Notice

DESCRIPTION CN118387891A

Preparation method of metal boride water electrolysis catalyst and flash evaporation Joule heating technology

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金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法

[0001]

Technical Field

技术领域

[n0001]

This invention relates to the field of inorganic functional materials technology, and in particular to a method for preparing a metal boride electrolysis water catalyst using flash evaporation Joule heating technology.

本发明涉及无机功能材料技术领域，特别涉及金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法。

[0003]

Background Technology

背景技术

[n0002]

With social development and population growth, energy consumption is increasing, and energy mainly comes from traditional fossil fuels (coal, oil, natural gas, etc.). Therefore, it is necessary to find clean and renewable energy sources.

随着社会的发展，人口的增加，能源消耗也日益增多，而能源主要来自传统的化石燃料(煤、石油、天然气等)，因此，需要寻找清洁、可再生的能源。

Hydrogen, as a clean energy source, produces zero pollution upon combustion and is widely regarded as an ideal clean energy carrier.

其中氢气作为一种清洁能源，燃烧产物可以达到零污染，被广泛视为一种理想的清洁能源载体。

Industrial methods for producing hydrogen mainly include methane steam reforming, coal gasification, and water electrolysis. The first two methods produce the greenhouse gas carbon dioxide, and the production process still consumes fossil fuels.

而工业上制备氢气的方法主要有甲烷蒸汽重整、煤气化过程和电解水，其中前两种会产生温室气体二氧化碳，并且制备过程依旧会消耗化石燃料。

Electrolysis of water is the most ideal method for producing hydrogen. Among the traditional electrolysis catalysts, platinum has the best properties, but it has drawbacks such as high price and low reserves. Therefore, in order to improve conversion efficiency, a suitable non-metallic water electrolysis catalyst is proposed.

电解水制氢是最为理想的制备方法，其中传统的电解水催化剂中铂的性质最优，但是存在价格昂贵，储量少等不足。 因此，为了提高转化效率，提出适合的非金属电解水催化剂。

[n0003]

Currently, metal sulfides (such as MoS₂, WS₂), carbides (W₂C, Mo₂C), nitrides (such as NiMoN_x/C), phosphides (such as Ni₂P, MoP), and borides (such as Mo₂B, MoB) can all be used as catalysts for hydrogen production through water electrolysis.

目前，金属硫化物(如MoS₂、WS₂)，碳化物(W₂C、Mo₂C)，氮化物(如NiMoN_x/C)，磷化物(如Ni₂P、MoP)，硼化物(如Mo₂B、MoB)等都可以作为电解水制氢催化剂。

Among them, metal borides are a new type of metal borides that have attracted great attention in the fields of chemistry and materials science. Among them, the borophene structural units and metal-metal bond structure of metal borides have excellent electron transport capabilities, making them a potential material for hydrogen production through water electrolysis. However, borides are more difficult to synthesize than carbides, sulfides, and phosphides. At present, metal borides have the following main problems: (1) They are difficult to synthesize, requiring high temperature and high pressure, which takes a long time.

其中金属硼化物是一种新兴的金属硼化物，在化学以及材料学领域受到极大地关注。 其中金属硼化物中硼烯结构单元和金属-金属键结构，而具有优异的电子传输能力，是一种潜在的电解水裂解制氢

材料。 但是由于硼化物相比于碳化物、硫化物、磷化物合成难一些。 目前，金属硼化物主要存在以下问题：(1)合成难，需要在高温高压下合成，耗时长。

(2)

High temperature and high pressure will result in larger particle size, producing mixed phase products, and impurities are not easy to remove. Therefore, we propose a method for preparing a metal boride electrolysis water catalyst using flash evaporation Joule heating technology, which can reduce preparation time and energy consumption, and can prepare pure phase metal borides.

高温高压会导致粒径较大，产生混合相产物，杂质不易去除。 因此，我们提出一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，能够减少制备时间以及能耗，并且能够制备纯相的金属硼化物。

[0006]

Summary of the Invention

发明内容

[n0004]

In view of this, the purpose of this invention is to propose a method for preparing a metal boride electrolysis water catalyst and a flash evaporation Joule heating technique, which can reduce the preparation time and prepare pure phase metal borides, effectively solving the technical problems in the background art.

有鉴于此，本发明的目的在于提出金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，能够减少制备时间，且能够制备纯相的金属硼化物，可以有效地解决背景技术中的技术问题。

[n0005]

The further defined technical solution of this invention is: a method for preparing a metal boride catalyst using flash Joule heating technology, wherein a metal salt and a boron source are ground and mixed, placed in a Joule heating reactor and sealed, evacuated, and then a gas is introduced for heating to obtain a metal boride; this invention mainly adopts a one-step grinding process to obtain a solid powder precursor, and then obtains the metal boride catalyst by flash Joule heating in a gas.

本发明作为进一步限定的技术方案是：金属硼化物催化剂及闪蒸焦耳热技术制备方法，其通过金属盐、硼源进行研磨混匀，置于焦耳热反应装置中进行密封，抽真空，而后通入气体，进行加热，得到金属硼化物；本发明主要采用一步研磨得到固体粉末前驱物，然后在气体中通过闪蒸焦耳热加热的方式得到金属硼化物催化剂。

[n0006]

The beneficial effects of this invention are:

本发明的有益效果是：

[n0007]

(1) The metal salt and boron source provided by the present invention are ground and mixed, placed in a Joule heating reaction device for sealing and vacuuming, and then gas is introduced and heated to obtain a metal boride catalyst. The present invention obtains a solid powder precursor by one-step grinding, and then obtains metal boride by flash evaporation Joule heating in an atmosphere. The present invention mainly obtains metal boride by flash evaporation Joule heating technology. The material preparation method is fast, simple and green, which can reduce preparation time and energy consumption, and can prepare pure phase metal boride.

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(1)本发明提供的金属盐、硼源进行研磨混匀，置于焦耳热反应装置中进行密封、抽真空，而后通入气体，进行加热，得到金属硼化物催化剂；本发明通过采用一步研磨得到固体粉末前驱物，然后在气

氛中通过闪蒸焦耳热加热的方式得到金属硼化物，本发明主要通过闪蒸焦耳热技术方式得到金属硼化物，该材料制备方法快速、简单、绿色，能够减少制备时间以及能耗，并且能够制备纯相的金属硼化物。

[n0008]

(2) The flash Joule heating provided by the present invention has a heating temperature of 700-1100°C and a heating time of 5s-125s. The flash Joule heating temperature and time are conducive to rapid heating, thereby reducing the preparation time. And by rapidly cooling down, the generation of crystalline nanocrystals is promoted, thereby improving the stability of the catalyst in the hydrogen evolution reaction of water electrolysis.

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(2)本发明提供的闪蒸焦耳热的加热温度为700-1100°C，加热的时间为5s-125s；其闪蒸焦耳热的加热温度以及时间有利于使其进行快速升温，进而减少制备的时长；并通过急速降温冷却，促进结晶纳米晶粒的生成，进而提高催化剂在电解水析氢反应的稳定性。

[0012]

Attached Figure Description

附图说明

[n0009]

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

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

[n0010]

Figure 1 is an X-ray diffraction pattern of the noble metal boride (RuB₂) prepared in Example 1 of this invention;

图1是本发明中，实施例1制备得到的贵金属硼化物(RuB₂)的X射线衍射图；

[n0011]

Figure 2 is a transmission electron microscope image of the noble metal boride (RuB₂) prepared in Example 1 of this invention;

图2是本发明中，实施例1制备得到的贵金属硼化物(RuB₂)的透射电镜图；

[n0012]

Figure 3 is the X-ray diffraction pattern of the alkaline earth (CaB₆) and transition metal borides (TiB₂, VB₂, CrB₂) prepared in Examples 2-5 of this invention;

图3是本发明中，实施例2-5制备得到的碱土(CaB₆)、过渡金属硼化物(TiB₂、VB₂、CrB₂)的X射线衍射图；

[n0013]

Figure 4 is the X-ray diffraction pattern of the rare earth metal borides (LaB₆, CeB₆) prepared in Examples 6 and 7 of this invention;

图4是本发明中，实施例6、7制备得到的稀土金属硼化物(LaB₆、CeB₆)的X射线衍射图；

[n0014]

Figure 5 shows the polarization curve of the noble metal boride (RuB₂) prepared in Example 1 of this invention under acidic conditions.

图5是本发明中，实施例1中制备得到的贵金属硼化物(RuB₂)在酸性条件下的极化曲线；

[n0015]

Figure 6 shows the polarization curves of the noble metal boride (RuB₂) prepared in Example 1 of this invention under neutral and alkaline conditions.

图6是本发明中，实施例1制备得到的贵金属硼化物(RuB₂)在中性、碱性条件下的极化曲线；

[n0016]

Figure 7 shows the stability curve of the noble metal boride (RuB₂) prepared in Example 1 of this invention for hydrogen production by electrolysis of water in acidic solution;

图7是本发明中，实施例1制备得到的贵金属硼化物(RuB₂)在酸性溶液中电解水制氢稳定曲线；

[n0017]

Figure 8 is the XRD pattern of the noble metal boride (RuB₂) prepared in Comparative Example 1 in this invention;

图8是本发明中，对比例1制备得到的贵金属硼化物(RuB₂)的XRD图；

[n0018]

Figure 9 shows the polarization curve of the noble metal boride (RuB₂) prepared in Comparative Example 1 under acidic conditions in this invention.

图9是本发明中，对比例1制备得到的贵金属硼化物(RuB₂)在酸性条件下的极化曲线。

[0023]

Detailed Implementation

具体实施方式

[n0019]

To make the objectives, technical solutions, and advantages of the embodiments of the present invention clearer, the technical solutions of 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.

为使本发明实施方式的目的、技术方案和优点更加清楚，下面将结合本发明实施方式中的附图，对本发明实施方式中的技术方案进行清楚、完整地描述，显然，所描述的实施方式是本发明一部分实施方式，而不是全部的实施方式。

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

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

Therefore, the following detailed description of embodiments of the invention provided in the accompanying drawings is not intended to limit the scope of the claimed invention, but merely to illustrate selected embodiments of the invention.

因此，以下对在附图中提供的本发明的实施方式的详细描述并非旨在限制要求保护的本发明的范围，而是仅仅表示本发明的选定实施方式。

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

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

[n0020]

The present invention provides a method for preparing a metal boride electrolysis water catalyst and a flash evaporation Joule heating technology, comprising the following steps: grinding and mixing a metal salt and a boron source, placing them in a Joule heating reaction device for sealing, evacuating a vacuum, then introducing gas and heating to obtain a metal boride catalyst.

本发明实施例提供的是：金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：将金属盐、硼源进行研磨混匀，置于焦耳热反应装置中进行密封，抽真空，而后通入气体，进行加热，得到金属硼化物催化剂。

[n0021]

Preferably, the heating temperature of the Joule thermal reaction device is 700-1100°C, and the heating time is 5s-125s. The Joule thermal flash pulse is an ultrafast high-temperature calcination technology. Its millisecond-level current pulse passes through the precursor, making the sample temperature reach ultra-high temperature (>3000K), and then rapidly cools it to room temperature (10⁴K/s).

作为优选的，焦耳热反应装置的加热温度为700-1100°C，加热的时间为5s-125s，其中焦耳热闪蒸脉冲是一种超快高温煅烧技术，其毫秒级的电流脉冲通过前驱体，使样品温度达到超高温(>3000K)，然后迅速冷却到室温(10⁴K/s)。

Rapid, instantaneous high temperatures and rapid temperature rise and fall rates allow the reaction to be completed in a few seconds to tens of seconds.

快速的瞬间高温及升降温速率可促使反应在几秒到几十秒即可完成。

Meanwhile, the second-level calcination time can effectively avoid phenomena such as sintering and agglomeration of active components caused by long-term heat treatment, ensuring the rapid and effective dispersion of active atoms, thereby effectively controlling the microstructure, composition and structure of the synthesized material.

同时，秒级煅烧时间可有效避免长时间热处理引发的活性组分烧结、团聚等现象，保证了活性原子的快速、有效分散，从而可有效调控合成材料的微观形貌、组成和结构等。

The heating temperature and time facilitate rapid heating, thereby reducing the preparation time; and the rapid cooling promotes the formation of crystalline nanocrystals, thereby improving the stability of the catalyst in the hydrogen evolution reaction of water electrolysis.

其加热的温度以及时间有利于使其进行快速升温，进而减少制备的时长；并通过急速降温冷却，促进结晶纳米晶粒的生成，进而提高催化剂在电解水析氢反应的稳定性。

Preferably, the heating temperature of the Joule heating apparatus is 800°C.

优选的，焦耳热反应装置的加热温度为800°C。

[n0022]

Preferably, the metal salt includes one or more of sulfates, chlorides, and ammonium salts.

作为优选的，金属盐包括硫酸盐、氯化盐、铵盐中的一种或多种。

Preferably, the metal salt is a chloride salt.

优选的，金属盐为氯化盐。

[n0023]

Preferably, the boron source is one or more of boron powder, sodium borohydride, boron hydride, boric acid, and boron trichloride.

作为优选的，硼源为硼粉、硼氢化钠、氢化硼、硼酸、三氯化硼中的一种或几种。

Preferably, sodium borohydride is used as the boron source, in which sodium ions in sodium borohydride combine with chloride ions in the precursor to form sodium chloride. Then, at a reaction temperature greater than 700°C, the sodium chloride volatilizes, so it will not remain in the product sample, thereby improving the purity of the product.

优选的，硼源选用硼氢化钠，其中硼氢化钠中的钠离子与前驱体中的氯离子结合形成氯化钠，而后在反应温度大于700℃，氯化钠发生挥发，因此不会残留在产品的样品中，进而提高产品的纯度。

[n0024]

Preferably, the metal salt is ruthenium trichloride and the boron source is sodium borohydride; preferably, the molar ratio of ruthenium trichloride to sodium borohydride is 1:2-2.2, which is conducive to the full reaction of the metal salt and the boron source and does not produce other by-products.

作为优选的，金属盐为三氯化钌，硼源为硼氢化钠；优选的，三氯化钌与硼氢化钠的摩尔比为1：2-2.2，其摩尔比的设置有利金属盐与硼源的充分反应，不产生其他副产物。

Preferably, the upper limit of the Joule heating reaction temperature is 750-850°C, and the heating time is 5s-70s.

优选的，焦耳热反应的温度上限为750-850°C，加热的时间为5s-70s。

Preferably, the current is 60-90A and the voltage is 10-40V.

优选的，电流的大小为60-90A，电压的大小为10-40V。

[n0025]

Preferably, the gas atmosphere is one or more of argon, nitrogen, and hydrogen.

作为优选的，气体氛围为氩气、氮气、氢气中的中的一种或几种。

Argon and nitrogen are inert gases. When the boron source is sodium borohydride, boron hydride, boric acid, or boron trichloride, the boron source and metal salt can react directly.

Hydrogen is a reducing gas. When the boron source is boron powder, hydrogen can reduce the boron powder without the need for impurity removal. Preferably, the gas atmosphere is nitrogen.

其中氩气与氮气属于惰性气体，当硼源采用硼氢化钠、氢化硼、硼酸或三氯化硼时，硼源与金属盐能够直接进行反应；而氢气为还原性气体，当硼源为硼粉时，氢气能够将硼粉进行还原，而不需要进行除杂；采用优选的，气体氛围为氮气。

[n0026]

Preferably, the metal boride catalyst has the structural formula MxBy, where M includes Mg, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Sr, Y, Zr, Nb, Mo, Hf, Ta, W, Re, Ru, Rh, Pd, Os, Ir, La, Ce, Pr, and Nd.

作为优选的，金属硼化物催化剂的结构式为MxBy，所述M包括Mg、Ca、Ti、V、Cr、Mn、Fe、Co、Ni、Sr、Y、Zr、Nb、Mo、Hf、Ta、W、Re、Ru、Rh、Pd、Os、Ir、La、Ce、Pr、Nd。

[n0027]

The present invention is an improvement on the metal boride catalyst.

本发明作为改进的是金属硼化物催化剂。

[n0028]

As a further improvement, this invention relates to the application of metal boride catalysts in hydrogen production through water electrolysis.

本发明作为进一步改进的是金属硼化物催化剂在电解水裂解制氢中的应用。

[n0029]

Example 1

实施例1

[n0030]

A method for preparing a metal boride water electrolysis catalyst using flash evaporation Joule heating technology includes the following steps:

一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：

[n0031]

Weigh 118 mg of ruthenium trichloride and 45 mg of sodium borohydride into a mortar and grind for 1 minute to mix them thoroughly. Place the uniformly mixed and dried mixture into a Joule heating reaction mold and shake it to spread it evenly in the mold. Then fix the Joule heating reaction mold in the Joule heating reaction device, seal it, and evacuate or introduce nitrogen gas for a period of time to remove the air from the device.

称取118mg三氯化钌、45mg硼氢化钠置于研钵中，进行研磨1min，使其进行充分混合均匀，得到混合物；将均匀混合且干燥的混合物置于焦耳热反应模具内，振荡使其均匀地平铺在模具中，而后将焦耳热反应模具固定在焦耳热反应装置内，进行密封，抽真空或通入一段时间氮气排除装置中的空气。

The current was set to 70A, the voltage to 40V, the heating time to 60s, and the upper temperature limit to 800°C. The Joule heating reaction was carried out by applying electricity. After the reaction was completed, ruthenium diboride was obtained and taken out for use.

其中电流大小设置为70A，电压设置为40V，加热时间为60s，温度上限设置为800°C，通电进行焦耳热反应，待反应结束后，得到二硼化钌，取出待用。

[n0032]

Example 2

实施例2

[n0033]

A method for preparing a metal boride water electrolysis catalyst using flash evaporation Joule heating technology includes the following steps:

一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：

[n0034]

Weigh 118 mg of calcium dichloride and 242 mg of sodium borohydride into a mortar and grind for 1 minute to mix them thoroughly. Place the uniformly mixed and dried mixture into a Joule heating reaction mold and shake it to spread it evenly in the mold. Then fix the Joule heating reaction mold into the Joule heating reaction device, seal it, and evacuate or introduce nitrogen gas for a period of time to remove the air from the device.

称取118mg二氯化钙、242mg硼氢化钠置于研钵中，进行研磨1min，使其进行充分混合均匀，得到混合物；将均匀混合且干燥的混合物置于焦耳热反应模具内，振荡使其均匀地平铺在模具中，而后将焦耳热反应模具固定在焦耳热反应装置内，进行密封，抽真空或通入一段时间氮气排除装置中的空气。

The current was set to 70A, the voltage to 47.5V, the heating time to 60s, and the upper temperature limit to 800°C. The Joule heating reaction was carried out by applying electricity. After the reaction was completed, calcium hexaboride was obtained and taken out for use.

其中电流大小设置为70A，电压设置为47.5V，加热时间为60s，温度上限设置为800°C,通电进行焦耳热反应，待反应结束后，得到六硼化钙，取出待用；

[n0035]

Example 3

实施例3

[n0036]

A method for preparing a metal boride water electrolysis catalyst using flash evaporation Joule heating technology includes the following steps:

一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：

[n0037]

Weigh 108 mg of titanium tetrachloride and 103 mg of sodium borohydride into a mortar and grind for 1 minute to mix them thoroughly. Place the uniformly mixed and dried mixture into a Joule heating reaction mold and shake it to spread it evenly in the mold. Then fix the Joule heating reaction mold into the Joule heating reaction device, seal it, and evacuate or introduce nitrogen gas for a period of time to remove the air from the device.

称取108mg四氯化钛、103mg硼氢化钠置于研钵中，进行研磨1min，使其进行充分混合均匀，得到混合物；将均匀混合且干燥的混合物置于焦耳热反应模具内，振荡使其均匀地平铺在模具中，而后将焦耳热反应模具固定在焦耳热反应装置内，进行密封，抽真空或通入一段时间氮气排除装置中的空气。

The current was set to 70A, the voltage to 47.5V, the heating time to 60s, and the upper temperature limit to 1000°C. The Joule heating reaction was carried out by applying electricity. After the reaction was completed, titanium diboride was obtained and taken out for use.

其中电流大小设置为70A，电压设置为47.5V，加热时间为60s，温度上限设置为1000°C，通电进行焦耳热反应，待反应结束后，得到二硼化钛，取出待用。

[n0038]

Example 4

实施例4

[n0039]

A method for preparing a metal boride water electrolysis catalyst using flash evaporation Joule heating technology includes the following steps:

一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：

[n0040]

Weigh 30 mg of vanadium trichloride and 15 mg of sodium borohydride into a mortar and grind for 1 minute to mix them thoroughly and evenly. Place the evenly mixed and dried mixture into a Joule heating reaction mold and shake it to spread it evenly in the mold. Then fix the Joule heating reaction mold into the Joule heating reaction device, seal it, and evacuate or introduce nitrogen gas for a period of time to remove the air from the device.

称取30mg三氯化钒、15mg硼氢化钠置于研钵中，进行研磨1min，使其进行充分混合均匀，得到混合物；将均匀混合且干燥的混合物置于焦耳热反应模具内，振荡使其均匀地平铺在模具中，而后将焦耳热反应模具固定在焦耳热反应装置内，进行密封，抽真空或通入一段时间氮气排除装置中的空气。

The current was set to 70A, the voltage to 47.5V, the heating time to 60s, and the upper temperature limit to 1000°C. The Joule heating reaction was carried out by applying electricity. After the reaction was completed, vanadium diboride was obtained and taken out for later use.

其中电流大小设置为70A，电压设置为47.5V，加热时间为60s，温度上限设置为1000°C，通电进行焦耳热反应，待反应结束后，得到二硼化钒，取出待用。

[n0041]

Example 5

实施例5

[n0042]

A method for preparing a metal boride water electrolysis catalyst using flash evaporation Joule heating technology includes the following steps:

一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：

[n0043]

Weigh 30 mg of chromium trichloride and 15 mg of sodium borohydride into a mortar and grind for 1 minute to mix them thoroughly. Place the uniformly mixed and dried mixture into a Joule heating reaction mold and shake it to spread it evenly in the mold. Then fix the Joule heating reaction mold into the Joule heating reaction device, seal it, and evacuate or introduce nitrogen gas for a period of time to remove the air from the device.

称取30mg三氯化铬、15mg硼氢化钠置于研钵中，进行研磨1min，使其进行充分混合均匀，得到混合物；将均匀混合且干燥的混合物置于焦耳热反应模具内，振荡使其均匀地平铺在模具中，而后将焦耳热反应模具固定在焦耳热反应装置内，进行密封，抽真空或通入一段时间氮气排除装置中的空气。

The current was set to 70A, the voltage to 47.5V, the heating time to 60s, and the upper temperature limit to 1000°C. The Joule heating reaction was carried out by applying electricity. After the reaction was completed, vanadium diboride was obtained and taken out for later use.

其中电流大小设置为70A，电压设置为47.5V，加热时间为60s，温度上限设置为1000℃，通电进行焦耳热反应，待反应结束后，得到二硼化钒，取出待用。

[n0044]

Example 6

实施例6

[n0045]

A method for preparing a metal boride water electrolysis catalyst using flash evaporation Joule heating technology includes the following steps:

一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：

[n0046]

Weigh 78 mg of cerium chloride and 72 mg of sodium borohydride into a mortar and grind for 1 minute to mix them thoroughly. Place the uniformly mixed and dried mixture into a Joule heating reaction mold and shake it to spread it evenly in the mold. Then fix the Joule heating reaction mold into the Joule heating reaction device, seal it, and evacuate or introduce nitrogen gas for a period of time to remove the air from the device.

称取78mg氯化铈、72mg硼氢化钠置于研钵中，进行研磨1min，使其进行充分混合均匀，得到混合物；将均匀混合且干燥的混合物置于焦耳热反应模具内，振荡使其均匀地平铺在模具中，而后将焦耳热反应模具固定在焦耳热反应装置内，进行密封，抽真空或通入一段时间氮气排除装置中的空气。

The current was set to 60A, the voltage to 40V, the heating time to 120s, and the upper temperature limit to 750°C. The Joule heating reaction was carried out by applying electricity. After the reaction was completed, cerium hexaboride was obtained and taken out for use.

其中电流大小设置为60A，电压设置为40V，加热时间为120s，温度上限设置为750°C，通电进行焦耳热反应，待反应结束后，得到六硼化铈，取出待用。

[n0047]

Example 7

实施例7

[n0048]

A method for preparing a metal boride water electrolysis catalyst using flash evaporation Joule heating technology includes the following steps:

一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：

[n0049]

Weigh 33 mg of lanthanum chloride and 43 mg of sodium borohydride into a mortar and grind for 1 minute to mix them thoroughly. Place the uniformly mixed and dried mixture into a Joule heating reaction mold and shake it to spread it evenly in the mold. Then fix the Joule heating reaction mold into the Joule heating reaction device, seal it, and evacuate or introduce nitrogen gas for a period of time to remove the air from the device.

称取33mg氯化镧、43mg硼氢化钠置于研钵中，进行研磨1min，使其进行充分混合均匀，得到混合物；将均匀混合且干燥的混合物置于焦耳热反应模具内，振荡使其均匀地平铺在模具中，而后将焦耳热反应模具固定在焦耳热反应装置内，进行密封，抽真空或通入一段时间氮气排除装置中的空气。

The current was set to 60A, the voltage to 40V, the heating time to 100s, and the upper temperature limit to 800°C. The Joule heating reaction was carried out by applying electricity. After the reaction was completed, lanthanum hexaboride was obtained and taken out for later use.

其中电流大小设置为60A，电压设置为40V，加热时间为100s，温度上限设置为800°C，通电进行焦耳热反应，待反应结束后，得到六硼化镧，取出待用。

[n0050]

Comparative Example 1

对比例1

[n0051]

A method for preparing a metal boride water electrolysis catalyst using flash evaporation Joule heating technology includes the following steps:

一种金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法，包括以下步骤：

[n0052]

(1) Weigh 118 mg of ruthenium trichloride and 45 mg of sodium borohydride into a mortar and grind for 1 min to mix them thoroughly and evenly to obtain a mixture; place the evenly mixed and dried mixture into a crucible and then place it in a muffle furnace for heating for 30 s-120 s at a temperature of 800 °C. After the reaction is complete, ruthenium diboride is obtained and taken out for use.

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(1)称取118mg三氯化钌、45mg硼氢化钠置于研钵中，进行研磨1min，使其进行充分混合均匀，得到混合物；将均匀混合且干燥的混合物放置于坩埚中，而后进行放置于马弗炉中，进行加热，加热时间为30s-120s，加热的温度为800°C，待反应结束后，得到二硼化钌，取出待用。

[n0053]

Application Example 1

应用例1

[n0054]

In this application example 1, the metal borides prepared in Examples 1-7 and Comparative Example 1 were ground into powder, and then the ground samples were pressed into sheets and placed in an XRD diffractometer for characterization, resulting in Figures 1, 3, 4 and 8.

本应用例1通过将实施例1-7以及对比例1制备获得的金属硼化物进行研磨成粉，而后将研磨后的样品压制成片，放置于XRD衍射仪中进行表征，得到图1、图3、图4、图8。

[n0055]

Figure 1 shows the X-ray diffraction pattern of the metal boride RuB₂ prepared in Example 1. As can be seen from Figure 1, the metal boride RuB₂ prepared in Example 1 is a pure phase. Figure 3 shows the X-ray diffraction patterns of the alkaline earth metal borides CaB₆ and transition metal borides TiB₂, VB<sub>2< /sub>, and CrB₂ prepared in Examples 2-5. As can be seen from Figure 3, the alkaline earth metal borides CaB₆ and transition metal borides TiB₆ and CrB₂ prepared in Examples 2-5 are... 9_, VB₂, and CrB<sub>2< /sub> are pure phases; Figure 4 shows the X-ray diffraction patterns of rare earth metal borides LaB₆ and CeB₆ prepared in Examples 6 and 7. As can be seen from Figure 4, the rare earth metal borides LaB₆ and CeB₆ prepared in Examples 6 and 7 are pure phases; Figure 8 shows the X-ray diffraction pattern of ruthenium diboride RuB₂ prepared in Comparative Example 1. As can be seen from Figure 8, the metal boride RuB₂ prepared in Comparative Example 1 is a non-pure phase.

图1为实施例1制备获得的金属硼化物RuB₂的X射线衍射图，由图1中可以看出实施例1制备获得的金属硼化物RuB₂为纯相；图3为实施例2-5制备得到的碱土金属硼化物CaB₆以及过渡金属硼化物TiB₂、VB₂、CrB₂的X射线衍射图，由图3中可以看出实施例2-5制备获得的碱土金属硼化物CaB₆以及过渡金属硼化物TiB₂、VB₂、CrB₂为纯相；图4为实施例6、

实施例7制备获得的稀土金属硼化物LaB₆、CeB₆的X射线衍射图，由图4可以看出实施例6、实施例7制备获得的稀土金属硼化物LaB₆、CeB₆为纯相；图8为对比例1制备获得的二硼化钌RuB₂的X射线衍射图，由图8可以看出对比例1制备获得的为金属硼化物RuB₂为非纯相。

[n0056]

Application Example 2

应用例2

[n0057]

In this application example 2, the metal boride prepared in Examples 1-7 was cut into a size of 1cm × 1cm and then placed under a transmission microscope for testing, resulting in the transmission electron microscope image of Example 1, as shown in Figure 2.

本应用例2利用上述实施例1-7制备得到的金属硼化物进行裁剪为1cm×1cm的尺寸大小，而后置于透射显微镜中进行测试，得到实施例1的透射电镜图，如图2。

[n0058]

Figure 2 on the left is a transmission electron microscope (TEM) image of the metal boride RuB₂ prepared in Example 1; the morphology of the sample is composed of particles with a size of 50-100 nm. Figure 2 on the right is a high-resolution TEM image that further confirms that the synthesized sample is ruthenium diboride.

图2左侧为实施例1制备获得的金属硼化物RuB₂的透射电镜图；样品的形貌为50-100nm的粒子组成，图2右侧为高分辨透射电镜照片进一步证明合成样品为二硼化钌。

[n0059]

Application Example 3

应用例3

[n0060]

In this application example 3, the metal boride RuB₂ prepared in Example 1 was dissolved in a 10 mg/mL mixture of water, alcohol, and Nafion, and sonicated for 30 minutes to obtain a mixture. 10 μL of the mixture was dropped onto a conductive base such as a glassy carbon electrode, carbon cloth, conductive glass, or titanium sheet, and dried to serve as the working electrode.

本应用例3利用实施例1制备获得的金属硼化物RuB₂分别溶解于10mg/mL的水、醇、nafion混合溶液，超声处理30分钟后，得到混合液；取10μL混合液滴加在玻碳电极、碳布、导电玻璃、钛片等的导电基地上，待干燥后作为工作电极。

The reference electrode was saturated calomel, the counter electrode was a graphite rod, and the electrolyte consisted of 0.5 M H₂SO₄, 1.0 M phosphate buffer solution, and 1.0 M KOH solution. The polarization curves were then tested on an electrochemical workstation, as shown in Figures 5, 6, and 7.

其中饱和甘汞为参比电极，石墨棒为对电极，电解液为0.5M H₂SO₄、1.0 M磷酸缓冲溶液、1.0M KOH溶液；而后置于电化学工作站进行极化曲线测试，如图5、图6以及图7。

[n0061]

Figure 5 shows the polarization curve of the metal boride electrolysis catalyst RuB₂ in Example 1 for hydrogen evolution (HER) by electrolysis of water in acidic solution (0.5 M H₂SO₄).

图5为实施例1金属硼化物电解水催化剂RuB₂在酸性溶液(0.5M H₂SO₄)电解水析氢(HER)的极化曲线。

When the current density is 10 mA/cm², the overpotential is 15 mV, exhibiting properties similar to Pt (when the current density is 10 mA/cm², the overpotential is 17 mV); Figure 6 shows the polarization curve of the metal boride electrolysis catalyst RuB₂ in Example 1 in 1M KOH/1M PBS solution. In 1M KOH solution, when the current density is 10 mA/cm², the overpotential is 110 mV; in 1M PBS solution, when the current density is 10 mA/cm², the overpotential is 75 mV.

当电流密度为10mA/cm²时，过电势为15mV，具有类Pt(电流密度为10mA/cm²时，过电势为17mV)的性质；图6为实施例1金属硼化物电解水催化剂RuB₂在1M KOH/1MPBS溶液中的极化曲线，在1M KOH溶液中，当电流密度为10mA/cm²时，过电势为110mV；在1MPBS溶液中，当电流密度为10mA/cm²时，过电势为75mV。

Figure 9 shows the polarization curves of comparative example 1 metal boride RuB₂ in acidic solution (0.5M H₂SO₄) during water electrolysis and hydrogen evolution (HER).

图9为对比例1金属硼化物RuB₂在酸性溶液(0.5M H₂SO₄)电解水析氢(HER)的极化曲线。

When the current density is 10 mA/cm², the overpotential is 115 mV.

当电流密度为10mA/cm²时，过电势为115mV。

[n0062]

Figure 7 shows the overpotential and time curves of the hydrogen production reaction of metal boride RuB₂ in 0.5M H₂SO₄ solution, where the current density is maintained at 10mA/cm². This metal boride exhibits the highest catalytic stability in the hydrogen production reaction environment under the test conditions, and its catalytic performance remains stable for more than 20 hours, demonstrating that the catalyst has good catalytic stability.

图7为实施例1金属硼化物RuB₂在在0.5M H₂SO₄溶液中的电解水制氢反应电流密度保持在10mA/cm²的反应过电势和时间曲线；该金属硼化物在该测试条件下的制氢反应环境中，具有最高的催化稳定性，在其催化性能能够稳定20小时以上，表现出该催化剂具有良好的催化稳定性。

[n0063]

The metal boride electrolysis catalyst and flash Joule heating method provided by this invention involve a one-step grinding process to obtain a solid powder precursor, followed by flash Joule heating in a gas atmosphere to obtain the metal boride. In acidic solution, the catalyst can achieve a current density of 10 mA/cm², with an overpotential as low as 15 mV, and its catalytic performance can remain stable for more than 20 hours, demonstrating that the catalyst has high catalytic activity and stability.

本发明提供的金属硼化物电解水催化剂及闪蒸焦耳热技术制备方法采用一步研磨得到固体粉末前驱体，然后气体氛围中通过闪蒸焦耳热加热的方式得到金属硼化物，其中在酸性溶液中，能够达到电流密度10mA/cm²，所需过电位低至15mV，且催化性能能够稳定20小时以上，表现出该催化剂具有高催化剂活性和稳定性。

This catalyst reduces the hydrogen evolution overpotential of borides, and the rapid cooling rate promotes the formation of crystalline nanocrystals, thereby improving the stability of the catalyst in the electrocatalytic hydrogen evolution reaction. It can also reduce preparation time and energy consumption, and can prepare pure-phase metal boride catalysts.

该催化剂在降低硼化物析氢过电位的同时，由于急速冷却率可以促进结晶纳米晶粒的生成，进而提高催化剂在电催化析氢反应中的稳定性；并且能够减少制备时间以及能耗，能够制备纯相的金属硼化物催化剂。

[n0064]

The above description is only a preferred embodiment of the present invention and is not intended to limit the present invention. For those skilled in the art, the present invention can have various modifications and variations.

以上所述仅为本发明的优选实施方式而已，并不用于限制本发明，对于本领域的技术人员来说，本发明可以有各种更改和变化。

Any modifications, equivalent substitutions, or improvements made within the spirit and principles of this invention shall be included within the scope of protection of this invention.

凡在本发明的精神和原则之内，所作的任何修改、等同替换、改进等，均应包含在本发明的保护范围之内。