二方面还提供一种根据本申请第一方面提供的方法制备出的铜基石墨烯复合材料，所述复合材料为由石墨烯和铜基底交替复合形成的层状复合材料，所述铜基底在所述层状复合材料的厚度方向上呈单晶态，且呈(111)晶面择优取向。

[0093]

The above description is merely a preferred embodiment of this application and is not intended to limit this application. Any modifications, equivalent substitutions, improvements, etc., made within the spirit and principles of this application should be included within the scope of protection of this application.

以上所述仅为本申请的较佳实施例而已，并不用以限制本申请，凡在本申请的精神和原则之内，所做的任何修改、等同替换、改进等，均应包含在本申请保护的范围之内。