Notice

DESCRIPTION CN115888718A

Preparation and application of a chestnut-shaped hollow NiCu composite material

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[0001]

Technical Field

[n0001]

This invention belongs to the field of nanomaterial preparation technology, specifically relating to a chestnut-shaped hollow NiCu composite material, its preparation method, and its application.

[0003]

Background Technology

[n0002]

Semiconductor photocatalysis is considered one of the most promising strategies in the energy and environment fields of the 21st century.

Therefore, a great deal of research has focused on developing semiconductor photocatalysts.

Among them, one-dimensional nanomaterial photocatalysts, including nanorods, nanoribbons, nanofibers, nanowires, and nanotubes, are considered to be among the most promising materials in the field of photocatalysis.

[n0003]

One-dimensional nanomaterials have a large surface area and a large number of catalytic surface active centers.

Generally speaking, a larger surface area can promote the absorption of reactants, and abundant active centers can promote charge separation and interfacial reactions, thus exhibiting excellent photocatalytic activity.

Furthermore, the channel structure of one-dimensional nanomaterials can serve as a charge transport pathway to accelerate electron-hole pair transport. Due to their unique one-dimensional structure, one-dimensional semiconductor photocatalysts are very suitable as important basic units for manufacturing multi-level hierarchical composite photocatalysts.

[n0004]

However, the rapid recombination of photogenerated charge carriers and the poor selectivity of reaction products limit the practical application of one-dimensional nanomaterials in photocatalysis.

To address these challenges, numerous strategies have been employed to modify one-dimensional photocatalysts, including morphology control, elemental doping, defect engineering, and heterojunction structures. Among these methods, constructing

heterojunctions is considered a promising and effective approach to improve photocatalytic efficiency. In particular, considering the outstanding advantages of one-dimensional semiconductor photocatalysts, such as their unique structure, high specific surface area, numerous active centers, and direct charge transport pathways, they are considered an important basic unit for combining with another type of semiconductor.

[n0005]

Inspired by the rapid development of one-dimensional photocatalysts, one-dimensional/one-dimensional heterojunction photocatalysts focus on solving the key problem of high recombination rate of photogenerated electrons and holes, which greatly improves photocatalytic performance.

Traditionally, the preparation of one-dimensional/one-dimensional hybrid structures has relied heavily on the use of organic surfactants or polymers. Therefore, it is of great

significance to design a simple, one-step method for preparing highly dispersed one-dimensional/one-dimensional nanomaterials.

[0008]

Summary of the Invention

[n0006]

The purpose of this invention is to provide a chestnut-shaped hollow NiCu composite material, its preparation method, and its application.

[n0007]

To achieve the above objectives, the present invention adopts the following technical solution:

[0011]

A chestnut-shaped hollow NiCu composite material is prepared by adding divalent nickel salt, divalent copper salt and precipitant to deionized water, stirring thoroughly until completely dispersed to obtain a uniformly dispersed precursor solution, transferring the precursor solution into a stainless steel high-temperature reactor lined with polytetrafluoroethylene,

carrying out a hydrothermal reaction in a drying oven, and then cooling, centrifuging, washing and drying until the water is completely evaporated to obtain a chestnut-shaped hollow NiCu nanocomposite material with uniform particle size distribution and a green color.

[n0008]

Furthermore, the millimole ratio of the divalent nickel salt, divalent copper salt, and precipitant used is 25:3:150.

[n0009]

Furthermore, the divalent nickel salt is nickel chloride hexahydrate (NiCl<sub>2<

/sub>・6H₂O); the divalent copper salt is copper chloride dihydrate (CuCl₂・6H₂O); and the precipitant is urea (CH₄N₂O).

[n0010]

Furthermore, the hydrothermal reaction is carried out at a temperature of 120 °C for 24 h.

[n0011]

Furthermore, the washing process involves rinsing three times with deionized water.

[n0012]

Furthermore, the drying process involves freeze-drying at -53 °C for 12 hours under vacuum conditions.

[n0013]

The obtained chestnut-shaped hollow NiCu composite material can be used for photocatalytic reduction of CO₂. Specifically, the chestnut-shaped hollow NiCu composite material is used as a catalyst, 2,2'-bipyridine is used as a co-catalyst, and triethanolamine is used as an electron donor. The photocatalytic reduction of CO<sub>2<

/sub> is carried out in a deionized water/acetonitrile (2:3, v/v) mixed solvent system under visible light (λ> 420 nm, 300 W Xe light source).

[n0014]

Since most fossil carbon on Earth is stored in the form of carbonate minerals, it is of particular importance to explore metal carbonate catalysts for selective CONER reduction.

However, carbonates are generally considered a poor matrix for accommodating photocatalytically active species, and there are currently few reports on carbonate-based photocatalytic materials.

This invention provides a chestnut-shaped hollow NiCu heterostructure composed of

Ni₂(OH)₂CO₃・4H₂O and Cu(OH)₂.

Hollow one-dimensional/one-dimensional structures enhance the separation of photogenerated charges by introducing heterojunctions with suitable materials, thus enabling them to be used for the photochemical reduction of CO₂.

Compared with ordinary heterojunctions, the carbonate vacancies in the chestnut-shaped hollow NiCu heterostructure significantly enhance the adsorption and activation of CO₂.

The inert CO₂ molecule is highly adsorbed on the NiCO₃ surface, which makes it easy to be activated into the key intermediate CO₂[−] for photoreduction reaction.

[n0015]

One-dimensional/two-dimensional structures suffer from a low interface region between the two materials and limited interaction.

One-dimensional/one-dimensional heterostructures created between different materials can effectively control the properties of the interface, maximize the interface area, and form a uniform heterojunction between the semiconductor and a suitable electronic medium, which can greatly promote electron transport and prevent electron-hole recombination.

Therefore, one-dimensional/one-dimensional hollow structures are good candidate materials for effectively combining specific shapes and good interfacial contact, and their application in improving charge transport and separation in CO₂ photocatalytic reduction is significant.

[n0016]

The beneficial effects of this invention are as follows:

[0021]

(1) The chestnut-shaped hollow NiCu nanocomposite material prepared by the present invention can overcome the shortcomings of the corresponding individual components to a large extent based on the tight binding between different components and the synergistic catalytic effect between components, and shows higher charge separation efficiency and charge migration rate.

[n0017]

(2) The present invention uses a one-step hydrothermal synthesis method to generate uniform and highly dispersed chestnut hollow NiCu nanocomposite microspheres in situ. These microspheres are composed of a one-dimensional/one-dimensional NiCu heterostructure made up of many needle-shaped nanoparticles.

By enhancing the charge conversion at the interface through a one-dimensional nanoneedle array, carbon dioxide can be photoreduced to carbon monoxide with high selectivity, providing a new approach for constructing favorable interfacial heterostructures.

[n0018]

(3) The equipment and materials required for the preparation method of the present invention are easy to obtain, the process operation is simple, the process conditions are concise, the cost is low, safe and efficient, and large-scale industrialization can be realized. Compared with other precious metals, it has less impact on the environment and is a green and environmentally friendly material that is beneficial to the environment. Moreover, it provides a new idea for the synthesis and application of carbonate photocatalysts.

[0024]

Attached Figure Description

[n0019]

Figure 1 shows the microstructure of NiCu nanocomposites under different hydrothermal times;

[0026]

Figure 2 shows the microstructure of the chestnut-shaped hollow NiCu nanocomposite material prepared in the example.

[0027]

Figure 3 shows the microstructure and EDS spectrum of the Ni₂(OH)<sub>2<

/sub>CO₃・4H₂O nanocomposite material prepared in Comparative

Example 1.

[0028]

Figure 4 shows the microstructure of Cu(OH)₂ in Comparative Example 2;

[0029]

Figure 5 shows the transmission electron microscope (TEM) image and EDS spectrum of the chestnut-shaped hollow NiCu nanocomposite material prepared in the example.

[0030]

Figure 6 shows a comparison of X-ray diffraction (XRD) images of chestnut-shaped hollow NiCu nanocomposites prepared in the examples, Ni₂(OH)₂CO₃・4H₂O nanocomposites prepared in Comparative Example 1, and Cu(OH)₂ prepared in Comparative Example 2.

[0031]

Figure 7 shows a comparison of the performance of NiCu nanocomposites under different hydrothermal times;

[0032]

Figure 8 is a performance comparison diagram of chestnut-shaped hollow NiCu nanocomposite material prepared in the example, Ni₂(OH)₂CO₃・4H₂O prepared in Comparative Example 1 and Cu(OH)₂ prepared in Comparative Example 2.

[0033]

Figure 9 shows the cycling performance of the chestnut-shaped hollow NiCu nanocomposite material prepared in the example.

[0034]

Figure 10 shows a comparison of the microstructure of the chestnut-shaped hollow NiCu nanocomposite material prepared in the example before and after the photocatalytic reaction.

[0035]

Figure 11 shows the photocurrent spectra of chestnut-shaped hollow NiCu nanocomposites prepared in the examples, Ni₂(OH)₂CO₃・4H₂O prepared in Comparative Example 1, and Cu(OH)₂ prepared in Comparative Example 2.

[0036]

Figure 12 shows the impedance comparison spectra of the chestnut-shaped hollow NiCu nanocomposite material prepared in the example, Ni₂(OH)₂CO₃・4H₂O prepared in Comparative Example 1, and Cu(OH)₂ prepared in Comparative Example 2.

[0037]

Figure 13 shows the PL spectra of the chestnut-shaped hollow NiCu nanocomposite material prepared in the examples, Ni₂(OH)₂CO₃・4H₂O prepared in Comparative Example 1, and Cu(OH)₂ prepared in Comparative Example 2.

[0038]

Detailed Implementation

[n0020]

To make the content of this invention easier to understand, the technical solution of this invention will be further described below with reference to specific embodiments, but this invention is not limited thereto.

[n0021]

Example: Preparation of chestnut-shaped hollow NiCu nanocomposites

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[0041]

1) Add 1.18 g (5 mmol) nickel chloride hexahydrate (NiCl₂・6H₂O) and 0.1 g (0.6 mmol) copper chloride dihydrate (CuCl₂・2H₂O) to 50 mL of deionized water, and obtain solution A by ultrasonic diffusion;

[0042]

2) Add 1.8 g (30 mmol) of urea (CH₄N₂O) to solution A and stir magnetically at 500 rpm for 10 min to obtain a uniformly distributed precursor solution;

[0043]

3) The obtained precursor solution was transferred into a stainless steel autoclave containing polytetrafluoroethylene and reacted in a drying oven at 120°C for 24 hours. After the reaction was completed, the autoclave was cooled to room temperature.

[0044]

4) The reaction solution was centrifuged at 8000 rpm to separate the green solid powder, and then washed three times with deionized water.

[0045]

5) The mixture was freeze-dried overnight at -53 °C under vacuum to allow the moisture to evaporate completely, thus obtaining a chestnut-shaped hollow NiCu nanocomposite material.

[n0022]

To further investigate the effect of hydrothermal time on the growth process of NiCu hollow heterostructures, the microstructures of the structures after hydrothermal treatment for 30 min, 1 h, 3 h, 6 h, 12 h and 24 h were compared. The results are shown in Figure 1.

As shown in Figure 1, in the first 30 minutes of the reaction, NiCu is not a needle-like nanosphere structure, but is composed of hexagonal blocks (a). As time progresses, after 1 hour of reaction, it completes the transformation from hexagonal to nanospheres. At this time, the edges of the nanospheres agglomerate together, still without obvious needle-like

structures (b). When the hydrothermal time is extended to 3 hours, tiny nanoneedles begin to grow at the edges, and numerous nanoneedles connect with each other to complete the surface modification of the nanospheres (c). The growth of nanoneedles mainly occurs during the hydrothermal process from 3 to 6 hours. At this time, the slender nanoneedles are distributed in a staggered and interwoven manner (d). When the time is further extended, the chestnut-like structure remains unchanged (e), but when the hydrothermal time reaches 24 hours, the internal structure of the broken NiCu heterostructure can be observed to be hollow (Figure f).

This indicates that during the hydrothermal process from 30 min to 24 h, the NiCu heterostructure underwent a structural transformation from hexagonal to nano-flower-like structures, and finally to hollow chestnut-like structures.

[n0023]

Preparation of Ni₂(OH)₂CO₃・4H₂O

(Comparative Example 1)

[0048]

1) Add 3.56 g (15 mmol) of nickel chloride hexahydrate (NiCl₂・6H<sub>2<
/sub>O) and 2.8 g (47 mmol) of urea (CH₄N₂O) to 50 mL of deionized water. After ultrasonic diffusion, stir magnetically at 500 rpm for 10 min to obtain a uniformly dispersed precursor solution.

[0049]

2) The obtained precursor solution was transferred into a stainless steel autoclave containing polytetrafluoroethylene and reacted in a drying oven at 100°C for 20 hours. After the reaction was completed, the autoclave was cooled to room temperature.

[0050]

3) The reaction solution was centrifuged at 8000 rpm to separate the green solid powder, and then washed three times with deionized water.

[0051]

4) The Ni₂(OH)₂CO₃・4H₂O nanocomposite material was freeze-dried overnight at -53 °C under vacuum conditions to allow the moisture to evaporate completely, resulting in uniform and highly dispersed Ni₂(OH)₂CO₃・4H₂O nanocomposite material.

[n0024]

Comparative Example 2

[0053]

Commercial Cu(OH)NER70 was purchased from Sinopharm Group.

[n0025]

Figures 2-4 show the microstructures of the chestnut-shaped hollow NiCu nanocomposite material prepared in the examples, the Ni₂(OH)₂CO₃・4H₂O nanocomposite material prepared in Comparative Example 1, and the Cu(OH)₂ nanocomposite material prepared in Comparative Example 2, respectively.

As can be seen from Figure 2, the overall microstructure of the nanocomposite material obtained in the example looks like a chestnut. Compared with Figures 3 and 4, it can be seen that the chestnut-shaped hollow NiCu nanocomposite material prepared in the example has well preserved the needle-like micro/nano structure and has a hollow structure.

[n0026]

Figure 5 shows the transmission electron microscope (TEM) image and EDS spectrum of the chestnut-shaped hollow NiCu nanocomposite material prepared in the example.

As can be seen from the figure, two types of stripes exist simultaneously on the obtained composite nanowires. A more detailed study of the NiCu heterostructure was conducted using STEM, revealing interplanar spacings (c) of 0.26 nm and 0.30 nm, which correspond to the (002) plane of Cu(OH)₂ and Ni₂(OH)₂CO₃・4H₂O. This further illustrates that NiCu is a heterostructure composed of Ni₂(OH)₂CO₃・4H₂O and Cu(OH)₂.

Meanwhile, the elemental mapping images of Ni, Cu, and O show that Ni, Cu, and O are evenly distributed in the marked area.

[n0027]

Figure 6 shows a comparison of X-ray diffraction (XRD) images of the chestnut-shaped hollow NiCu nanocomposite material prepared in the examples, the Ni₂(OH)₂CO₃・4H₂O nanocomposite material prepared in Comparative Example 1, and the Cu(OH)₂ nanocomposite material prepared in Comparative Example 2.

As can be seen from the figure, the X-ray diffraction peak angles of NiCu are consistent with those of Ni₂(OH)₂CO₃・4H₂O and Cu(OH)₂. Therefore, it can be inferred that the phases of the NiCu heterostructure are

Ni₂(OH)₂CO₃・4H₂O and Cu(OH)₂.

Among them, the diffraction peaks at 10.03°, 17.46°, 47.34°, and 59.97° can be attributed to Ni₂(OH)₂CO₃・4H₂O, while the diffraction peaks at 26.86°, 30.56°, 33.98°, 36.75°, and 39.86° are consistent with the angles of Cu(OH)₂.

[n0028]

Application Example 1

[0058]

The catalyst samples from the examples and comparative examples were used for photocatalytic carbon dioxide reduction, and the specific steps are as follows:

[0059]

1) Take 1 mg of catalyst sample, 8 mg of 2,2'-bipyridine as co-catalyst, 1 mL of triethanolamine as electron donor, 2 mL of deionized water and 3 mL of acetonitrile as solvent, and add them to a 25 mL quartz glass reactor;

[0060]

2) Seal the reactor, use a vacuum pump to remove the air from the reactor, and then introduce CO₂. Repeat this process three times to ensure that the reactor is filled with CO₂ gas.

[0061]

3) Place the reactor under a 300 W Pofil xenon lamp (which has a 400 nm cutoff filter) and maintain a constant temperature with stirring at 30°C;

[0062]

4) Every hour, 500 μL of gas is extracted from the reactor using a sampling needle and quantitatively determined using a gas chromatograph (Agilent 7890BGC).

[n0029]

Figure 7 is a comparison of the performance of the NiCu heterostructures prepared in the examples under different hydrothermal times.

As can be seen from the figure, when the hydrothermal time is 24h, the photocatalytic reduction of CO₂ is optimal due to the chestnut hollow structure of NiCu.

[n0030]

Figure 8 is a performance comparison diagram of the chestnut-shaped hollow NiCu nanocomposite material prepared in the examples, Ni₂(OH)₂CO₃・4H₂O prepared in Comparative Example 1, and Cu(OH)₂ prepared in Comparative Example 2.

As can be seen from the figure, the photocatalytic reduction performance of CO₂ by Ni₂(OH)₂CO₃・4H₂O is 6.65 μmol・h⁻¹, and the catalytic performance of NiCu nanocomposite material is 12.26 μmol・h⁻¹, which is 1.84 times that of Ni₂(OH)₂CO₃・4H₂O and 43.79 times that of Cu(OH)₂ (0.28 μmol・h⁻¹).

[n0031]

Figure 9 shows the cycling performance of the chestnut-shaped hollow NiCu nanocomposite material prepared in the example.

As can be seen from the figure, it still maintains excellent catalytic reduction performance for carbon dioxide after four cycles.

[n0032]

Figure 10 shows a comparison of the microstructure of the chestnut-shaped hollow NiCu nanocomposite material before and after the catalytic reaction.

As can be seen from the figure, the NiCu nanocomposite material still maintains a chestnut-shaped hollow morphology, indicating that it has good chemical and catalytic stability.

[n0033]

Application Example 2

[0068]

Using Ag/AgCl as the reference electrode, platinum as the counter electrode, and FTO glass

coated with the catalyst sample as the working electrode, the electrical properties and charge separation effect of the material were studied under different illumination conditions.

[n0034]

Figures 11 and 12 show the photocurrent and impedance spectra of the chestnut-shaped hollow NiCu nanocomposite material prepared in the examples, Ni₂(OH)₂CO₃・4H₂O prepared in Comparative Example 1, and Cu(OH)₂ prepared in Comparative Example 2, respectively.

As can be seen from the figure, the interaction between the heterojunction arrays in the NiCu nanocomposite enhances the charge conversion at the interface and accelerates the electron-hole separation efficiency, which is consistent with the performance comparison in Figure 9.

[n0035]

Figure 13 shows the PL spectra of the chestnut-shaped hollow NiCu nanocomposite material prepared in the examples, Ni₂(OH)₂CO₃・4H₂O prepared in Comparative Example 1, and Cu(OH)₂ prepared in Comparative Example 2.

The signal strength of a PL can typically reflect the recombination efficiency of electrons and holes.

As can be seen from the figure, compared with Ni₂(OH)₂CO₃・4H₂O and Cu(OH)₂, NiCu exhibits the weakest PL signal intensity. This indicates that the addition of Cu element effectively promotes the separation of

photogenerated carriers, thereby allowing the chestnut-shaped hollow NiCu heterostructure to exhibit the highest catalytic activity.

[n0036]

The above description is only a preferred embodiment of the present invention. All equivalent changes and modifications made within the scope of the claims of the present invention should be included in the scope of the present invention.
