DESCRIPTION CN114622237A

Preparation method and application of nickel-copper bimetallic nanotube catalyst material

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[0001]

Technical Field

[n0001]

This invention belongs to the field of catalytic preparation technology, and relates to the preparation of a nickel-copper bimetallic nanotube catalyst material and its application as an electro-oxidation of biomass derivatives.

[0003]

Background Technology

[n0002]

Electrocatalytic water splitting is generally considered one of the most promising routes for the production of H₂ and has been extensively studied for decades.

However, the oxygen evolution reaction (OER) involves a four-electron oxidation process, which is thermodynamically unfavorable and typically requires a high overpotential to promote overall water splitting.

Furthermore, the oxygen generated at the anode is almost worthless, and a large amount of energy is required to separate the gaseous products in order to avoid cross-permeation of H₂ and O₂.

In view of this, replacing the kineticly sluggish OER with the thermodynamically more favorable organic reforming reaction can couple hydrogen production while preparing high-value-added organic compounds, thereby further improving energy utilization efficiency and economic benefits. In particular, the conversion of biomass into fuel and high-value chemicals, known as "biorefining technology," has a long history. Taking 5-hydroxymethylfurfural (HMF) as an example, important furan-based chemicals can be prepared through catalytic oxidation. One of the products, 2,5-furandicarboxylic acid (FDCA), can be used to replace terephthalic acid, a monomer material for the synthesis of polyethylene terephthalate (PET), due to its similar chemical structure. Biomass-based polyester poly(ethylene furandicarboxylate) (PEF) synthesized by FDCA polymerization performs better than PET in many plastic products. FDCA is also listed by the U.S. Department of Energy as one of the 12 most important high-value-added chemicals produced from biomass conversion.

[0005]

Summary of the Invention

[n0003]

This invention provides a method for preparing a nickel-copper bimetallic nanotube catalyst material and its application in the electro-oxidation catalytic reaction of organic biomass, achieving a 100% conversion rate of HMF and a 99% yield of FDCA.

[n0004]

In addition, this catalyst also exhibits excellent catalytic activity for the electro-oxidation of other small-molecule alcohols/aldehydes from biomass, with conversion rates and selectivity of 98-100% for the corresponding products.

[n0005]

The technical solution of the present invention is as follows:

[n0006]

A method for preparing a nickel-copper bimetallic nanotube catalyst material includes the following steps:

[n0007]

Nickel-copper alloy nanotube catalysts (NiCuNTs) were obtained in situ on a nickel foam substrate using nickel sulfate and copper sulfate as reactants, deionized water as solvent, and nickel foam as current collector substrate via electrodeposition-dealloying method.

[n0008]

A method for preparing a nickel-copper bimetallic nanotube catalyst material specifically includes the following steps:

[n0009]

(1) Nickel sulfate, copper sulfate and boric acid are dissolved in deionized water to form a reaction solution. Stir until completely dissolved to obtain a homogeneous dark green solution, which is used as the electrolyte for electrodeposition.

[n0010]

(2) Using nickel foam as the working electrode, platinum sheet as the counter electrode, and saturated calomel electrode as the reference electrode, current is applied to the electrolyte obtained in step (1) above for electrodeposition to obtain NiCu alloy precursor material (denoted as NiCuNPs).

[n0011]

(3) Then a constant potential (0.5-1.2V) is applied to remove the alloy. After the reaction, the foamed nickel is taken out, and after washing and drying, the nickel-copper alloy nanotube catalyst material (NiCu NTs) is obtained.

[n0012]

In step (1), the concentration of NiSO₄ in the reaction solution is 0.2-0.8 mol/L, the concentration of CuSO₄ in the reaction solution is 0.05-0.2 mol/L, and the concentration of H₃BO₃ in the reaction solution is 0.2-0.8 mol/L.

Most preferably, the concentration of NiSO₄ in the reaction solution is 0.5 mol/L, the concentration of CuSO₄ in the reaction solution is 0.075 mol/L, and the concentrations of H₃BO₃ in the reaction solution are 0.5 mol/L respectively.

[n0013]

The stirring conditions are: magnetic stirring for 20 to 40 minutes, with a rotation speed of 400 to 800 rpm.

Most preferably, the stirring conditions are: magnetic stirring for 30 minutes at a speed of 600 rpm.

[n0014]

In step (2), the nickel foam needs to be cleaned.

[n0015]

Electrodeposition is performed in the electrolyte obtained in step (1) above at 10–40°C (preferably 20–30°C).

The conditions for applying current electrodeposition are: 60-120 mA current electrodeposition for 5-20 minutes.

[n0016]

In step (3), the constant potential is 0.5 to 1.2V.

Remove the nickel foam after reacting for 5-10 minutes.

[n0017]

The most preferred method for preparing a nickel-copper bimetallic nanotube catalyst material specifically includes the following steps:

[n0018]

NiSO, CuSO, and HSOBO were weighed and added to deionized water to form a reaction solution. The concentrations of NiSO, CuSO, and HSOBO in the reaction solution were 0.5 M, 0.075 M, and 0.5 M, respectively. The solution was then magnetically stirred for 30 min at 600 rpm to obtain a uniform dark green solution. Next, the dried and clean nickel foam was wrapped with raw material tape to facilitate electrodeposition. The area was fixed at 1×1.

5cm², with nickel foam (NF) as the working electrode, platinum sheet as the counter electrode, and saturated calomel electrode as the reference electrode. Electrodeposition was performed using a constant current method at 100mA for 10 minutes at room temperature (25°C) to obtain the NiCuNPs precursor. Then, dealloying was performed at 1.0V with a dissolution time of 400s and a stirring speed of 30rpm. The prepared material was rinsed with deionized water and ethanol to remove residual electrolyte, and then dried in a vacuum drying oven for later use, which is the nickel-copper bimetallic nanotube catalyst material.

[n0019]

The prepared nickel-copper bimetallic nanotube catalyst was used as an organic biomass electro-oxidation catalyst, achieving a 100% HMF conversion and a 99% FDCA yield.

Specifically, it is used as a catalyst and electrode material in the electro-oxidation of HMF (5-hydroxymethylfurfural) to FDCA (2,5-furandicarboxylic acid).

In the reaction, it can be used not only directly as an electrode material, but also as a catalyst.

[n0020]

In addition, this catalyst also exhibits excellent catalytic activity for the electro-oxidation of other small-molecule alcohols/aldehydes from biomass, with conversion rates and selectivity of 98-100% for the corresponding products.

Small biomass molecules such as benzyl alcohol (BA), furfural (FF), and furfuryl alcohol (FFA).

In the reaction, it can be used not only directly as an electrode material, but also as a catalyst.

[n0021]

Traditional biomass oxidation mainly uses a thermocatalytic approach, which requires the addition of an oxidant. The reaction process is usually carried out under high temperature and high pressure, which is costly and pollutes the environment.

In contrast, electrocatalytic biomass oxidation can decompose water into reactive oxygen species with high oxidizing power at room temperature and normal pressure, efficiently catalyzing the conversion of biomass into high-value-added organic chemicals.

It has the advantages of green and mild reaction conditions and high reaction selectivity, while reducing carbon emissions, making it an effective way to achieve the goal of "carbon peak and carbon neutrality".

[n0022]

Compared with the prior art, the beneficial effects of the present invention are:

[n0023]

This invention employs a simple electrodeposition-dealloying method to construct an in-situ grown NiCu alloy nanotube catalyst material based on nickel foam substrate.

Nickel and copper are abundant and inexpensive on Earth, meeting the cost requirements of industrial applications; nanotube morphology has a high specific surface area and favorable charge transport channels, which significantly increases the reaction area between the catalyst material and the organic substrate, exhibiting excellent catalytic activity and versatility.

The preparation method described in this invention is simple to operate, has good reproducibility, low cost, and is environmentally friendly.

[n0024]

This invention directly grows nickel-copper alloy nanotube array materials in situ on a conductive substrate through a simple one-step electrodeposition-dealloying method.

This preparation method has the advantages of simple process, short time and low cost. The material obtained has self-supporting characteristics and can be used directly as electrode material or as catalyst.

Its unique hollow tubular structure can provide a large effective surface area for electrochemical activity, greatly enriching the active sites for catalytic reactions.

The introduction of copper effectively reduces the intrinsic resistance and mass transfer resistance of the catalyst material, which is beneficial to promoting the kinetic process of the catalytic reaction.

This catalyst can electrocatalyze the oxidation of biomass derivatives (such as 5-hydroxymethylfurfural (HMF), benzyl alcohol (BA), furfural (FF), and furfuryl alcohol (FFA)) to prepare corresponding biomass acid products, exhibiting extremely high conversion rates and selectivity, and demonstrating excellent catalytic versatility.

Taking HMF as an example, the conversion rate can reach over 98%, and the selectivity is over 99%.

[0028]

Attached Figure Description

[n0025]

Figure 1 shows physical images of blank nickel foam, NiCuNPs precursor, and NiCuNTs electrode material;

[n0026]

Figure 2 shows scanning electron microscope images of (a,b) NiCuNPs precursor and (c,d) NiCuNTs electrode material;

[n0027]

Figure 3 shows the X-ray diffraction patterns of the NiCuNPs precursor and the NiCuNTs electrode material;

[n0028]

Figure 4 shows the (a) linear sweep voltammetry curves and (b) Tafel slope plots of the NiCu NTs electrode material with and without HMF substrate;

[n0029]

Figure 5 shows the possible reaction pathway of HMF directional oxidation to FDCA in NiCu NTs electrode material (a), the concentration of organic matter during HMF oxidation to FDCA by high performance liquid chromatography and its relative concentration change (c), and the Faraday efficiency of HMF to FDCA in 5 consecutive cycles.

[n0030]

Figure 6 shows the electrocatalytic performance of NiCu NTs electrode materials at different HMF concentrations: (a) peak current density, (b) Tafel slope plot, (c) electrochemically effective active area, and (d) conversion, selectivity, and Faraday efficiency.

[n0031]

Figure 7 shows the catalytic performance of NiCu NTs electrode materials on different substrates: (a) electro-oxidation of benzyl alcohol (BA), (b) oxidation of furfural (FF), and (c) electro-oxidation of furfuryl alcohol (FFA).

[n0032]

Figure 8 shows the general catalytic results of the NiCu NTs electrode material.

[n0033]

Figure 9 shows (a) a scanning electron microscope image of the Cu-free sample with copper electrode material, (b) linear scanning voltammetry curves with and without HMF substrate, and (c) electrolysis current-time and charge-time curves in 20 mM HMF solution.

[n0034]

Figure 10 shows (a) the electrochemically effective active area of NiCuNTs, NiCuNPs precursors, and Cu-free electrode materials in HMF solution, and (b) their electrochemical impedance spectroscopy.

[0039]

Detailed Implementation

[n0035]

To facilitate understanding of the present invention, the present invention will be further described below with reference to specific embodiments. These embodiments are only used to illustrate the present invention and do not limit the scope of the present invention.

The technical terms used in this document are for the purpose of describing specific embodiments only and are not intended to limit the scope of protection of this invention.

[n0036]

Example 1: Preparation of NiCu NTs Electrode Material

[n0037]

The preparation steps are as follows:

[n0038]

Weigh out NiSO₄, CuSO₄, and H₃BO₃ and add them to 50 mL of deionized water to form a reaction solution. The concentrations of NiSO₄, CuSO₄, and H₃BO₃ in the reaction solution are 0.5 M, 0.075 M, and 0.5 M, respectively. Then, stir magnetically for 30 min at a speed of 600 rpm to obtain a uniform dark green solution.

Next, the dry and clean nickel foam is wrapped with raw material tape to fix the electrodeposition reaction area to 1×1.5cm².

The experiment was conducted on a CHI760E electrochemical workstation using nickel foam (NF) as the working electrode, a platinum sheet as the counter electrode, and a saturated calomel electrode as the reference electrode.

The first step of electrodeposition was performed using a constant current method, with continuous electrodeposition at 100 mA for 10 minutes at room temperature (25°C) to obtain the NiCuNPs precursor.

Then, dealloying was performed at 1.0V for 400s with a stirring speed of 30rpm.

The prepared material was rinsed with deionized water and ethanol to remove residual electrolyte, and then dried in a vacuum drying oven for later use, which is the NiCu NTs material.

[n0039]

Figure 1 shows the physical images of blank nickel foam, NiCuNPs precursor, and NiCuNTs electrode material in Example 1. Figure 2 shows the scanning electron microscope images of the obtained NiCuNTs material at different magnifications.

Figures 2a-b show the surface morphology of the NiCuNPs precursor generated by the first step of electrodeposition, exhibiting a large-area uniformly distributed nanoparticle morphology.

Figures 2c-d are scanning electron microscope images of the NiCu NTs sample. It can be clearly seen that NiCu NTs is an array structure composed of nanotubes. The nanotubes have smooth surfaces and are densely packed, exhibiting a large specific surface area and large pores, which is conducive to full contact with the electrolyte and provides more active sites for catalytic reactions.

Figure 3 is the X-ray diffraction pattern of the NiCu NTs material obtained in Example 1.

The NiCu NPs precursor has three pairs of distinct characteristic peaks, corresponding to Ni (JCPDS No. 70-1849) and Cu (JCPDS No. 04-0836) metals, respectively. However, for NiCu NTs materials, the three characteristic peaks of Ni metal are retained, while the three characteristic peaks of Cu metal disappear. This may be attributed to the low Cu content after dealloying.

[n0040]

Example 2: Application of NiCu NTs electrode material in the electro-oxidation of HMF to generate FDCA

[n0041]

In a 1M KOH solution, using NiCuNTs electrode material as the working electrode, a platinum sheet as the counter electrode, and an Hg/HgO electrode as the reference electrode, the performance of NiCuNTs catalyst for the electrochemical oxidation of HMF was systematically studied in an H-type electrolytic cell.

Figure 4a compares the linear sweep voltammetry (LSV) curves of water oxidation (without HMF) and HMF oxidation (20 mM) using NiCu NTs electrode catalysts, and it can be observed at 1.42 V vs.

RHE and significant oxygen bubble release at the corrected potential, with a current density of 100 mA cm⁻² at a potential of 1.58 V (overpotential η = 350 mV), are comparable to the catalytic performance of most Ni-based OER catalysts reported in the literature.

The appearance of redox peaks (Ni²⁺/Ni³⁺) indicates the formation of β-NiOOH, which is also considered to be the true active site for water oxidation.

After adding 20 mM HMF, the current density increased significantly, peaking at approximately 136 mA cm⁻² at 1.424 V.

This indicates that HMF has a greater advantage in electro-oxidation compared to OER.

This is also confirmed by the Tafel slope results in Figure 4b. The Tafel slope in 20 mM HMF is 24.9 mVdec⁻¹, which is much smaller than the 36.9 mVdec⁻¹ in the water oxidation process, indicating that the electro-oxidation of HMF is thermodynamically more favorable than water oxidation.

[n0042]

Figure 5a shows the possible reaction pathway for the directional oxidation of HMF to FDCA. As the electrolysis reaction proceeds (1.424 V vs RHE), the intermediate products HMFCA (5-hydroxymethyl-2-furanocarboxylic acid) and FFCA (5-formyl-2-furanocarboxylic acid) detected by high performance liquid chromatography (Figure 5b) indicate that the above reaction pathway is followed on the NiCu NTs catalyst: the aldehyde group is first oxidized to form the HMFCA intermediate, then the hydroxymethyl group is continuously oxidized to produce FFCA, and finally FDCA is obtained. This is basically consistent with the aerobic oxidation reaction pathway.

After 120 minutes of electrolysis, it was found that the conversion rate of FDCA was approximately 100%, the FDCA yield was approximately 99%, and the Faraday efficiency (FE) was [not specified].

The saturation rate was 96.4% (Figure 5c), which is comparable to the catalysts recently reported in the literature.

The catalyst was recycled five times consecutively, and the Faraday efficiency was always above 90% (Figure 5d), indicating that the material has excellent catalytic stability.

[n0043]

Figure 6 shows the electrocatalytic performance of NiCu NTs electrode materials at different HMF concentrations.

As the HMF concentration increases, the peak current density of the LSV curve continuously increases, and the slopes of the Tafel curves are 71.3 mV・dec⁻¹(35 mM), 85.8 mV・dec⁻¹(50 mM), 85.3 mV・dec⁻¹(75 mM), and 148.4 mV・dec⁻¹(100 mM), respectively, indicating that the electro-oxidation catalytic reaction is a diffusion-controlled process as the substrate concentration increases.

The electrochemically effective active area (ECSA, Figure 6c) results show that the double-layer specific capacitance (C_{dl}) increases with increasing substrate concentration. In a system with 100 mM HMF, C_{dl} is 96.2 mF・cm⁻², and the converted ECSA is 2405 cm². This huge electrochemically effective area can undoubtedly provide more electrocatalytic active sites.

When the substrate HMF concentration is 100 mM (Figure 6d), it can be completely electrolyzed in 240 minutes with a conversion rate of 96.7%. This excellent catalytic performance at a high substrate concentration undoubtedly confirms that NiCuNTs electrode materials have great commercial prospects.

[n0044]

Example 3: Application of NiCu NTs in the electro-oxidation of BA, FF, and FFA

[n0045]

To further explore the versatility of NiCuNTs catalysts, we selected three other organic substrates, such as benzyl alcohol (BA), furfural (FF), and furfuryl alcohol (FFA), to evaluate their electrocatalytic performance (Figure 7 and Table 1).

After adding the organic substrate, a significant increase in peak current (LSV curves, Figures

7a-c) can be easily observed, demonstrating a more desirable organic electro-oxidation capability than OER.

Electrolysis experiments were conducted using a voltage of 1.424V vs RHE. The catalytic results (Figure 8 and Table 1) showed that the conversion and selectivity were both above 98% when the corresponding acid products were generated, and the Faraday efficiency was above 85%, demonstrating excellent catalytic universality.

[n0046]

Table 1

[n0048]

Example 4: Preparation of Cu-free electrode material and its application in the electro-oxidation of HMF

[n0049]

The preparation steps are as follows:

[n0050]

Weigh out NiSO₄ and H₃BO₃ and add them to 50 mL of deionized water to form a reaction solution. The concentrations of NiSO₄ and H₃BO₃ in the reaction solution are 0.5 M and 0.5 M, respectively. Then, stir magnetically for 30 min at a speed of 600 rpm to obtain a uniform dark green solution.

Next, the dry and clean nickel foam is wrapped with raw material tape to fix the electrodeposition reaction area to 1×1.5cm².

The experiment was conducted on a CHI760E electrochemical workstation using nickel foam (NF) as the working electrode, a platinum sheet as the counter electrode, and a saturated calomel electrode as the reference electrode.

The first step of electrodeposition was performed using a constant current method, with continuous electrodeposition at 100mA for 10 minutes at room temperature (25°C) to obtain the precursor.

Then, dealloying was performed at 1.0V for 400s with a stirring speed of 30rpm.

The prepared material was rinsed with deionized water and ethanol to remove residual electrolyte, and then dried in a vacuum drying oven for later use, which is the Cu-free material.

Figure 9a is a scanning electron microscope image of the Cu-free material in Example 4. It can be observed that Ni metal particles are tightly packed on the surface of the nickel foam with almost no voids, and the loading of the material is reduced sharply. This indicates that without the copper salt precursor, the unique mesoporous tubular structure of NiCuNTs cannot be obtained, which is not conducive to the adsorption of the substrate and the catalytic reaction.

[n0051]

Further investigation into the application of Cu-free electrode materials in the electro-oxidation of HMF was conducted. For example, in 9b, the linear sweep voltammetry (LSV) curves of water oxidation (without HMF) and HMF oxidation (20 mM) using Cu-free electrode materials were compared. It can be observed that after adding 20 mM HMF, the current density increased significantly, with a peak value of approximately 47 mA at 1.467 V.

This indicates that HMF also has greater advantages in electro-oxidation compared to OER.

Figure 9c shows the current-time curve of electrolysis at 1.424V. After 2 hours of electrolysis, the yield of FDCA is 64.5%, which is much lower than that of the copper-containing samples NiCuNTs and NiCuNPs.

[n0052]

Figure 10 shows a systematic comparison of the electrochemical active specific surface area and resistivity of three catalyst materials to explore the fundamental reasons for the differences in catalytic activity among the three materials.

The introduction of copper reduces the intrinsic resistance R_s and mass transfer resistance R_{ct} of the catalyst material, greatly improving the kinetics of the catalytic reaction. At the same time, the deposition and removal of copper facilitates the creation of mesoporous channels, greatly increasing the electrochemically active specific surface area and providing more catalytic reaction sites, thus giving NiCuNTs electrode materials excellent electrocatalytic activity.