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DESCRIPTION CN113488376A

A two-dimensional silicon dioxide and its preparation method and application

[0001]

Technical Field

[n0001]

The present invention belongs to the field of material technology, and specifically relates to two-dimensional silicon dioxide and a preparation method and application thereof.

[0003]

Background Art

[n0002]

The information disclosed in this background technology section is only intended to enhance the understanding of the overall background of the invention, and should not necessarily be regarded as an admission or any form of suggestion that the information constitutes the prior art already known to a person skilled in the art.

[n0003]

Silica is one of the most common materials in our daily life and is the material that has been used by humans for the longest time since the Stone Age.

Two-dimensional silica has important potential value in nanomechanics and nanoelectronics due to its structural advantages. The existing preparation methods mainly include exfoliation method, CVD method and template method.

In nature, layered silicates have a sandwich structure of two tetrahedrons and one octahedron, which is also the main source for the preparation of SiO₂ nanosheets.

The exfoliation method mainly uses layered silicates as raw materials to prepare SiO₂ nanosheets, which not only contain impurities, but also often require complex exfoliation, and the exfoliation efficiency is low and cannot be mass-produced.

The template method usually uses some existing 2D materials as templates (such as graphene, MoS₂, etc.), and grows on the template surface through hydrolysis of silane precursors. However, this method requires other 2D materials as templates, which are generally not easy to obtain directly, and the templates used to prepare SiO₂nanosheets are difficult to remove, so pure SiO₂nanosheets cannot be obtained. For example, the prior art discloses a method for obtaining two-dimensional silica nanosheets by using graphene oxide as a template and tetraethyl orthosilicate as a silicon source, and freeze-drying and sintering. The use of the template complicates the entire preparation process, and requires the process of introducing a template agent and then removing the template agent, which may not be completely removed. Moreover, graphene oxide as a template agent greatly increases the preparation cost of two-dimensional silica, and is not suitable for large-scale industrial production. The CVD method is to grow a silicon precursor on a substrate (such as a silicon wafer) under specific pressure and temperature. This method requires special equipment, is costly, has harsh preparation conditions, has a low yield, and is difficult to prepare on a large scale.

[n0004]

Therefore, developing an efficient, low-cost, and large-scale method for producing two-dimensional silica is of great significance to promote the development of two-dimensional silica.

[0007]

Summary of the invention

[n0005]

In order to address the deficiencies in the prior art, the present invention provides a two-dimensional silica and a preparation method and application thereof. The present invention adopts a commercial precursor and obtains the two-dimensional silica by acid treatment and heat treatment in an air atmosphere. No expensive template is required in the entire preparation process, and the precursor is also a commercially available material. In addition, the entire preparation process has few steps and a simple process, thereby realizing large-scale and low-cost preparation of two-dimensional silica.

[n0006]

In order to achieve the above object, the first aspect of the present invention provides a method for preparing two-dimensional silicon dioxide, which specifically comprises the following steps:

[n0007]

Siloxene is obtained by acid treatment of calcium silicide alloy, and then two-dimensional silicon dioxide can be prepared by heat treating the siloxene in an air atmosphere.

[n0008]

A second aspect of the present invention provides two-dimensional silicon dioxide obtained by the above preparation method.

[n0009]

The third aspect of the present invention provides the use of the above two-dimensional silicon dioxide in the negative electrode of a lithium battery.

[n0010]

A fourth aspect of the present invention provides a high thermal stability diaphragm, the diaphragm is composed of two-dimensional silicon dioxide and a common battery diaphragm, and the two-dimensional silicon dioxide is coated on the common battery diaphragm;

[n0011]

One or more embodiments of the present invention have at least the following beneficial effects:

[n0012]

(1) The present invention uses commercial precursors to obtain two-dimensional silica by acid treatment and heat treatment in an air atmosphere. No expensive template is required in the entire preparation process. The precursor is also a commercially available material. The entire preparation process has few steps and a simple process. It is a method for preparing two-dimensional silica on a large scale and at low cost.

[n0013]

(2) The two-dimensional silicon dioxide prepared by the present invention can not only be used as the negative electrode material in lithium batteries, showing excellent cycle stability, but also can be used to prepare high thermal stability diaphragms.

[0017]

BRIEF DESCRIPTION OF THE DRAWINGS

[n0014]

The accompanying drawings in the specification, which constitute a part of the present invention, are used to provide a further understanding of the present invention. The exemplary embodiments of the present invention and their descriptions are used to explain the present invention and do not constitute improper limitations on the present invention.

[n0015]

FIG1 is an XRD test diagram in Example 1, a) two-dimensional silicon dioxide, b) siloxene;

[n0016]

FIG2 is a SEM image of the two-dimensional silicon dioxide in Example 1;

[n0017]

FIG3 is a SEM image of siloxene in Example 1;

[n0018]

FIG4 is a CV curve of the two-dimensional silicon dioxide used as the negative electrode active material in Example 1;

[n0019]

FIG5 is a charge and discharge curve when the two-dimensional silicon dioxide in Example 1 is used as the negative electrode active material;

[n0020]

FIG. 6 is a cycle performance diagram of the two-dimensional silicon dioxide in Example 1 as the negative electrode active material.

[0025]

DETAILED DESCRIPTION

[n0021]

It should be noted that the following detailed descriptions are exemplary and are intended to provide further explanation of the present invention.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[n0022]

It should be noted that the terms used herein are for describing specific embodiments only and are not intended to be limiting of exemplary embodiments according to the present invention.

As used herein, unless the context clearly indicates otherwise, the singular forms are intended to include the plural forms. In addition, it should be understood that when the terms "including" and/or "comprising" are used in this specification, they indicate the presence of features, steps, operations, devices, components and/or their combinations.

[n0023]

As introduced in the background art, the methods for preparing silicon dioxide in the prior art generally have the problems of high cost, complicated process and disadvantageous for large-scale production.

[n0024]

In order to solve the above technical problems, the first aspect of the present invention provides a method for preparing two-dimensional silicon dioxide, which specifically comprises the following steps:

[n0025]

Siloxene is obtained by acid treatment of calcium silicide alloy, and then two-dimensional silicon dioxide can be prepared by heat treating the siloxene in an air atmosphere.

[n0026]

The present invention uses commercial calcium silicide alloy as a precursor. Calcium silicide itself can provide silicon as a silicon source. During the acidification process, the acid can strip off the calcium atoms in the calcium silicide. The silicon in the calcium silicide structure reacts with the water in the acid solution and the oxygen in the air to generate siloxene with a regular layered structure. Heat treatment is continued on the basis of siloxene to remove H in the structure while maintaining the layered two-dimensional structure. At the same time, silicon can be oxidized in an air atmosphere to obtain two-dimensional silicon dioxide nanosheets.

[n0027]

The present invention particularly emphasizes that air atmosphere is the key to preparing two-dimensional silicon dioxide. The present invention can obtain two-dimensional silicon dioxide material in one step by heating in air and utilizing oxygen in the air. This method can avoid the problem of generating silicon or amorphous silicon oxide due to insufficient oxygen during the heat treatment process.

If heat treatment is performed in an inert atmosphere, the oxygen content in siloxane is limited, so only other silicon oxides can be generated.

[n0028]

For example: R.S.Fu immersed layered CaSi₂ in dilute hydrochloric acid under ultrasonic conditions to peel off and form siloxane, and then pyrolyzed the obtained siloxane in an Ar atmosphere to obtain flaky SiO1.1 rather than SiO₂.

At the same time, in order to obtain a physical phase containing silicon dioxide in this scheme, low-temperature + high-temperature treatment is required. Siloxene is first subjected to low-temperature heat treatment (300-500 ° C) to obtain amorphous silicon oxide (SiOx); after high-temperature heat treatment of siloxene (>800 ° C), silicon oxide undergoes a disproportionate reaction to form a dispersed mixture of nano-silicon and silicon oxide (nano-Si/a-SiO₂), and finally what is obtained is still a mixture of silicon and silicon oxide, and pure two-dimensional silicon dioxide material cannot be directly obtained.

[n0029]

The acid described in the present invention needs to play the role of stripping Ca from calcium silicide, so any strong acid that can achieve this effect can be used, such as permanganic acid, hydrochloric acid, sulfuric acid, nitric acid, perchloric acid, selenic acid, hydrobromic acid, hydroiodic acid, chloric acid, preferably hydrochloric acid;

[n0030]

The concentration of the acid will affect the stripping effect. If the concentration is too low, the stripping will be incomplete, resulting in the inclusion of Ca impurities in the product. As a preferred embodiment, the concentration of the acid is 1-12 mol L⁻¹, and more preferably 2 mol L⁻¹;.

[n0031]

Furthermore, the acidification treatment time is 5-32 hours, preferably 24 hours.

[n0032]

The temperature of the heat treatment affects the synthesis of two-dimensional silica. If the temperature is too low, only silicon oxide can be obtained. As a preferred embodiment, the heat treatment temperature is 800-1500 ° C, and more preferably 1000 ° C. Two-dimensional silica is obtained by high-temperature heating, and the structure is more stable.

[n0033]

Furthermore, the heating rate is: 0.1-10 ° C min⁻¹;

[n0034]

The present invention obtains silicon dioxide by utilizing oxygen in the air. In order to maintain its two-dimensional structure, the heating rate must be regulated. A slow heating rate is beneficial for obtaining a stable two-dimensional structure.

[n0035]

Furthermore, the heat treatment time is 0.1-10h.

[n0036]

A second aspect of the present invention provides two-dimensional silicon dioxide obtained by the above preparation method.

[n0037]

The third aspect of the present invention provides the use of the above two-dimensional silicon dioxide in the negative electrode of a lithium battery.

The application described here refers specifically to the application as a negative electrode active material. Two-dimensional silica can be used as a negative electrode material together with conventional binders and carbon.

[n0038]

A fourth aspect of the present invention provides a high thermal stability diaphragm, the diaphragm is composed of two-dimensional silicon dioxide and a common battery diaphragm, and the two-dimensional silicon dioxide is coated on the common battery diaphragm;

[n0039]

Furthermore, the coating has a thickness of 1-50 μ m, preferably 1-10 μ m;

[n0040]

Furthermore, the two-dimensional silica and the organic solution are configured into a slurry with a concentration of 2-30%, and then coated on a common separator.

[n0041]

The common diaphragm is a polyolefin diaphragm mainly composed of polyethylene (PE) and polypropylene (PP).

[n0042]

The solute in the organic solution is one or a mixture of two or more of polytetrafluoroethylene, polyoxyethylene and polyvinylidene fluoride polymer materials.

[n0043]

The solvent in the organic solution is one of nitrogen methyl pyrrolidone, N,N-dimethylformamide (DMF), ethanol, n-hexane, tetrahydrofuran, acetonitrile, petroleum ether, chlorobenzene, toluene, pyridine or benzonitrile, or a mixture thereof.

[n0044]

The coating method is spraying or rolling.

[n0045]

In order to enable those skilled in the art to more clearly understand the technical solution of the present invention, the technical solution of the present invention will be described in detail below in conjunction with specific embodiments.

[n0046]

Example 1

[n0047]

A method for preparing two-dimensional silica comprises taking 5.0 g of commercial calcium silicide and treating it with a 2 mol L⁻¹ hydrochloric acid solution for 24 hours to obtain a siloxane intermediate; heat treating the intermediate at 1000 ° C. in air for 5 hours, and then cooling it to room temperature to obtain a two-dimensional silica material.

[n0048]

The XRD patterns of the prepared two-dimensional silica and siloxane are shown in Figure 1, and the SEM patterns are shown in Figures 2 and 3. It can be seen from the SEM patterns that siloxane is a regularly arranged layered structure. After heat treatment, the layered structure is basically maintained, and a two-dimensional silica material is obtained.

[n0049]

Performance Testing:

[n0050]

The two-dimensional silicon dioxide prepared in Example 1 was used as the negative electrode material and metallic lithium was used as the positive electrode material to assemble a lithium ion half-cell, and the electrochemical performance was tested. The specific results are shown in Figures 4-6.

[n0051]

It can be seen from Figures 4-6 that the discharge capacity of the two-dimensional silicon dioxide prepared in Example 1 after 100 cycles is 461.6 mAh g⁻¹. Except for the first cycle, the capacity is basically stable, showing excellent cycle stability.

The unique two-dimensional structure is conducive to promoting the transport of ions and increasing the contact between electrodes and electrolytes, thereby achieving excellent electrochemical performance.

[n0052]

Example 2

[n0053]

A method for preparing two-dimensional silica comprises taking 5.0 g of commercial calcium silicide and treating it with a 5 mol L⁻¹ hydrochloric acid solution for 18 h to obtain a siloxane intermediate; heat treating the intermediate at 1400 ° C. in air for 2 h, and then cooling it to room temperature to obtain a two-dimensional silica material.

[n0054]

Example 3

[n0055]

A method for preparing two-dimensional silica comprises taking 5.0 g of commercial calcium silicide, treating it with a 10 mol L⁻¹ hydrochloric acid solution for 12 h, and obtaining a siloxane intermediate; heat treating the intermediate at 1200 ° C. in air for 4 h, and obtaining a two-dimensional silica material after cooling to room temperature.

[n0056]

Example 4

[n0057]

A method for preparing two-dimensional silica comprises taking 5.0 g of commercial calcium silicide and treating it with a 1 mol L⁻¹ hydrochloric acid solution for 30 h to obtain a siloxane intermediate; heat treating the intermediate at 1000 ° C. in air for 5 h, and then cooling it to room temperature to obtain a two-dimensional silica material.

[n0058]

Example 5

[n0059]

A method for preparing two-dimensional silica comprises taking 5.0 g of commercial calcium silicide and treating it with a 2 mol L⁻¹ hydrochloric acid solution for 24 hours to obtain a siloxane intermediate; heat treating the intermediate at 900 ° C. in air for 8 hours, and then cooling it to room temperature to obtain a two-dimensional silica material.

[n0060]

Example 6

[n0061]

A method for preparing two-dimensional silica comprises taking 5.0 g of commercial calcium silicide and treating it with a 2 mol L⁻¹ hydrochloric acid solution for 24 hours to obtain a siloxane intermediate; heat treating the intermediate at 800 ° C. in air for 10 hours, and then cooling it to room temperature to obtain a two-dimensional silica material.

[n0062]

Example 7

[n0063]

A high thermal stability diaphragm, formed by coating the two-dimensional silicon dioxide prepared in Example 1 on a polyethylene film, wherein the thickness of the silicon dioxide coating is 10 μ m;

[n0064]
Specific preparation method:

[n0065]
The two-dimensional silica and a DMF solution containing polytetrafluoroethylene were prepared into a slurry with a concentration of 10%, and then sprayed on a polyethylene film.

[n0066]
Comparative Example 1:

[n0067]
Take 5.0g of commercial aluminum silicon alloy, and then treat it with 2mol L⁻¹ hydrochloric acid solution for 24h to obtain a silicon intermediate product; heat treat the intermediate product at 1000°C in air for 5h, cool to room temperature, and obtain porous silicon dioxide.

[n0068]
Comparative Example 2:

[n0069]
Take 5.0 g of commercial calcium silicide and treat it with 2 mol L⁻¹ hydrochloric acid solution for 24 hours to obtain an intermediate product of siloxane; heat treat the intermediate product at 1000 ° C in nitrogen for 5 hours, cool to room temperature, and obtain a composite of silicon and silicon oxide.

[n0070]
Comparative Example 3:

[n0071]
Take 5.0 g of commercial calcium silicide and treat it with 0.5 mol L⁻¹ hydrochloric acid solution for 24 hours to obtain an intermediate product of siloxane and calcium salt; heat treat the intermediate product at 1000 ° C in air for 5 hours and cool it to room temperature to obtain a complex of silica and calcium salt.

[n0072]
Comparative Example 4:

[n0073]

466 Take 5.0 g of commercial calcium silicide and treat it with 2 mol L⁻¹ hydrochloric acid solution for 24 hours to obtain a siloxane intermediate; heat treat the intermediate at 400 ° C in air for 5 hours and cool to room temperature to obtain a silicon oxide composite material.

[n0074]

472 The above descriptions are only preferred embodiments of the present invention and are not intended to limit the present invention. For those skilled in the art, the present invention may be subject to various modifications and changes.

475 Any modifications, equivalent substitutions, improvements, etc. made within the spirit and principles of the present invention should be included in the protection scope of the present invention.