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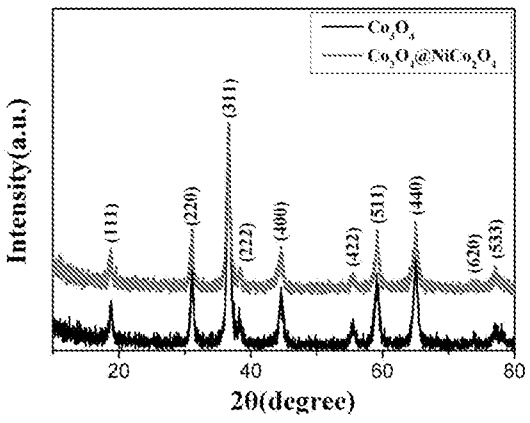
(54) **A PREPARATION METHOD AND APPLICATION OF A CO3O4@NICO2O4 CATALYST.**

(57) The invention relates to the technical field of electrocatalysis, in particular to a preparation method and application of a Co3O4@NiCo2O4 catalyst, which comprises the following steps: S1: Preparing Co3O4 nanowire layer by weighing CoCl2-6H2O, NH4F and urea; S2: NiCl2-6H2O, CoCl2-6H2O, NH4F, urea and the Co3O4 nanowire layer obtained by Step S1 are weighed, and Co3O4@NiCo2O4 catalyst is prepared. The Co3O4@NiCo2O4 nanowire layered array prepared by the invention exhibits A surprisingly high specific capacitance (1466 F g^{-1} at 2.5 A g^{-1}), which is far superior to the traditional capacitor materials. This high specific capacitor is mainly due to its unique layered heterostructural design, which provides a wide range of surface areas and electrochemically active sites, enhancing the diffusion and charge storage capacity of electrolyte ions. Drawing 1



Drawing 1

A Preparation Method and Application of A Co_3O_4@$NiCo_2O_4$ Catalyst

LU509305

Technical Field

The invention relates to the technical field of electrocatalysis, in particular to a preparation method and application of a Co_3O_4@$NiCo_2O_4$ catalyst.

Background Technology

In recent years, with the growing demand for sustainable clean energy, the development of efficient energy storage systems has attracted much attention. High-performance energy storage devices are an important part of clean energy technology and indispensable for next-generation electronics, biomedical devices and hybrid electric vehicles. Compared to other conventional energy storage devices, supercapacitors (also known as electrochemical capacitors) are well suited for numerous applications that require high energy density and fast charge and discharge rates, such as hybrid electric vehicles and industrial equipment. However, the low energy density of supercapacitors limits their practical applications, making them unable to meet commercial needs. Therefore, it is very important to prepare electrocatalyst which is an efficient electrode material with excellent electrochemical properties. According to previous studies, building structurally unique electrode materials for pseudo-capacitors has also proved to be a very effective way to increase energy density. The ideal electrode material should have high conductivity to promote electron transport, rich electrochemical active sites to improve specific capacitance, and be environmentally friendly. Among many materials, Co_3O_4 nanomaterials are widely considered to be the most promising catalyst materials for solar cells.

The construction of three-dimensional layered nanostructures based on Co_3O_4 on conductive substrates is still an inherent property of Co_3O_4 on conductive substrates. This can improve weaknesses and improve electrochemical performance. Heterostructures can provide a larger specific surface area and multiple accessible electroactive sites, thus facilitating electron transport and ion diffusion. Electron transfer and ion diffusion enhance the redox reaction. For

example, Sun and collaborators fabricated core-shell Co_3O_4@$NiCo_2O_4$ composites on nickel foam to achieve high specific capacitance at a current of 1514 $F \cdot g^{-1}$. The current density is 1 A g^{-1}. To date, controllable fabrication of layered arrays of bimetallic oxide nanowire with ideal surface area and porosity on nickel foam (NF) remains a major challenge for researchers designing highly efficient electrocatalysts for supercapacitors. Efficient electrocatalysts for supercapacitors remain a major challenge for researchers.

Contents of Invention

The invention aims to provide a preparation method and application of Co_3O_4@$NiCo_2O_4$ catalyst, and provides a self-supporting Co_3O_4@$NiCo_2O_4$ nanowire laminated array as a high efficiency electrocatalyst, and is used as a high performance supercapacitor electrocatalyst material. This method provides a new strategy for the development of advanced electrode materials.

In order to realize the technical purpose and achieve the technical effect, the invention is realized through the following technical schemes:

A method for preparing Co_3O_4@$NiCo_2O_4$ catalyst comprises the following steps:

S1: Co_3O_4 nanowire layer is prepared by weighing $CoCl_2$-$6H_2O$, NH_4F and urea;

S2: $NiCl_2$-$6H_2O$, $CoCl_2$-$6H_2O$, NH_4F, urea and the Co_3O_4 nanowire layer obtained by step S1 are weighed, and Co_3O_4@$NiCo_2O_4$ catalyst is prepared.

Further, the step S1 specifically comprises the following sub-steps:

S1.1: Weighing 1.5mmol $CoCl_2$-$6H_2O$, 1mmol NH_4F and 2mmol urea into 40mL H_2O and stirring them for 20 minutes;

S1.2: The evenly stirred solution is transferred to a 50mL polytetrafluoroethylene reactor, which is filled with 2cm×3cm nickel foam that had been pre-treated in 6M HCl and reacted at 120 ℃ for 6 hours;

S1.3: Samples obtained by washing with deionized water and anhydrous ethanol several times; After drying under vacuum at 60 °C, and then calcination at 5 °C min^{-1} to 300 °C for 2 hours, Co_3O_4 nanowire layer is obtained.

Further, the step S2 specifically comprises the following sub-steps:

S2.1: 0.1mmol $NiCl_2$-$6H_2O$, 0.2mmol $CoCl_2$-$6H_2O$, 0.1mmol NH_4F and 0.2mmol urea are accurately weighed and added into 40mL H_2O, stirring them for 20 minutes;

S2.2: The homogenized solution is transferred to a 50mL polytetrafluoroethylene reactor, in which foamed nickel coated Co_3O_4 nanowires are added and reacted at 120 °C for 6 hours;

S2.3: After the reaction, the sample obtained by washing with deionized water and anhydrous ethanol several times; Finally, the washed sample is dried under vacuum at 60 °C, and then calcined at 5 °C·min^{-1} to 300 °C for 2 hours to obtain Co_3O_4@$NiCo_2O_4$ catalyst.

On the other hand, the invention provides the application of the Co_3O_4@$NiCo_2O_4$catalyst in the preparation of supercapacitors.

The invention has the following beneficial effects:

The Co_3O_4@$NiCo_2O_4$ nanowire layered array prepared by the invention exhibits A surprisingly high specific capacitance (1466 F g^{-1} at 2.5 A g^{-1}), which is far superior to the traditional capacitor materials. This high specific capacitor is mainly due to its unique layered heterostructural design, which provides a wide range of surface areas and electrochemically active sites, enhancing the diffusion and charge storage capacity of electrolyte ions. The composite containing Co_3O_4 and $NiCo_2O_4$ improves the kinetic properties of the redox reaction through synergistic action, thus significantly improving the capacitive properties.

Co_3O_4@$NiCo_2O_4$ The nanowire array can maintain a specific capacitance of 93.8% after 5000 charge and discharge cycles, showing excellent cycle stability. This performance is due to the high structural stability of the prepared materials, and the heterostructures are able to maintain strong mechanical strength in repeated

electrochemical processes such as redox reactions and ion exchange. At the same time, the introduction of $NiCo_2O_4$ not only enhances the conductivity of the material, but also improves the chemical stability, thus reducing the material degradation in the long-term electrochemical cycle.

Compared with pure Co_3O_4 nanowires, Co_3O_4@$NiCo_2O_4$ exhibits superior electrochemical properties. It illustrates enhanced electrochemical activity at various scanning speeds and current densities, which is due to the involvement of Ni^{2+}/Ni^{3+} redox pairs, which expands the redox reaction range of the material, thereby increasing the charge storage capacity. In addition, the three-dimensional conductive network structure of $NiCo_2O_4$ improves the electron conduction rate, making the electrochemical reaction more efficient.

The layered nanowire arrays at Co_3O_4@$NiCo_2O_4$ demonstrate low charge-transfer resistance, as verified by electrochemical impedance spectroscopy (EIS). Low charge transfer resistors benefit from the material's heterostructural design, which provides a continuous electron transport path, reducing interface impedance and energy loss. $NiCo_2O_4$ plays a role in regulating the electronic structure in this system, improving the electron density and distribution uniformity, thus accelerating the charge transfer process.

And indeed, the implementation of any product of the invention does not necessarily need to achieve all the advantages described above.

Explanation on Drawings

In order to more clearly state the technical scheme of the implementation method of the invention, the following is a brief introduction of the drawings required for the description of the implementation method. It is obvious that the drawings described below are only some implementation methods of the invention, and other drawings can be obtained according to these drawings for ordinary technicians in the field without creative labor.

Drawing 1 illustrates the XRD pattern of the sample. (a) Co_3O_4 nanowires, (b) Co_3O_4@$NiCo_2O_4$ nanowires layered array;

Drawing 2 illustrates the low-power and high-power SEM images of the sample. (a, b) Co_3O_4 nanowires, (c, d) Co_3O_4@$NiCo_2O_4$ nanowires layered array;

Drawing 3 illustrates TEM and HRTEM images of the sample. (a, b) Co_3O_4 nanowires, (c, d) Co_3O_4@$NiCo_2O_4$ nanowires layered array;

Drawing 4 illustrates the EDS image of Co_3O_4 nanowire @@$NiCo_2O_4$ nanosheet sample.

Drawing 5 illustrates the cyclic voltammetry curve and constant current charge-discharge curve of the sample. (a, b) Co_3O_4 nanowires, (c, d) Co_3O_4@$NiCo_2O_4$ nanowires layered array.

Drawing 6 is a comparison diagram of the electrochemical properties of the samples. (a) CV value at 25mV s^{-1}; (b) Charge and discharge curve at 5A g^{-1}; (c) The functional relationship between specific capacitance and scanning rate; (d) Specific capacitance as a function of current density.

Drawing 7 illustrates the cyclic performance and Nyquist diagram of the sample. (a) Charge and discharge 5000 times under 5A g^{-1} conditions; (b) Nyquist diagram under conditions 1A g^{-1}.

Specific Implementation Method

The following is a clear and complete description of the technical scheme in the implementation method of the invention in combination with the drawings attached to the implementation method of the invention. Obviously, the described implementation method is only a part of the implementation method of the invention, but not the whole implementation method. Based on the implementation methods of the invention, all other implementation methods obtained by ordinary technicians in the field without creative labor fall within the scope of protection of the invention.

Implementation method 1

A method for preparing a Co_3O_4@$NiCo_2O_4$ catalyst described in the present implementation method comprises the following steps:

S1: Co_3O_4 nanowire layer is prepared by weighing $CoCl_2$-$6H_2O$, NH_4F, and urea;

S2: $NiCl_2$-$6H_2O$, $CoCl_2$-$6H_2O$, NH_4F, urea and the Co_3O_4 nanowire layer obtained by step S1 are weighed, and Co_3O_4@$NiCo_2O_4$ catalyst is prepared.

In this implementation method, step S1 specifically comprises the following sub-steps:

S1.1: Weighing 1.5mmol $CoCl_2$-$6H_2O$, 1mmol NH_4F and 2mmol urea into 40mL H_2O and stirring them for 20 minutes;

S1.2: The homogenized solution is transferred to a 50mL polytetrafluoroethylene reactor filled with 2cm×3cm nickel foam that had been pretreated in 6M HCl and reacted at 120 ℃ for 6 hours.

S1.3: Sample obtained by multiple washing with deionized water and anhydrous ethanol. Finally, the washed sample is dried under vacuum at 60 ℃, and then calcined at 5 ℃ min^{-1} to 300 ℃ for 2 hours to obtain the Co_3O_4 nanowire layer.

In this implementation method, step S2 specifically comprises the following sub-steps:

S2.1:0.1mmol $NiCl_2$-$6H_2O$, 0.2mmol $CoCl_2$-$6H_2O$, 0.1mmol NH_4F and 0.2mmol urea are accurately weighed into 40mL H_2O and stirred for 20 minutes.

S2.2: The evenly stirred solution is transferred to a 50mL polytetrafluoroethylene reactor, where foamed nickel coated Co3O4 nanowires are added and reacted at 120 ℃ for 6 hours.

S2.3: Samples obtained by washing with deionized water and anhydrous ethanol several times after the reaction. Finally, the washed sample is dried under vacuum at 60 ℃, and then calcined at 5℃·min^{-1} to 300 ℃ for 2 hours to obtain Co_3O_4@$NiCo_2O_4$ catalyst.

On the other hand, the invention provides the application of the Co_3O_4@$NiCo_2O_4$ catalyst in the preparation of supercapacitors.

Implementation method 2

Synthesis of Co_3O_4 nanowire arrays

Weighing 1.5mmol $CoCl_2$-$6H_2O$, 1mmol NH_4F and 2mmol urea into 40mL H_2O and stirring them for 20 minutes. The evenly stirred solution is transferred to a 50mL polytetrafluoroethylene reactor, which is filled with 2cm×3cm nickel foam that had been pretreated in 6M HCl and reacted at 120 °C for 6 hours. After the reaction, the samples are washed several times with deionized water and anhydrous ethanol. Finally, the washed sample is dried under vacuum at 60 °C and then calcined at 5 °C min^{-1} to 300 °C for 2 hours.

Synthesis of Co_3O_4@$NiCo_2O_4$ electrocatalysts

0.1mmol $NiCl_2$-$6H_2O$, 0.2mmol $CoCl_2$-$6H_2O$, 0.1mmol NH_4F and 0.2mmol urea are accurately weighed into 40mL H_2O and stirred for 20 minutes. Then, the evenly stirred solution is transferred to a 50mL polytetrafluoroethylene reactor, where foam-coated Co_3O_4 nanowires are added and reacted at 120 °C for 6 hours. After the reaction, the samples are washed several times with deionized water and anhydrous ethanol. Finally, the washed sample is dried under vacuum at 60 °C and then calcined at 5 °C min^{-1} to 300 °C for 2 hours.

Representation

The phase purity of the sample is characterized by X-ray powder diffraction with graphite monochromator and high intensity CuKa radiation (λ=0.154060 nm). The scanning speed is 8° min^{-1} and the scanning range is 10° to 80°. The samples are analyzed using a Hitachi S-4800 field emission scanning electron microscope (accelerated voltage 5.0kV).

The electrochemical properties of an electrocatalyst Co_3O_4@$NiCo_2O_4$, in particular its specific capacitance (C_{sp}), are calculated by the following formula:

$$C_{sp} = \frac{\int IdV}{S \cdot \Delta V \cdot m}$$

$$C_{sp} = \frac{I \cdot \Delta t}{m \cdot \Delta V}$$

I is the current density of constant current charge and discharge, Δt is the discharge time, m is the sample quality, ΔV is the potential window, and S is the scanning speed.

XRD-6000 X-ray powder diffractometer is used to characterize the phase purity and structure of Co_3O_4@$NiCo_2O_4$ electrocatalyst. Drawing 1 (red line) illustrates the X-ray powder diffraction pattern of Co_3O_4@$NiCo_2O_4$ nanowire layered array. Compared with the diffraction pattern of Co_3O_4 nanowire (black line), the diffraction peak intensity is slightly enhanced, but there is basically no change. The diffraction peaks (111), (220), (311), (222), (400), (422), (511), (400), (650) and (533) can be used as the characteristic peaks of the cubic phase Co_3O_4 (JCPDS:78-1969) and the spinel phase $NiCo_2O_4$ (JCPDS:73-1702) . The pattern of the Co_3O_4@$NiCo_2O_4$ structure contains diffraction peaks of Co_3O_4 and $NiCo_2O_4$, indicating the presence of these two phases on the nickel foam substrate.

The shape and size of the electrocatalyst are observed by field emission scanning electron microscopy. Drawings 2a and 2b show low - and high-power scanning electron microscopy images of Co_3O_4 nanowires. The prepared Co_3O_4 nanowire array is neat and uniform. Drawings 2c and 2d show low - and high-power SEM images of the Co_3O_4@$NiCo_2O_4$ nanowire layered array. Nickel-cobalt oxide nanowires grow through Co_3O_4 nanowires. These nanowires are interconnected to form a highly porous surface morphology. Therefore, due to the presence of efficient diffusion channels, almost all layered nanowire arrays can be easily used by electrolytes to store energy. This structure greatly increases the active surface area and provides more sites for Faraday reactions, resulting in higher specific capacitance.

Drawing 4 illustrates the EDS spectrum. Drawing 4a illustrates that nickel has a weight percentage of 19.15 and an atomic percentage of 10.48. Drawings 4b and c show a uniform distribution of nickel elements. This proves the successful construction of $NiCo_2O_4$ nanowires on Co_3O_4 nanowires.

To evaluate the electrochemical capacitance performance of Co_3O_4@$NiCo_2O_4$ nanowires, cyclic voltammetry (CV) is first recorded in a three-electrode system. The Co_3O_4@$NiCo_2O_4$ electrocatalyst is assembled into a three-electrode system with platinum electrode and standard saturated calomel electrode to measure the electrochemical properties and compare with the Co_3O_4 nanowire array. The CV curve of the sample is measured at different scanning speeds of 5 to 50 mV s^{-1} over a voltage range of -0.1 to 0.5V. In Drawing 5a, the redox peak of Co_3O_4 nanowire is caused by Co^{2+}/Co^{3+} and Co^{3+}/Co^{4+} redox reactions:

$$Co_3O_4 + OH^- + H_2O = 3CoOOH + e^-$$

$$CoOOH + OH^- = CoO_2 + H_2O + e^-$$

Drawing 5c, Co_3O_4@$NiCo_2O_4$ the expansion and migration of redox peaks in the layered nanowire array are mainly due to the increase of Ni^{2+}/Ni^{3+}reactions:

$$NiCo_2O_4 + OH^- + H_2O = NiOOH + 2CoOOH + e^-$$

All of the electrodes showed significant redox peaks, indicating that they have Faraday battery-like properties. Notably, the Co_3O_4@$NiCo_2O_4$ electrocatalyst exhibits a higher peak current density and a larger cyclic voltamogram (CV) sealing area than Co_3O_4, which indicates a stronger charge storage capacity. According to the electrochemical calculation formula (1), the specific capacitance at different scanning speeds is calculated. At scanning speeds of 5mV s^{-1}, 10mV s^{-1}, 25mV s^{-1} and 50mV s^{-1}, the specific capacitance of Co_3O_4@$NiCo_2O_4$ nanowire arrays is 1895 F g^{-1}, 1723 F g^{-1}, 1518 F g^{-1} and 1239 F g^{-1}, respectively. The specific capacitance of Co_3O_4 nanowire arrays is 1267 F g^{-1}, 1108 F g^{-1}, 941 F g^{-1} and 715 F g^{-1}, respectively. The main reason for this limitation is that the high scanning rate limits the entry of ions into the internal microstructure of the electrode material. As a result, ion transport is limited by slow diffusion and can only use the outer surface for charge storage. With the increase of scanning speed, the specific capacitance decreases gradually. The constant current charge-discharge curves of the samples are measured in the voltage range of -0.1-0.45V at different current densities of 2.5, 5, 10 and 20 A g^{-1}. The specific capacitance of constant

current charge and discharge can be calculated according to formula (2). Drawing 5d illustrates the constant current charge and discharge curve of the Co_3O_4@$NiCo_2O_4$ nanowire layered array.

Drawing 6a illustrates the comparison of cyclic voltammetry curves of Co_3O_4 nanowire array and Co_3O_4@$NiCo_2O_4$ nanowire layered array at 25 mV s^{-1} current density. Obviously, the enclosed area of the layered nanowire array is significantly larger than that of pure Co_3O_4, indicating that the layered array has a larger area capacitance. Drawing 6b illustrates A comparison of constant current charge and discharge at a current density of 5A g^{-1}.

The specific capacitance of Co_3O_4@$NiCo_2O_4$ nanowire-layered arrays is better than that of Co_3O_4-based nanocomposites reported in the literature, such as three-dimensional Co_3O_4@$Ni(OH)_2$(1330 F g^{-1}@2.5mA cm^{-1}). Co_3O_4@MnO_2(1532.4 F g^{-1}@1 A g^{-1}), Co_3O_4@porous carbon (1307 F g^{-1}@1 A g^{-1}) and Co_3O_4@$NiCo_2O_4$ (672 F g^{-1}@0.5 A g^{-1}). The excellent electrochemical performance of the Co_3O_4@$NiCo_2O_4$ nanowire layered array in the present implementation method is due to the reasonable design and fabrication of layered heterostructures on nickel foam.

The cyclic performance of the sample is studied by conducting 5000 charge and discharge cycles at the current density of 5Ag-^{1}. As shown in Drawing 7a, the specific capacitance of the Co_3O_4@$NiCo_2O_4$ nanowire layered array is maintained at 93.8%, while that of the Co_3O_4 nanowire array is maintained at 91.2%. The previous literature reported that Co_3O_4/MnO_2 had a permittivity of 93.4% after 5000 cycles and $CoMnO_4$/Co_3O_4 had a permittivity of 90.38% after 2000 cycles. Co_3O_4@$NiCo_2O_4$ The excellent cycling properties of layered nanowire arrays provide a solid theoretical basis for the practical application of supercapacitor electrode materials.

To further understand the fundamental behavior of the supercapacitor electrodes, the researchers performed an electrochemical impedance spectroscopy (EIS) analysis of them. The EIS has a measurement frequency range of 100kHz to

0.05Hz and an open circuit voltage of 5mV. The ionic resistance of the electrolyte, the inherent resistance of the active material and the contact resistance constitute the electrochemical impedance. The diameter of the quasi-semicircular fitting circle in the high frequency region represents the charge transfer resistance of the electrode material in an electrochemical system. As shown in Drawing 7b, the resistance of $CoMnO_4/Co_3O_4$ nanowire layered arrays is lower than that of Co_3O_4 nanowire arrays. The lower charge transfer resistance enables the layered array to have better electrochemical performance.

In summary, the invention adopts hydrothermal method to develop an $Co_3O_4@NiCo_2O_4$ electrocatalyst with nanowire layered array. Due to the synergistic action of Co_3O_4 and $NiCo_2O_4$, $Co_3O_4@NiCo_2O_4$ nanowire layered arrays exhibit high specific capacitance of 1466 F g^{-1} and excellent cycling performance at 2.5 A g^{-1}, and can maintain 93.8% specific capacitance after 5000 charge-discharge cycles. These results indicate that $Co_3O_4@NiCo_2O_4$ nanowire layered arrays will be a suitable electrocatalyst for practical energy conversion devices. From a methodological point of view, the invention makes it possible to prepare a promising $Co_3O_4@NiCo_2O_4$ pseudo-capacitor material electrocatalyst by a simple and low-cost hydrothermal method.

The above disclosed preferred implementation methods of the invention are only used to assist in the elaboration of the invention. The preferred implementation method does not elaborate on all the details and does not limit the invention to the specific implementation method. Obviously, according to the contents of this manual, many modifications and changes can be made. These implementation methods are selected and specifically described in this specification for the purpose of better explaining the principle and practical application of the invention, so that technicians in the technical field can better understand and utilize the invention. The present invention is limited only by the claims and their full scope and equivalents.

Claims

1. A method for preparing Co_3O_4@$NiCo_2O_4$ catalyst is characterized in that: It comprises the following steps:

S1: Co_3O_4 nanowire layer is prepared by weighing $CoCl_2$-$6H_2O$, NH_4F and urea;

S2: $NiCl_2$-$6H_2O$, $CoCl_2$-$6H_2O$, NH_4F, urea and the Co_3O_4 nanowire layer obtained by step S1 are weighed, and Co_3O_4@$NiCo_2O_4$ catalyst is prepared.

2. The preparation method of Co_3O_4@$NiCo_2O_4$ catalyst described in Claim 1 is characterized in that: The step S1 specifically includes the following sub-steps:

S1.1: Weighing 1.5mmol $CoCl_2$-$6H_2O$, 1mmol NH_4F and 2mmol urea into 40mL H_2O and stirring them for 20 minutes;

S1.2: The evenly stirred solution is transferred to a 50mL polytetrafluoroethylene reactor, which is filled with 2cm×3cm nickel foam that had been pre-treated in 6M HCl and reacted at 120 ℃ for 6 hours;

S1.3: Samples obtained by washing with deionized water and anhydrous ethanol several times; After drying under vacuum at 60 ℃, and then calcination at 5 ℃ min^{-1} to 300 ℃ for 2 hours, Co_3O_4 nanowire layer is obtained.

3. The preparation method of Co_3O_4@$NiCo_2O_4$ catalyst described in Claim 1 is characterized in that: The step S2 specifically includes the following sub-steps:

S2.1: 0.1mmol $NiCl_2$-$6H_2O$, 0.2mmol $CoCl_2$-$6H_2O$, 0.1mmol NH_4F and 0.2mmol urea are accurately weighed and added into 40mL H_2O, stirring them for 20 minutes;

S2.2: The homogenized solution is transferred to a 50mL polytetrafluoroethylene reactor, in which foamed nickel coated Co_3O_4 nanowires are added and reacted at 120 ℃ for 6 hours;

S2.3: After the reaction, the sample obtained by washing with deionized water and anhydrous ethanol several times; Finally, the washed sample is dried under vacuum at 60 ℃, and then calcined at 5 ℃·min^{-1} to 300 ℃ for 2 hours to obtain Co_3O_4@$NiCo_2O_4$ catalyst.

4. Application of Co_3O_4@$NiCo_2O_4$ catalyst prepared by any of the methods mentioned in Claim 1-3 in the preparation of supercapacitors.

Ansprüche

1. Ein Herstellungsverfahren für einen Co3O4@NiCo2O4-Katalysator, dadurch gekennzeichnet, dass es die folgenden Schritte umfasst:

S1: Wiegen von CoCl2 •6H2O, NH4F und Harnstoff zur Herstellung einer Co3O4-Nanodrahtschicht;

S2: Wiegen von NiCl2 • 6H2O, CoCl2 • 6H2O, NH4F, Harnstoff sowie der in Schritt S1 erhaltenen Co3O4-Nanodrahtschicht zur Herstellung des Co3O4@NiCo2O4-Katalysators.

2. Das nach Anspruch 1 beschriebene Herstellungsverfahren für einen Co3O4@NiCo2O4-Katalysator, dadurch gekennzeichnet, dass Schritt S1 die folgenden Teilschritte umfasst:

S1.1: 1,5 mmol CoCl2 •6H2O, 1 mmol NH4F und 2 mmol Harnstoff werden in 40 mL H2O eingewogen und 20 Minuten lang gerührt;

S1.2: Die homogenisierte Lösung wird in einen 50-mL-PTFE-Reaktor (Polytetrafluorethylen) überführt, in dem sich ein 2 cm × 3 cm großes Nickelschaumstück befindet, das zuvor in 6 M HCl vorbehandelt wurde. Die Reaktion erfolgt 6 Stunden lang bei 120 ° C;

S1.3: Das erhaltene Material wird mehrfach mit deionisiertem Wasser und wasserfreiem Ethanol gewaschen, dann bei 60 ° C im Vakuum getrocknet und anschließend bei einer Heizrate von 5 ° C/min auf 300 ° C für 2 Stunden kalziniert, um die Co3O4-Nanodrahtschicht

zu erhalten.

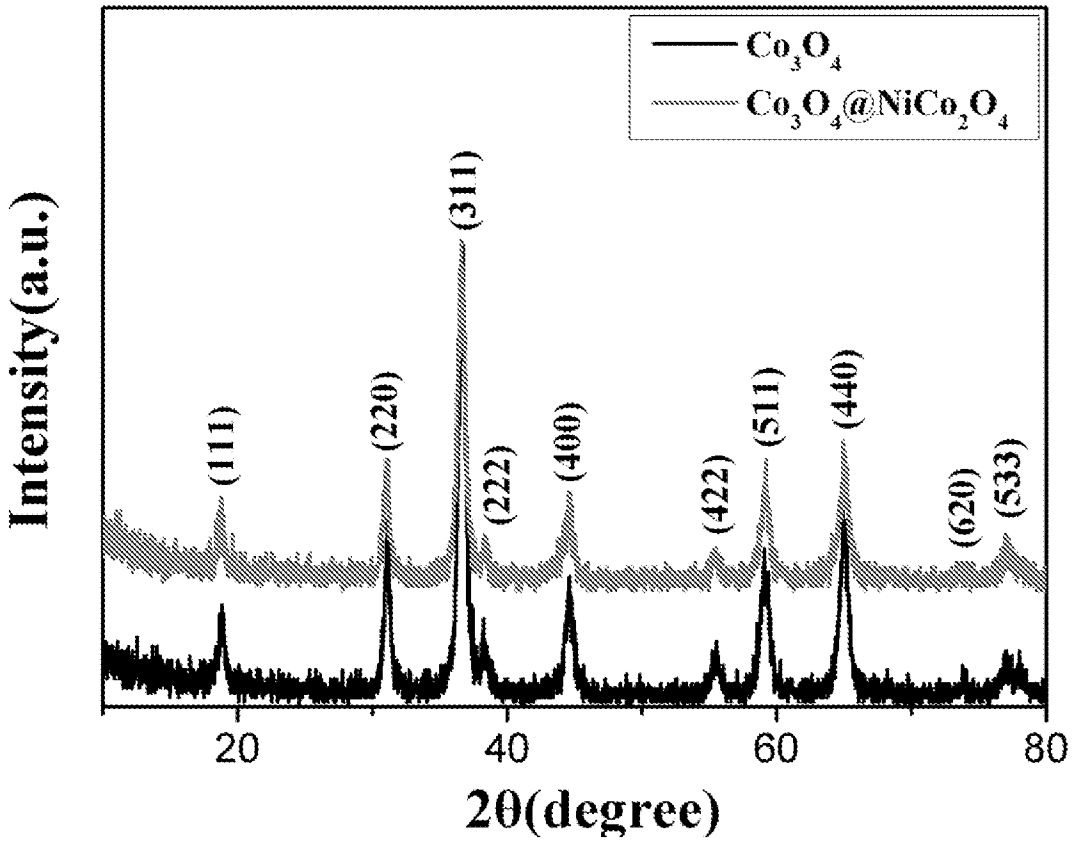
3. Das nach Anspruch 1 beschriebene Herstellungsverfahren für einen Co3O4@NiCo2O4-Katalysator, dadurch gekennzeichnet, dass Schritt S2 die folgenden Teilschritte umfasst:

S2.1: 0,1 mmol NiCl2 • 6H2O, 0,2 mmol CoCl2 • 6H2O, 0,1 mmol NH4F und 0,2 mmol Harnstoff werden genau eingewogen und in 40 mL H2O gelöst, anschließend 20 Minuten lang gerührt;

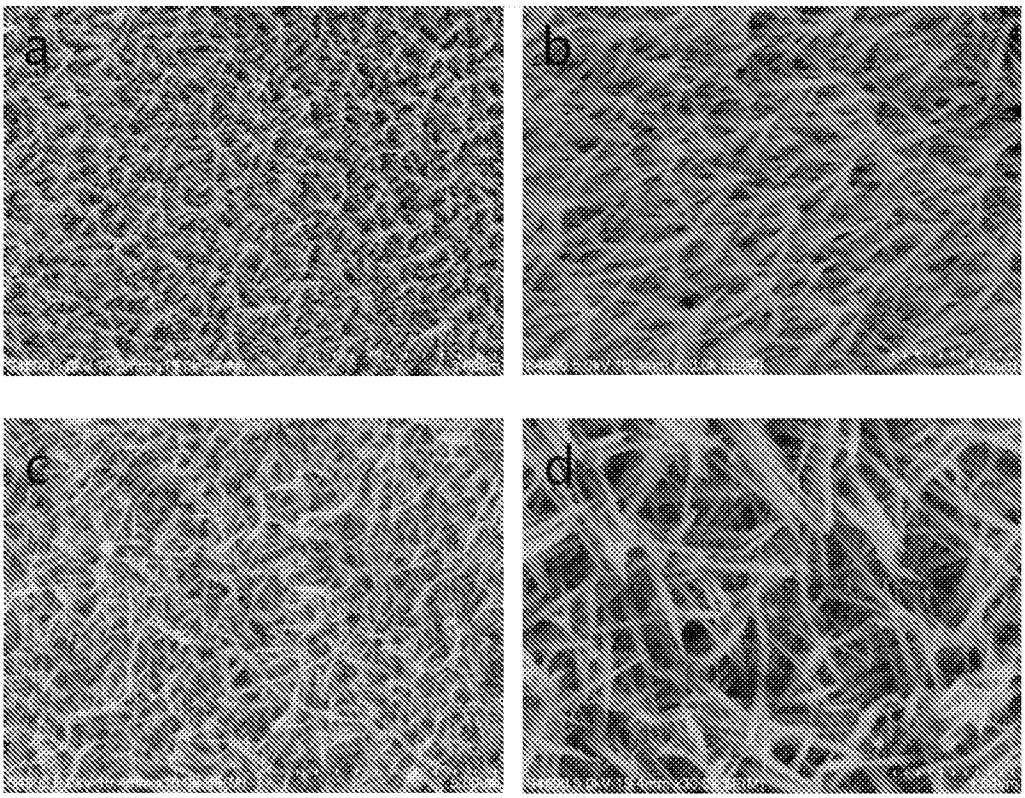
S2.2: Die homogenisierte Lösung wird in einen 50-mL-PTFE-Reaktor überführt, in dem die mit Co3O4-Nanodrähten beschichteten Nickelschaumstücke hinzugefügt werden. Die Reaktion erfolgt 6 Stunden lang bei 120 ° C;

S2.3: Nach Abschluss der Reaktion wird das erhaltene Material mehrfach mit deionisiertem Wasser und wasserfreiem Ethanol gewaschen. Anschließend wird das gewaschene Material bei 60 ° C im Vakuum getrocknet und bei einer Heizrate von 5 ° C/min auf 300 ° C für 2 Stunden kalziniert, um den Co3O4@NiCo2O4-Katalysator zu erhalten.

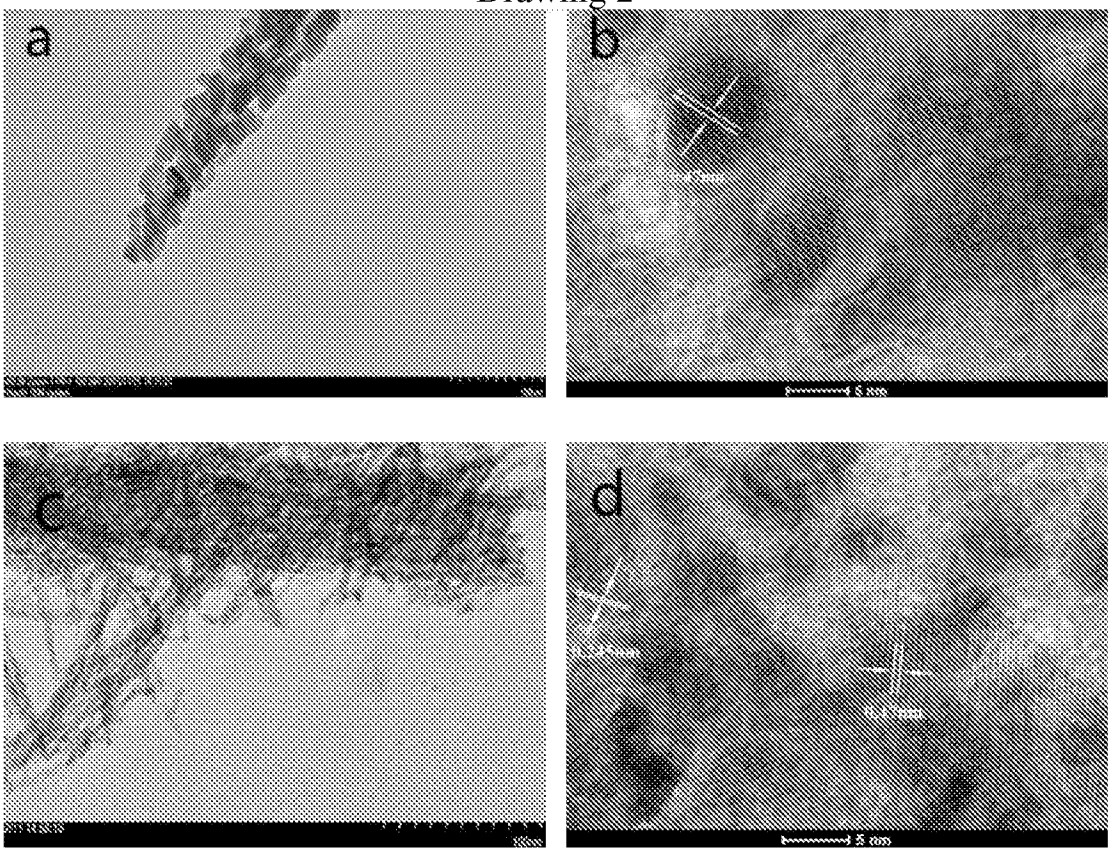
4. Die Anwendung des nach einem der Ansprüche 1 bis 3 hergestellten Co3O4@NiCo2O4-Katalysators bei der Herstellung von Superkondensatoren.


Co3O4
Co3O4@NiCo2O4
Intensity(a.u.)
(111)
(220)
(311)
(222)
(400)
(422)
(511)
(440)
(620)
(533)
20
40
60
80
2θ(degree)

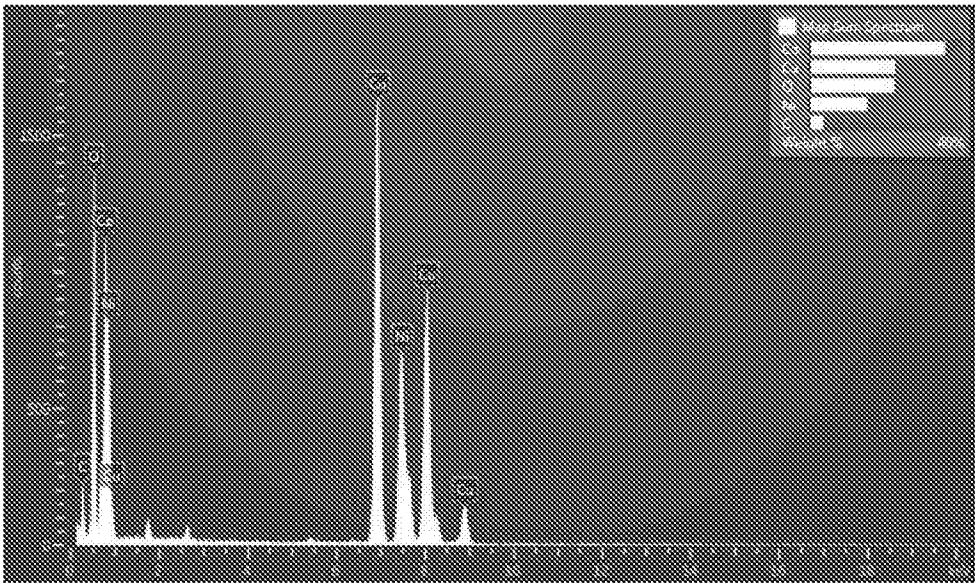
Drawing 1



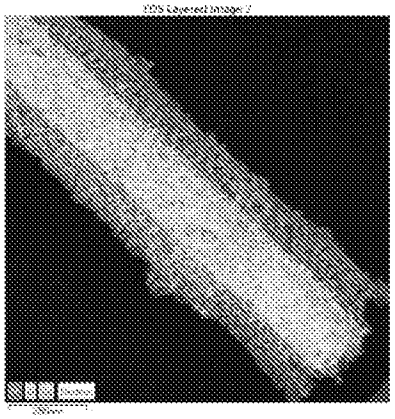
Drawing 2



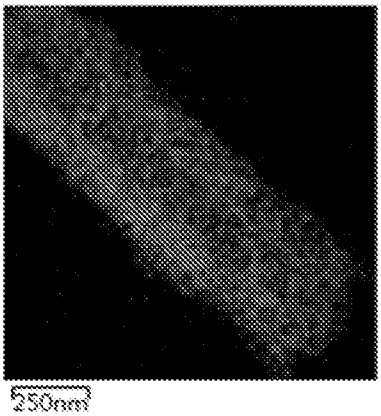
Drawing 3



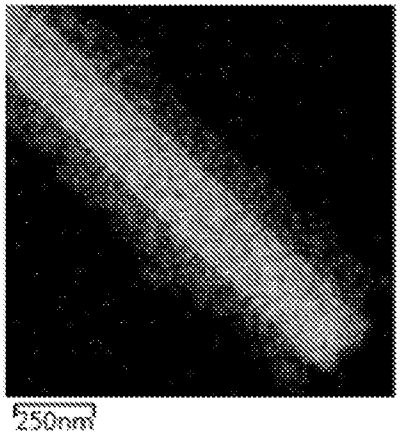
(a)



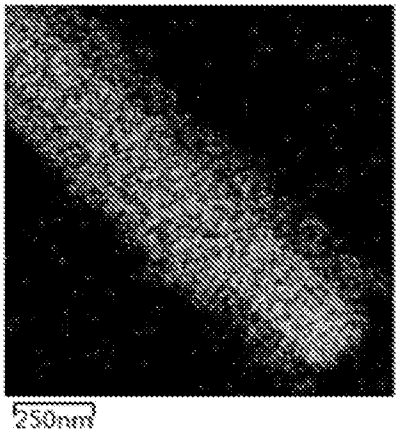
(b)



(c)

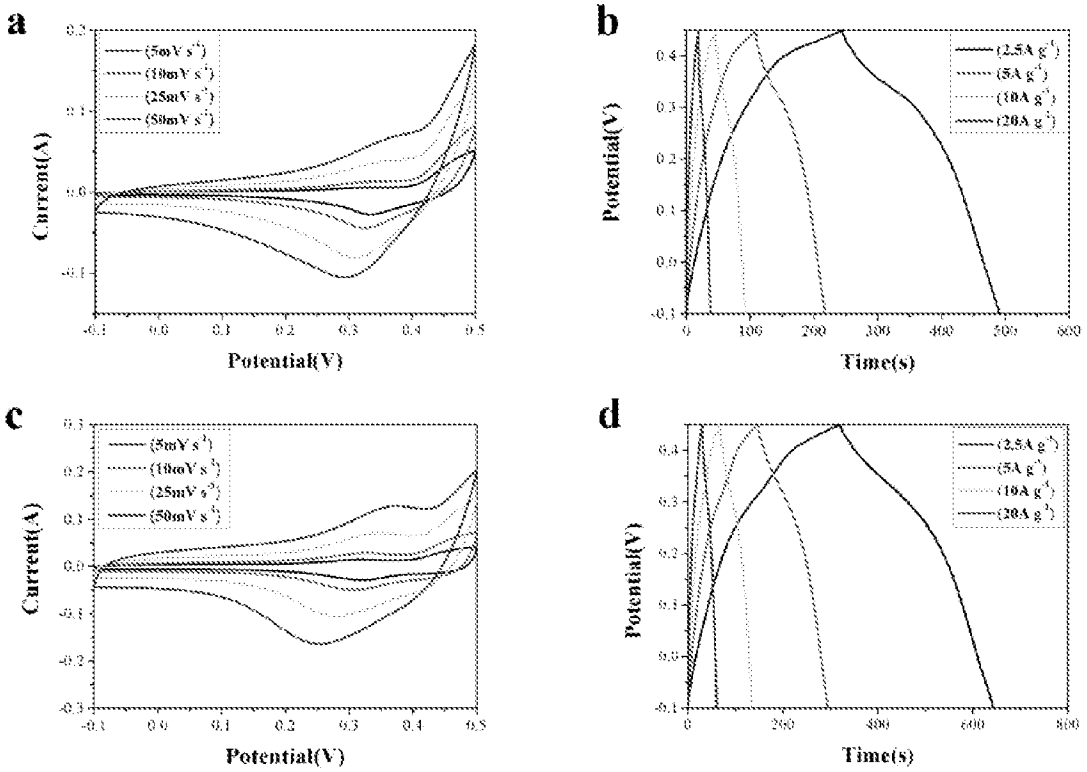


(d)

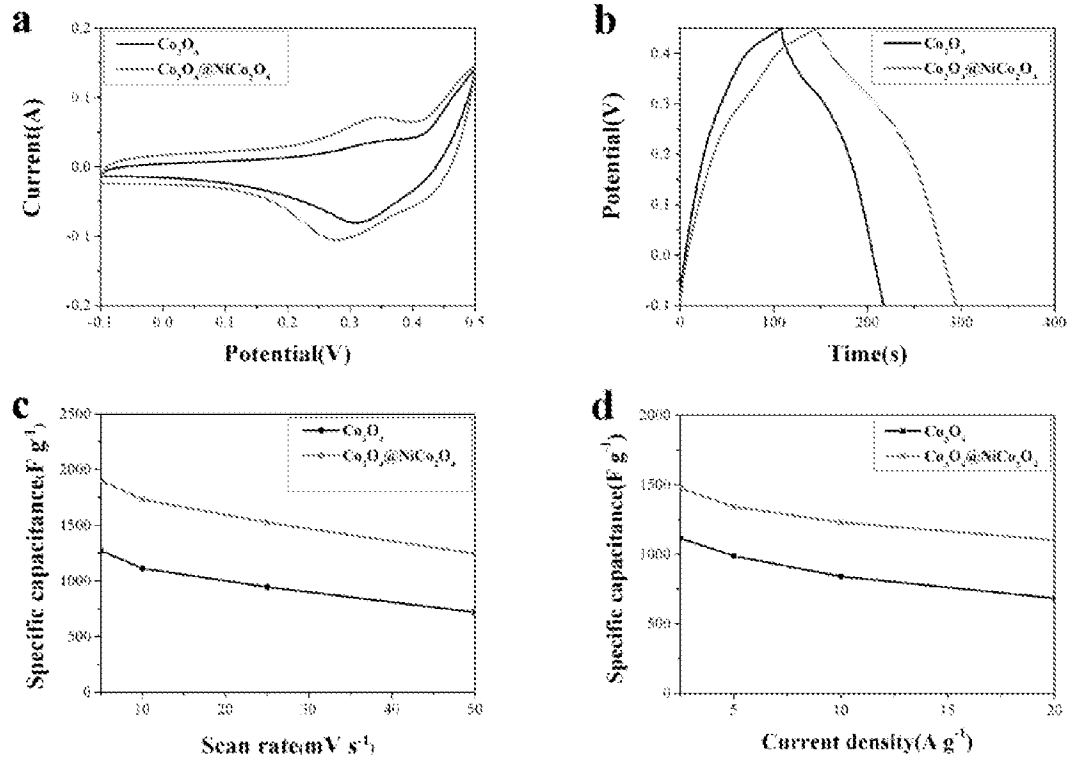


(e)

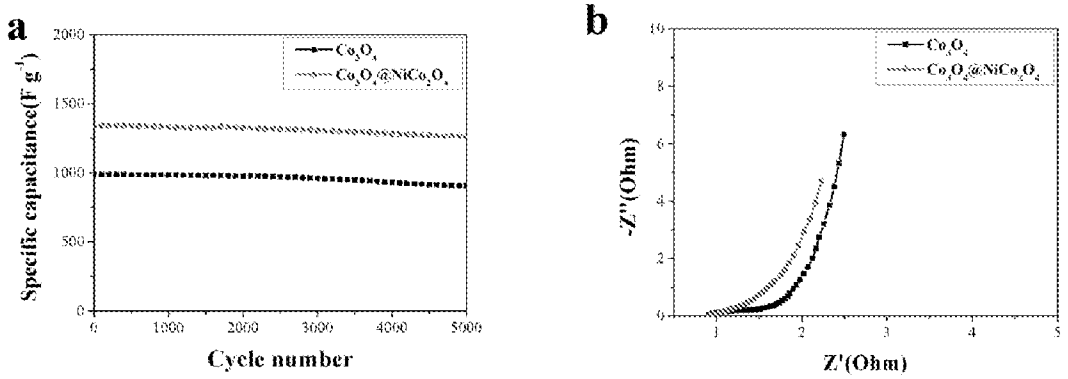
Drawing 4



Drawing 5



Drawing 6


a
Specific capacitance(F g-1)
Cycle number
Co3O4
Co3O4@NiCo2O4
b
-Z''(Ohm)
Z'(Ohm)
Co3O4
Co3O4@NiCo2O4

Drawing 7