Notice

DESCRIPTION CN118996481A

A Joule thermal flash mass production method for biomass carbon-based composite materials and its applications

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一种焦耳热法闪速宏量制备生物质碳基复合材料及其应用

[0001]

Technical Field

技术领域

[n0001]

This invention relates to the field of electrocatalytic materials technology, specifically to a Joule thermal flash mass production method for preparing biomass carbon-based composite materials and its applications.

本发明涉及电催化材料技术领域，具体为一种焦耳热法闪速宏量制备生物质碳基复合材料及其应用。

[0003]

Background Technology

背景技术

[n0002]

Generally, the yield ratio between corn and corn stalks is roughly 1:0.8, which means that about 231 million tons of corn stalks can be harvested each year.

一般情况下，玉米与玉米秸秆之间的产量比例大致为1:0.8，这意味着每年可收获约2.31亿吨玉米秸。

Straw residues are a byproduct of agricultural resources in many regions and are widely used in many agricultural industries.

秸秆残留物是许多地区农业资源的副产品，在许多农业产业中得到了广泛的利用。

However, the most common method of utilization at present is burning straw back into the field, which not only has a low resource utilization rate but also brings a lot of CO2 emissions, causing secondary damage to the environment.

然而，当前最常用的利用方式秸秆燃烧还田，不仅资源化利用率低还会带来大量CO₂排放问题，对环境造成二次伤害。

[n0003]

Currently, various CO2 emission reduction and utilization schemes have been proposed, such as carbon capture and storage technology and electrochemical CO2 reduction technology.

目前，人们已经提出了多种CO₂减排和利用的方案，例如运用碳捕获和储存技术、电化学CO₂还原技术等。

Among these technologies, the use of carbon-based materials for CO_NER4 adsorption, conversion and storage is generally considered a promising approach.

在这些技术中，普遍认为利用碳基材料进行CO₂吸附、转化和储存是一种具有前景的处理办法。

[n0004]

Research has found that biomass carbon-based materials co-doped with nickel and nitrogen exhibit particularly outstanding CO₂RR performance.

研究发现，镍与氮元素共同掺杂的生物质碳基材料具有尤为出色的CO₂RR性能。

However, its preparation process has many problems, such as complicated operation, long preparation process, low product yield, and large batch-to-batch variability, which prevents biomass carbon-based catalysts from being widely used in the market.

但其制备工艺存在诸多问题，无法规避操作繁琐、制备流程漫长、产物产量少、批次差异性大等问题，使得生物质碳基催化剂尚未得到广泛的市场化应用。

Therefore, to realize the industrial application of agricultural waste, the problem of large-scale preparation must first be solved. In recent years, the application of methods such as laser induction, high-voltage pulse, and Joule rapid heating has gradually become a new approach for the research on the large-scale preparation of solid carbon-based materials. In recent years, the Joule rapid heating method has been considered an innovative and efficient method based on electric Joule heating. The target temperature can be reached in an ultra-short processing time, which can overcome the problem of uneven distribution of active sites caused by differences in thermal migration rate. Rapid recombination of carbon structures can be achieved through instantaneous high-energy and high-heat methods, thereby enabling the functional modification and large-scale preparation of biomass carbon-based materials.

因此，要实现农业废弃物的工业化应用必须首先解决宏量化制备难题。 近年来，激光诱导、高电压脉冲和焦耳快速加热等方法的应用逐步成为固体碳基物质宏量制备研究的新思路。 近年来，焦耳快速加热方法被认为是一种基于电焦耳加热的创新且高效的方法。 可以在超短的处理时间内达到目标温度，这可以克服由于热迁移速率差异导致的活性位点分布不均匀的问题。 通过瞬间高能、高热的手段可实现碳结构快速重组，从而实现生物质碳基材料的功能化修饰和宏量制备。

[0007]

Summary of the Invention

发明内容

[n0005]

The purpose of this invention is to address the shortcomings of traditional corn stalk electrocatalysts, such as complex preparation steps and low efficiency, by utilizing the Joule rapid heating method to achieve efficient and large-scale preparation of electrocatalysts using corn stalks as precursors, thereby realizing the industrial-scale, kilogram-scale preparation of biomass carbon-based materials.

本发明的目的是针对传统玉米秸秆电催化剂的制备步骤复杂，效率低下等缺陷，利用焦耳快速加热法实现高效大量的以玉米秸秆为前驱体的电催化CO2催化剂的制备，实现生物质碳基材料的工业化、公斤级制备。

[n0006]

To achieve the above-mentioned objectives, the present invention provides the following technical solution: a Joule thermal flash mass production method for preparing biomass carbon-based composite materials, comprising the following preparation steps:

为了实现上述发明目的，本发明提供如下技术方案：一种焦耳热法闪速宏量制备生物质碳基复合材料，包括以下制备步骤：

[n0007]

(1) The corn stalks were ball-milled for 30-60 minutes, then crushed and passed through a 200-mesh sieve. After ultrasonic washing with deionized water, the stalks were filtered, the solid was collected, and freeze-dried to obtain corn stalk powder.

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(1)将玉米秸秆进行球磨30～60min，随后粉碎过200目筛，经去离子水超声洗涤，过滤，取固体，冷冻干燥，得玉米秸秆粉末；

[n0008]

(2) The corn stalk powder was calcined to obtain corn stalk carbon precursor;

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(2)将玉米秸秆粉末进行煅烧，得玉米秸秆碳前驱物；

[n0009]

(3) Mix the corn straw carbon precursor with an alkali source evenly, and then activate it by calcination to obtain intermediate A;

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(3)将玉米秸秆碳前驱物与碱源混合均匀，而后经煅烧活化，得中间物A；

[n0010]

(4) Disperse intermediate A in hydrochloric acid solution, acid wash for 2 h, wash with 50 wt% ethanol aqueous solution until the pH of the washing solution is 7, dry at 80°C for 24-48 h to obtain biomass carbon powder;

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(4)将中间物A分散于盐酸溶液中，酸洗2h，用50wt%乙醇水溶液洗涤至洗涤液pH为7，80°C干燥24～48h，得生物质碳粉；

[n0011]

(5) Mix biomass carbon powder, dicyandiamide and nickel chloride hexahydrate evenly to obtain a mixture;

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(5)将生物质碳粉、双氰胺和六水合氯化镍混合均匀，得混合物；

[n0012]

(6) The mixture is subjected to Joule calcination to obtain a biomass carbon-based composite material.

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(6)将混合物进行焦耳煅烧，得生物质碳基复合材料。

[n0013]

Furthermore, the ultrasonic rate in step (1) is 21 kHz and the duration is 2 to 3 hours.

进一步的，步骤(1)所述超声速率为21kHz、时间为2～3h。

[n0014]

Furthermore, the freeze-drying temperature in step (1) is -45°C and the time is 24 to 48 hours.

进一步的，步骤(1)所述冷冻干燥的温度为-45°C、时间为24～48h。

[n0015]

Furthermore, the mass ratio of corn stalks to deionized water in step (1) is 5-8:10-15.

进一步的，步骤(1)所述玉米秸秆与去离子水的质量比为5～8:10～15。

[n0016]

Furthermore, the calcination conditions in step (2) are: nitrogen atmosphere, temperature of 500°C, and time of 5h.

进一步的，步骤(2)所述煅烧的条件：气氛为氮气、温度为500°C、时间为5h。

[n0017]

Furthermore, the calcination conditions in step (3) are: nitrogen atmosphere, heating rate of 5°C/min, temperature of 800°C, and time of 2h.

进一步的，步骤(3)所述煅烧的条件：气氛为氮气、升温速率为5°C/min、温度为800°C、时间为2h。

[n0018]

Furthermore, the alkali source in step (3) is potassium hydroxide, and the mass ratio of corn straw carbon precursor to potassium hydroxide is 1:2.

进一步的，步骤(3)所述碱源为氢氧化钾，玉米秸秆碳前驱物与氢氧化钾的质量比为1:2。

[n0019]

Furthermore, in step (5), the mass ratio of biomass carbon powder, dicyandiamide, and nickel chloride hexahydrate is 1–5:0.28–0.56:1.18–2.37.

进一步的，步骤(5)所述生物质碳粉、双氰胺和六水合氯化镍的质量比为1～5:0.28～0.56:1.18～2.37。

[n0020]

Furthermore, the Joule calcination temperature in step (6) is 500–1000°C and the heating time is 1–10 seconds.

进一步的，步骤(6)所述焦耳煅烧温度为500～1000°C、升温时间为1～10s。

[n0021]

Compared with existing technologies, the beneficial effects achieved by this invention are as follows: This invention adopts the Joule rapid heating method, uses corn stalks as raw materials, and introduces nitrogen and nickel sources to achieve flash mass production of biomass carbon-based composite materials, realizing a virtuous cycle of "taking from carbon and using it for carbon"; in addition, this invention has the characteristics of mild processing conditions, short reaction time, low energy consumption, and environmental friendliness, and is suitable for mass production, with certain application prospects.

与现有技术相比，本发明所达到的有益效果是：本发明采用焦耳快速加热法，利用玉米秸秆为原料，引入氮源和镍源，实现闪速宏量制备生物质碳基复合材料，实现材料的“取之于碳，用之于碳”的良性循环；此外，本发明具有处理条件温和、反应时间短、能耗低、环境友好的特点，适用于大批量生产，有一定的应用前景。

This study not only provides new ideas for improving the preparation efficiency of biomass carbon-based materials, but also enables the efficient electrochemical reduction and resource utilization of CO₂.

通过本研究，不仅可以为提高生物质碳基材料的制备效率提供新思路，而且可以实现CO₂高效的电化学还原和资源化利用。

[0025]

Attached Figure Description

附图说明

[n0022]

The accompanying drawings are provided to further illustrate the invention and form part of the specification. They are used together with the embodiments of the invention to explain the invention and do not constitute a limitation thereof.

附图用来提供对本发明的进一步理解，并且构成说明书的一部分，与本发明的实施例一起用于解释本发明，并不构成对本发明的限制。

In the attached diagram:

在附图中：

[n0023]

Figure 1 shows the XRD patterns of the biomass carbon-based composite materials prepared by the Joule heating method in Examples 1-3;

图1为实施例1-3中焦耳热法制备的生物质碳基复合材料的XRD图谱；

[n0024]

Figure 2 shows the SEM image of the biomass carbon-based composite material prepared by the Joule heating method in Example 1;

图2为实施例1中焦耳热法制备的生物质碳基复合材料的SEM图谱；

[n0025]

Figure 3 shows the Faraday efficiencies of CO and H₂ in the biomass carbon-based composite materials prepared by the Joule heating method in Examples 1 and 4.

图3为实施例1、4中焦耳热法制备的生物质碳基复合材料的CO和H₂的法拉第效率。

[0030]

Detailed Implementation

具体实施方式

[n0026]

The technical solutions of the present invention will be clearly and completely described below with reference to the embodiments of the present invention. Obviously, the described embodiments are only some embodiments of the present invention, and not all embodiments.

下面将结合本发明实施例，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。

[n0027]

Example 1

实施例1

[n0028]

(1) The corn stalks were ball-milled for 45 min, then pulverized and passed through a 200-mesh sieve, washed with deionized water at 21 kHz for 2.5 h, filtered, and the solid was dried at -45 °C for 36 h to obtain corn stalk powder; the mass ratio of corn stalks to deionized water was 7:12.

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(1)将玉米秸秆进行球磨45min，随后粉碎过200目筛，经去离子水，于21kHz超声洗涤2.5h，过滤，取固体，于-45°C干燥36h，得玉米秸秆粉末；所述玉米秸秆与去离子水的质量比为7:12；

[n0029]

(2) The corn stalk powder was calcined at 500°C in a nitrogen atmosphere for 5 hours to obtain corn stalk carbon precursor.

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(2)将玉米秸秆粉末于500°C的氮气氛围下进行煅烧，时间为5h，得玉米秸秆碳前驱物；

[n0030]

(3) Mix the corn stalk carbon precursor with potassium hydroxide evenly, and calcine and activate it at 800°C at 5°C/min under a nitrogen atmosphere for 2 hours to obtain intermediate A; the mass ratio of the corn stalk carbon precursor to potassium hydroxide is 1:2.

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(3)将玉米秸秆碳前驱物与氢氧化钾混合均匀，在氮气氛围下，以5°C/min升温至800°C，进行煅烧活化，时间为2h，得中间物A；所述玉米秸秆碳前驱物与氢氧化钾的质量比为1:2；

[n0031]

(4) Disperse intermediate A in hydrochloric acid solution, acid wash for 2 h, wash with 50 wt% ethanol aqueous solution until the pH of the washing solution is 7, dry at 80°C for 36 h to obtain biomass carbon powder;

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(4)将中间物A分散于盐酸溶液中，酸洗2h，用50wt%乙醇水溶液洗涤至洗涤液pH为7，80°C干燥36h，得生物质碳粉；

[n0032]

(5) Mix biomass carbon powder, dicyandiamide and nickel chloride hexahydrate evenly to obtain a mixture; the mass ratio of biomass carbon powder, dicyandiamide and nickel chloride hexahydrate is 1:0.28:1.18;

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(5)将生物质碳粉、双氰胺和六水合氯化镍混合均匀，得混合物；生物质碳粉、双氰胺和六水合氯化镍的质量比为1:0.28:1.18；

[n0033]

(6) The mixture is heated to 700°C within 5 seconds and subjected to Joule calcination to obtain biomass carbon-based composite material, namely Ni/NC-5-700.

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(6)将混合物在5s内，升温至700°C，进行焦耳煅烧，得生物质碳基复合材料，即Ni/NC-5-700。

[n0034]

Example 2

实施例2

[n0035]

(1) The corn stalks were ball-milled for 45 min, then pulverized and passed through a 200-mesh sieve, washed with deionized water at 21 kHz for 2.5 h, filtered, and the solid was dried at -45 °C for 36 h to obtain corn stalk powder; the mass ratio of corn stalks to deionized water was 7:12.

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(1)将玉米秸秆进行球磨45min，随后粉碎过200目筛，经去离子水，于21kHz超声洗涤2.5h，过滤，取固体，于-45°C干燥36h，得玉米秸秆粉末；所述玉米秸秆与去离子水的质量比为7:12；

[n0036]

(2) The corn stalk powder was calcined at 500°C in a nitrogen atmosphere for 5 hours to obtain corn stalk carbon precursor.

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(2)将玉米秸秆粉末于500°C的氮气氛围下进行煅烧，时间为5h，得玉米秸秆碳前驱物；

[n0037]

(3) Mix the corn stalk carbon precursor with potassium hydroxide evenly, and calcine and activate it at 800°C at 5°C/min under a nitrogen atmosphere for 2 hours to obtain intermediate A; the mass ratio of the corn stalk carbon precursor to potassium hydroxide is 1:2.

---

(3)将玉米秸秆碳前驱物与氢氧化钾混合均匀，在氮气氛围下，以5°C/min升温至800°C，进行煅烧活化，时间为2h，得中间物A；所述玉米秸秆碳前驱物与氢氧化钾的质量比为1:2；

[n0038]

(4) Disperse intermediate A in hydrochloric acid solution, acid wash for 2 h, wash with 50 wt% ethanol aqueous solution until the pH of the washing solution is 7, dry at 80°C for 36 h to obtain biomass carbon powder;

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(4)将中间物A分散于盐酸溶液中，酸洗2h，用50wt%乙醇水溶液洗涤至洗涤液pH为7，80°C干燥36h，得生物质碳粉；

[n0039]

(5) Mix biomass carbon powder, dicyandiamide and nickel chloride hexahydrate evenly to obtain a mixture; the mass ratio of biomass carbon powder, dicyandiamide and nickel chloride hexahydrate is 1:0.28:1.18;

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(5)将生物质碳粉、双氰胺和六水合氯化镍混合均匀，得混合物；生物质碳粉、双氰胺和六水合氯化镍的质量比为1:0.28:1.18；

[n0040]

(6) The mixture is heated to 800°C within 5 seconds and subjected to Joule calcination to obtain biomass carbon-based composite material, namely Ni/NC-5-800.

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(6)将混合物在5s内，升温至800°C，进行焦耳煅烧，得生物质碳基复合材料，即Ni/NC-5-800。

[n0041]

Example 3

实施例3

[n0042]

(1) The corn stalks were ball-milled for 45 min, then pulverized and passed through a 200-mesh sieve, washed with deionized water at 21 kHz for 2.5 h, filtered, and the solid was dried at -45 °C for 36 h to obtain corn stalk powder; the mass ratio of corn stalks to deionized water was 7:12.

---

(1)将玉米秸秆进行球磨45min，随后粉碎过200目筛，经去离子水，于21kHz超声洗涤2.5h，过滤，取固体，于-45°C干燥36h，得玉米秸秆粉末；所述玉米秸秆与去离子水的质量比为7:12；

[n0043]

(2) The corn stalk powder was calcined at 500°C in a nitrogen atmosphere for 5 hours to obtain corn stalk carbon precursor.

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(2)将玉米秸秆粉末于500°C的氮气氛围下进行煅烧，时间为5h，得玉米秸秆碳前驱物；

[n0044]

(3) Mix the corn stalk carbon precursor with potassium hydroxide evenly, and calcine and activate it at 800°C at 5°C/min under a nitrogen atmosphere for 2 hours to obtain intermediate A; the mass ratio of the corn stalk carbon precursor to potassium hydroxide is 1:2.

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(3)将玉米秸秆碳前驱物与氢氧化钾混合均匀，在氮气氛围下，以5°C/min升温至800°C，进行煅烧活化，时间为2h，得中间物A；所述玉米秸秆碳前驱物与氢氧化钾的质量比为1:2；

[n0045]

(4) Disperse intermediate A in hydrochloric acid solution, acid wash for 2 h, wash with 50 wt% ethanol aqueous solution until the pH of the washing solution is 7, dry at 80°C for 36 h to obtain biomass carbon powder;

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(4)将中间物A分散于盐酸溶液中，酸洗2h，用50wt%乙醇水溶液洗涤至洗涤液pH为7，80°C干燥36h，得生物质碳粉；

[n0046]

(5) Mix biomass carbon powder, dicyandiamide and nickel chloride hexahydrate evenly to obtain a mixture; the mass ratio of biomass carbon powder, dicyandiamide and nickel chloride hexahydrate is 1:0.28:1.18;

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(5)将生物质碳粉、双氰胺和六水合氯化镍混合均匀，得混合物；生物质碳粉、双氰胺和六水合氯化镍的质量比为1:0.28:1.18；

[n0047]

(6) The mixture is heated to 900°C within 5 seconds and subjected to Joule calcination to obtain biomass carbon-based composite material, namely Ni/NC-5-900.

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(6)将混合物在5s内，升温至900°C，进行焦耳煅烧，得生物质碳基复合材料，即Ni/NC-5-900。

[n0048]

Example 4

实施例4

[n0049]

(1) The corn stalks were ball-milled for 45 min, then pulverized and passed through a 200-mesh sieve, washed with deionized water at 21 kHz for 2.5 h, filtered, and the solid was dried at -45 °C for 36 h to obtain corn stalk powder; the mass ratio of corn stalks to deionized water was 7:12.

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(1)将玉米秸秆进行球磨45min，随后粉碎过200目筛，经去离子水，于21kHz超声洗涤2.5h，过滤，取固体，于-45°C干燥36h，得玉米秸秆粉末；所述玉米秸秆与去离子水的质量比为7:12；

[n0050]

(2) The corn stalk powder was calcined at 500°C in a nitrogen atmosphere for 5 hours to obtain corn stalk carbon precursor.

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(2)将玉米秸秆粉末于500°C的氮气氛围下进行煅烧，时间为5h，得玉米秸秆碳前驱物；

[n0051]

(3) Mix the corn stalk carbon precursor with potassium hydroxide evenly, and calcine and activate it at 800°C at 5°C/min under a nitrogen atmosphere for 2 hours to obtain intermediate A; the mass ratio of the corn stalk carbon precursor to potassium hydroxide is 1:2.

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(3)将玉米秸秆碳前驱物与氢氧化钾混合均匀，在氮气氛围下，以5°C/min升温至800°C，进行煅烧活化，时间为2h，得中间物A；所述玉米秸秆碳前驱物与氢氧化钾的质量比为1:2；

[n0052]

(4) Disperse intermediate A in hydrochloric acid solution, acid wash for 2 h, wash with 50 wt% ethanol aqueous solution until the pH of the washing solution is 7, dry at 80°C for 36 h to obtain biomass carbon powder;

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(4)将中间物A分散于盐酸溶液中，酸洗2h，用50wt%乙醇水溶液洗涤至洗涤液pH为7，80°C干燥36h，得生物质碳粉；

[n0053]

(5) Mix biomass carbon powder and dicyandiamide evenly to obtain a mixture; the mass ratio of biomass carbon powder to dicyandiamide is 1:0.28;

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(5)将生物质碳粉、双氰胺混合均匀，得混合物；生物质碳粉、双氰胺的质量比为1:0.28；

[n0054]

(6) The mixture is heated to 800°C within 5 seconds and subjected to Joule calcination to obtain biomass carbon-based composite material, namely NC-5-800.

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(6)将混合物在5s内，升温至800°C，进行焦耳煅烧，得生物质碳基复合材料，即NC-5-800。

[n0055]

It will be apparent to those skilled in the art that the present invention is not limited to the details of the exemplary embodiments described above, and that the present invention can be implemented in other specific forms without departing from the spirit or essential characteristics of the present invention.

对于本领域技术人员而言，显然本发明不限于上述示范性实施例的细节，而且在不背离本发明的精神或基本特征的情况下，能够以其他的具体形式实现本发明。

Therefore, the embodiments should be regarded as exemplary and non-limiting in all respects, and the scope of the invention is defined by the appended claims rather than the foregoing description. Thus, it is intended that all variations falling within the meaning and scope of the equivalents of the claims be included within the invention.

因此，无论从哪一点来看，均应将实施例看作是示范性的，而且是非限制性的，本发明的范围由所附权利要求而不是上述说明限定，因此旨在将落在权利要求的等同要件的含义和范围内的所有变化囊括在本发明内。

Any markings in the claims should not be construed as limiting the scope of the claims.

不应将权利要求中的任何标记视为限制所涉及的权利要求。