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(54) Title: BIFUNCTIONAL ELECTROCATALYST FOR WATER SPLITTING AND PREPARATION METHOD THEREOF

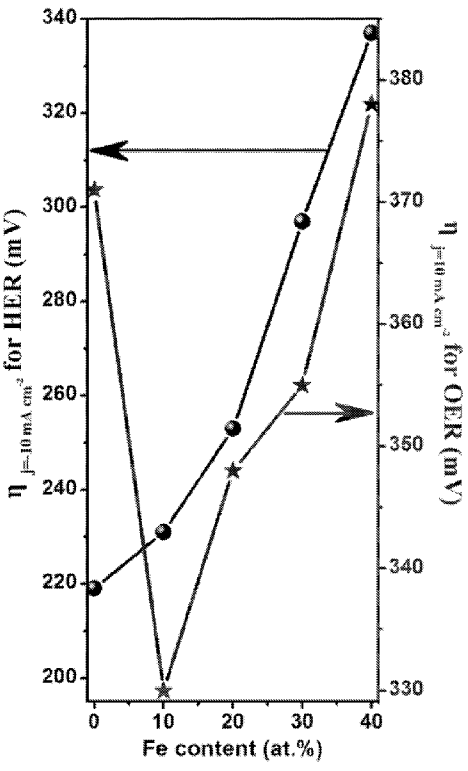


Figure 1

(57) Abstract: A method for preparing a bifunctional electrocatalyst is provided, which comprises: adding a nickel source compound and a ferric iron source compound into a solvent of ethanol; adding a urea into the obtained solution to give a mixture; drying the mixture; grinding the dried mixture into homogeneous powders and then subjecting the homogeneous powders to a heating process under inert atmosphere. The bifunctional electrocatalyst could simultaneously promote HER and OER processes in alkaline solution.

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BIFUNCTIONAL ELECTROCATALYST FOR WATER SPLITTING AND PREPARATION METHOD THEREOF

Technical Field

[0001] The present application relates to the field of water splitting by electrolysis, in particular, it relates to a preparation method of bifunctional electrocatalyst and a cell containing the bifunctional electrocatalyst.

Background Art

[0002] Molecular hydrogen (H_2) is extensively regarded as one of the most ideal energy vectors due to its zero-carbon emission, recyclability, and high energy conversion efficiency. Water splitting by electrolysis is an environmental-friendly way to generate H_2. Especially, when coupling to photovoltaic modules, it will be a sustainable and promising energy system for future society. Currently, the state-of-the-art electrocatalysts for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are often Pt-based and Ir-based or Ru-based materials, respectively. However, the scarcity and high-cost of these noble metal-based electrocatalysts limit their large-scale application. Therefore, developing active, stable and low-cost electrocatalysts in place of precious metal-based materials is a vital step towards future hydrogen economy.

[0003] Recently, transition metal (Mo, W, Ni, Co, Fe, Mn, Cu etc.) and their derivatives (carbide, oxide, sulfide, phosphide, hydroxide and mixed-metal alloy etc.) have been extensively invested as either HER or OER and even bifunctional electrocatalysts. Excitingly, some of them exhibited comparable or even better electrocatalytic performances than the existing Pt/C for HER or Ir/C for OER in some specific cases. For example, Chen et al. recently reported that a hierarchical nanoporous copper-titanium bimetallic electrocatalyst was able to produce hydrogen from water at more than twice the rate of the state-of-the-art Pt/C catalyst. As for the kinetically sluggish OER process, Dai et al. reported an electrocatalyst which could promote the OER process better than a commercial Ir/C catalyst through hybridizing ultrathin nickel–iron layered double hydroxide nanoplates with mildly oxidized multiwall CNTs. Notwithstanding these progresses, there are still very few success to develop bifunctional catalysts which could pair the two electrode reactions together in an integrated electrolyser for practical use. Although several feasible strategies to optimize the catalytic performance of transition metal based materials have been proposed, it remains highly challenging to develop facile synthetic methods to combine all these strategies for advanced catalysts.

Technical Problem

[0004] In order to improve the efficiency of water splitting by electrolysis, the present application provides a method for preparing a bifunctional electrocatalyst which could simultaneously promote HER and OER processes in alkaline solution. The preparation method comprises the following steps: (a) a nickel source compound and a ferric iron source compound being added into a solvent, wherein the molar ratio of the iron ion to the nickel ion in the obtained solution is in the range of from 0 to 2/3, and the total metal ion (the nickel ion plus the iron ion) content in the obtained solution is in the range of from 0.3 to 0.5 mmol; (b) a urea being added into the obtained solution to give a mixture; (c) the mixture obtained in step (b) being dried; (d) the dried mixture being ground into homogeneous powders and then subjected to a heating process under inert atmosphere.

Solution to Problem

Technical Solution

[0005] According to another embodiment of the present application, a bifunctional electrocatalyst is provided, which is made by the preparation method of the present application.

[0006] According to another embodiment of the present application, a symmetric two-electrode water splitting cell comprising the bifunctional electrocatalyst of the present application is provided.

Advantageous Effects of Invention

Advantageous Effects

[0007] The present application provides a method to prepare n Ni-based bifunctional electrocatalyst used in alkaline electrolyzers by simultaneously implementing nanostructuring, hybridizing with nanocarbon and doping with heterogeneous elements by a facile synthetic approach. The iron content of the obtained bifunctional electrocatalyst has significant influences on both the HER and OER activities of the catalyst. The preparation method according to the present application is simple and scalable, which is easy to carry out and can be performed by pyrolyzing a precursor composed of nickel and iron salts mixed with urea under inert atmosphere without any post-treatments.

Brief Description of Drawings

Description of Drawings

[0008] FIG. 1 shows the overpotentials for HER and OER with different Fe contents in $Ni_{1-x}Fe_x$/NC made by the method according to an embodiment of the present application.

[0009] FIG. 2 shows low-magnification (a) and high-resolution (b) SEM images of the bifunctional electrocatalyst according to an embodiment of the present application.

[0010] FIG. 3 shows TEM (a, b) and HRTEM (c) images of the $Ni_{0.9}Fe_{0.1}$/NC according an embodiment, and HAADF-TEM (d-g) image and the corresponding EDS mappings of C, Ni, Fe in the area marked in dotted rectangular frame; XRD (h) patterns of Ni/NC, $Ni_{0.9}Fe_{0.1}$/NC and standard XRD pattern of face-centered cubic metallic Ni.

[0011] FIG. 4 shows Full XPS spectrum (a) of the representative $Ni_{0.9}Fe_{0.1}$/NC sample; and high-resolution XPS spectra (b-e) of C 1s, N 1s, Ni 2p and Fe 2p, respectively.

[0012] FIG. 5 shows the performance of a cell containing the bifunctional catalyst according to the present application on overall electrochemical water splitting. The loading of the catalysts on carbon fiber paper was 2 mg cm^{-2}.

[0013] FIG. 6 shows the cyclic voltammogram of a water splitting cell composed of two symmetric $Ni_{0.9}Fe_{0.1}$/NC-NF electrodes. The loading of the catalysts on Ni foam was 2 mg cm^{-2}.

Mode for the Invention

Mode for Invention

[0014] Objects, advantages and embodiments of the present application will be explained below in detail with reference to the accompanying drawings. However, it should be appreciated that the following description of the embodiments is merely exemplary in nature and is not intended to limit the application, its application, or uses.

[0015] According to an embodiment of the present application, a method for preparing a bi-functional electrocatalyst is provided, wherein the bifunctional electrocatalyst could simultaneously promote HER and OER processes in alkaline solution. The method comprises the following steps: (a) a certain amount of nickel source compound and a certain amount of ferric iron source compound being added and dissolved into a solvent, wherein the molar ratio of the nickel ion to the iron ion in the obtained solution is in the range of from 100: 0 to 60: 40, and the total metal ion (the nickel ion plus the iron ion) content in the obtained solution is in the range of from 0.3 to 0.5 mmol; preferably, the molar ratio of the nickel ion to the iron ion in the obtained solution is in the range of from 99: 1 to 70: 30; (b) a certain amount of urea being added and dissolved into the obtained solution to give a mixture; (c) the mixture obtained in step (b) being dried in an oil bath with stirring; (d) the dried mixture being ground into homogeneous powders and then heated under inert atmosphere to give a black powder product.

[0016] According to a specific example of the present application, the nickel source compound in step (a) may be selected from the group consisting of nickel acetate, nickel chloride, nickel nitrate, nickel sulfate or the like and the combination thereof. The function of nickel source compound is to provide nickel ion in the solution.

[0017] According to a specific example of the present application, the ferric iron source

compound in step (a) can be selected from the group consisting of ferric chloride, ferric nitrate, ferric sulfate and the combination thereof.

[0018] In particular, the solvent in step (a) can be water, methanol, ethanol or propanol or the combination thereof, and the ethanol is preferred.

[0019] According to a preferable embodiment of the present application, in step (b) of the preparation method, the urea can be added in such an amount that the concentration of the urea in the solution is in the range of from 1 to 3 g/mL. More preferably, the concentration of urea in the solvent of ethanol is 1 g/mL.

[0020] In step (b) of the preparation method, after adding urea, the solution can be treated with ultrasound for 4 to 8 minutes so as to dissolve the urea into the solvent (water or ethanol) quickly. Alternatively, this solution can also be treated with stirring. More preferably, the period of the sonication treatment is 5 minutes.

[0021] According to a preferable embodiment of the present application, in step (c) of the preparation method, the mixture can be dried at 60 °C to 90 °C in an oil bath upon stirring for 5 to 10 hours to remove the solvent. More preferably, the mixture is dried at 70 °C in an oil bath with stirring for 6 hours.

[0022] According to a preferable embodiment of the present application, in step (d) of the preparation method, the dried mixture is thoroughly ground into homogeneous fine powders and then transferred into a ceramic crucible with an equipped cover. The heating process is preferably carried out with three stages: in the first stage, the temperature is raised from room temperature (about 25 °C) to a temperature of 520 °C to 580 °C at a programming rate of from 0.4 to 0.6 °C/min and then maintained at that temperature for 3 hours; in the second stage, the temperature is further raised to 650 °C to 750 °C within about 1 hour and maintained at that temperature for about 2 hours; in the third stage, the product is cooled naturally. The whole heating process is preferably proceeded under inert atmosphere with a gas flow rate of 40 to 60 sccm, wherein the inert atmosphere can be selected from the group consisting of Ar, N_2 and combination thereof.

[0023] During the heating process of the above step (b), the metal ions (Ni^{2+} and Fe^{3+}) are reduced to metallic state by the reduced species released from the pyrolysis of urea and then the metallic nanoparticles serve as catalysts to induce the growth of nitrogen-doped bamboo-like single-wall carbon nanotubes (CNTs), affording Ni-Fe/nitrogen doped nanocarbon hybrids (NiFe/NC). All these in-situ formed hybrids exhibit good electrocatalytic performances toward both OER and HER.

[0024] The doping amount of Fe into the NiFe/NC is found to have significant influences on both the HER and OER activities of the catalyst. The electrochemical water splitting activities of Ni-Fe/nitrogen doped nanocarbon hybrids (NiFe/NC) with different Fe contents on glass carbon (GC) electrodes in 1 M KOH (aq) electrolyte have been de-

termined. In this experiment, the Ni-Fe/nitrogen doped nanocarbon hybrid is denoted as $Ni_{1-x}Fe_x$/NC (with x = 0, 0.1, 0.2, 0.3 and 0.4, where x standing for the molar ratio of Fe to Fe+Ni). Figure 1 shows the result, i.e. the summaries of the overpotentials for HER and OER to achieve a current density of 10 mA cm^{-2} with different Fe contents in $Ni_{1-x}Fe_x$/NC. The mass loading of the catalyst is 0.2 mg/cm^2 in this experiment. It can be seen from Figure 1 that the most effective content of Fe for both HER and OER is about 10 at%. Accordingly, the molar ratio of the nickel ion to the iron ion in the obtained nanocarbon hybrid is preferably about 90:10, i.e., the atomic percent of Fe in the final alloy of Ni and Fe obtained in the above step (d) is about 10 at%.

[0025] According the preparation method of the present application, a black powder product is obtained after pyrolyzing the inexpensive starting materials, for example, ($Ni(CH_3COO)_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$ and urea) at a temperature in the range of 650 °C to 750 °C in inert atmosphere. Scanning electron microscopy (SEM) images (Figure 2a is a low-magnification SEM image, and Figure 2b is a high-resolution SEM image) show that nanoparticles with sizes ranging from 10 to 50 nm were well dispersed on or encapsulated in the bamboo-like nanotubes. No obvious morphology and size differences were observed among these samples with different Fe content in the hybrid. The XRD patterns (not shown) of these $Ni_{1-x}Fe_x$/NC samples were similar to each other, with three distinct diffraction peaks located around 44.3°, 51.7°, and 76.2° which can be assigned to the (111), (200), and (222) crystal-plane reflections of a face-centered cubic nickel phase (JCPDS card No. 89-7128). The incorporation of Fe into the Ni/NC didn't result in any additional crystal diffraction peaks. The TEM images also showed that some Ni-Fe alloy nanoparticles were completely encapsulated by a few carbon layers around them. The high-angle angular dark field TEM (HAADF-TEM) image and the corresponding EDS mapping demonstrated that the bamboo-like nanotubes were mainly composed of carbon and the nanoparticles were composed of Ni and Fe , the result is shown in Figure 3 (a-h), wherein Figures 3 (a) and 3 (b) are TEM images and Figure 3 (c) is HRTEM image of the $Ni_{0.9}Fe_{0.1}$/NC according an embodiment of the present disclosure, and Figures 3 (d-g) are HAADF-TEM images and the corresponding EDS mappings of C, Ni, Fe in the area marked in dotted rectangular frame in 3 (d); Figure 3 (h) shows XRD patterns of Ni/NC, $Ni_{0.9}Fe_{0.1}$/NC and standard XRD pattern of face-centered cubic metallic Ni .

[0026] The XRD patterns of these $Ni_{1-x}Fe_x$/NC samples are similar to each other, with three distinct diffraction peaks located around 44.3°, 51.7°, and 76.2° which can be assigned to the (111), (200), and (222) crystal-plane reflections of a face-centered cubic nickel phase. The incorporation of Fe into the Ni/NC doesn't result in any additional crystal diffraction peaks. However, a negative shift of 2θ angles with increasing iron concentrations could be observed, implying the substitutional incorporation of Fe atom into

the nickel cubic structure. Scherrer analysis of the broadening of (111) diffraction peak of $Ni_{0.9}Fe_{0.1}$/NC indicates an average grain size of 28 nm of Ni-Fe alloy nanoparticles along the (111) crystallographic axis direction, consistent with the results observed by SEM. Transmission electron microscopy (TEM) images (as shown in Fig. 3a and 3b) shows that the tube walls of bamboo-like nanotubes are composed of several dis-orderedly stacked graphene layers. This can explain why only a very weak diffraction peak could be observed at around 26.1°, corresponding to the graphitic (002) crystal-plane (see Fig. 3d). The high resolution TEM (HRTEM) image of the nanoparticles in Fig. 3c presents 0.21 nm lattice fringes, which can be attributed to the (111) lattice plane of the Ni-Fe alloy, in line with the XRD results. The TEM images also show that some Ni-Fe alloy nanoparticles are completely encapsulated by a few carbon layers around them. The high-angle angular dark field TEM (HAADF-TEM) image and the corresponding EDS mapping demonstrate that the bamboo-like nanotubes are mainly composed of carbon and the nanoparticles were composed of Ni and Fe (as shown in Fig. 3 (d-g)). The perfect superposition of the element distribution of Ni and Fe in their EDS mapping images further confirms the alloy nature of the Ni-Fe nanoparticles in $Ni_{0.9}Fe_{0.1}$/NC. All the characterization results above suggest that the pyrolyzed product is composed of metallic Ni-Fe alloy nanoparticles either encapsulated in or dispersed on bamboo-like CNTs. The specific surface area of a representative $Ni_{0.9}Fe_{0.1}$/NC catalyst is measured to be 153.7 $m^2 g^{-1}$ based on the Brunauer–Emmett–Teller (BET) surface area analysis, suggesting the hybrid owned a loose interior structure which could benefit the infiltration and flowage of electrolyte.

[0027] X-ray photoelectron spectroscopy (XPS) measurement has also been performed to in-vestigate the specific surface composition and chemical environment of the repre-sentative $Ni_{0.9}Fe_{0.1}$/NC, the result is shown in Figure 4 (a) shows Full XPS spectrum of the representative $Ni_{0.9}Fe_{0.1}$/NC sample; and Figure 4 (b-e) are high-resolution XPS spectra of C 1s, N 1s, Ni 2p and Fe 2p, respectively.

[0028] The full spectra of the $Ni_{0.9}Fe_{0.1}$/NC reveals the presence of C, Ni, Fe and slight N and O. The high-resolution C 1s core-level spectrum (as shown in Fig. 4b) could be de-convoluted into three peaks centered at ~284.5 eV, ~285.3 eV and ~286.4 eV, which is indexed to C=C/C-C, C=N and C-O/C-N, respectively. The sharpest peak corre-sponding to C=C/C-C indicates that most of the carbon atoms

[0029] The perfect superposition of the element distribution of Ni and Fe in their EDS mapping images further confirm the alloy nature of the Ni-Fe nanoparticles in $Ni_{0.9}Fe_{0.1}$/NC. All the characterization results above suggest that the pyrolyzed product is composed of metallic Ni-Fe alloy nanoparticles either encapsulated in or dispersed on bamboo-like CNTs.

[0030] According to another embodiment of the present application, the present bifunctional

electrocatalyst ($Ni_{1-x}Fe_x$/NC) can be loaded onto carbon fiber papers (CFPs) or on nickel foams. With a larger loading of 2 mg cm^{-2} on nickel foam, $Ni_{0.9}Fe_{0.1}$/NC exhibited overpotentials of 270 mV and 85 mV for OER and HER to reach a current density of 10 mA cm^{-2}, respectively. We integrated two $Ni_{0.9}Fe_{0.1}$/NC-NF electrodes into a symmetric two-electrode cell and studied the performance of this bifunctional catalyst for overall electrochemical water splitting. It can be seen from Figure 6 that a remarkable electrocatalytic activity was achieved with $Ni_{0.9}Fe_{0.1}$/NC-NF electrodes. The voltage needed to support a current density of 10 mA cm^{-2} was about 1.58 V determined from the reverse scan of the CV curve. Using more inert carbon fiber papers (CFPs) as substrate can get rid of the contribution of the intrinsic HER activity and derived OER activity of the commercial Ni foam. According to a preferred embodiment, with a larger loading of 2 mg cm^{-2}, $Ni_{0.9}Fe_{0.1}$/NC exhibits overpotentials of 191 mV and 270 mV for HER and OER to reach a current density of 30 mA cm^{-2}, respectively.

[0031] Furthermore, the performance of a cell containing integrated two identical $Ni_{0.9}Fe_{0.1}$ / NC-CFP electrodes for overall electrochemical water splitting has been studied. It can be seen from Figure 5 that the CFPs exhibit little activity for electrocatalytic water splitting while a remarkable electrocatalytic activity was achieved with $Ni_{0.9}Fe_{0.1}$/NC catalyst. For the symmetric two-electrode cell according to the present application, an overall voltage of 1.65 V is needed for maintaining a water splitting current density of 10 mA cm^{-2}.

[0032] The achieved electrocatalytic performance of the present $Ni_{1-x}Fe_x$/NC catalyst has been proved to be comparable or even superior to some existing advanced asymmetric and symmetric bifunctional water splitting electrocatalysts.

[0033] By pyrolyzing a mixture of metal salts and urea, the present application provides a $Ni_{1-x}Fe_x$/NC hybrid electrocatalyst which exhibits excellent performances to catalyze both HER and OER in alkaline electrolyte. And an efficient electrolyzer (cell) composed of two symmetric $Ni_{0.9}Fe_{0.1}$/NC loaded carbon fiber paper electrodes can achieve a current density of 10 mA cm^{-2} for overall water splitting at a voltage of 1.65 V, which is among the best performances for symmetric two-electrode water electrolyzer reported so far.

[0034] The present application will be described with following specific example, it should be acknowledged that other parameters within the scope of the present description can also be applied to this example.

[0035] Example 1

[0036] The metal salt precursors (nickel acetate tetrahydrate, $Ni(CH_3COO)_2 \cdot 4H_2O$ and Iron(III) chloride hexahydrate, $FeCl_3 \cdot 6H_2O$) were completely dissolved into 2 ml ethanol with a molar ratio of 9:1 while maintaining a total metal ion content of 0.5

mmol. Then, 2 g urea was added into the solution followed by a sonication treatment for 5 minutes. The obtained mixture was subsequently dried at 70 °C in an oil bath upon stirring for 6 hours to remove the ethanol. The dried mixture was thoroughly ground into homogeneous fine powders and then transferred into a ceramic crucible with an equipped cover. Next, the covered ceramic crucible was placed at the central of a tubular furnace and the temperature was raised from 25 °C to 550 °C at a programming rate of 0.5 °C/min and then maintained at 550 °C for 3 hours. After that, the temperature was further raised to 700 °C in 1 hour and maintained at that temperature for 2 hours and then cooled naturally. The whole heating process was proceeded under inert Ar/N_2 atmosphere with a gas flow rate of 50 sccm.

[0037] Example 2

[0038] The metal salt precursors (nickel chloride($NiCl_2$) and Iron(III) ferric nitrate, $Fe(NO_3)_3$) were completely dissolved into 4 ml of water with a molar ratio of 90:10 while maintaining a total metal ion content of 0.3 mmol. Then, 4 g urea was added into the solution followed by a sonication treatment for 8 minutes. The obtained mixture was subsequently dried at 90 °C in an oil bath upon stirring for 9 hours to remove the water. The dried mixture was thoroughly ground into homogeneous fine powders and then transferred into a ceramic crucible with an equipped cover. Next, the covered ceramic crucible was placed at the central of a tubular furnace and the temperature was raised from 25 °C to 580 °C at a programming rate of 0.4 °C/min and then maintained at 580 °C for 3 hours. After that, the temperature was further raised to 750 °C in 1 hour and maintained at that temperature for 2 hours and then cooled naturally. The whole heating process was proceeded under inert N_2 atmosphere with a gas flow rate of 50 sccm.

[0039] Example 3 Manufacture Of A Symmetric Two-Electrode Cell

[0040] A symmetric two-electrode water splitting cell containing two identical electrodes was made in this example, wherein these two electrodes were fabricated by the same method with the same catalyst. Firstly, 20 mg of catalyst obtained in Example 1 was dispersed in a mixture of 0.75 ml of water, 0.25 ml of ethanol and 100 μl of 5 wt% Nafion solution by at least 60 min sonication to form a homogeneous ink. After the sonication, 100 μl of the homogeneous ink was drop-dried onto carbon a fiber paper with a catalyst-covered-area of 1 cm^2 to achieve a catalyst-loading of 2 mg cm^{-2}. Secondly, one electrode was connected to the working electrode of the electrochemical workstation and another electrode was connected to the counter electrode and reference electrode of the electrochemical workstation. Finally, the two electrodes were inserted into 1 M KOH (aq) electrolyte with all the active areas being immersed.

[0041] The present application may be embodied in other forms without departing from the spirit or novel characteristics thereof. The embodiments disclosed in this application

are to be considered in all respects as illustrative and not limitative.

Claims

[Claim 1] A method for preparing a bifunctional electrocatalyst comprising:
(a) a nickel source compound and a ferric iron source compound being added into a solvent, wherein the molar ratio of the nickel ion to the iron ion in the obtained solution is in the range of from 93:7 to 85:15, and the total metal ion content in the obtained solution is in the range of from 0.3 to 0.5 mmol;
(b) a urea being added into the obtained solution to give a mixture;
(c) the mixture obtained in step (b) being dried;
(d) the dried mixture being ground into homogeneous powders and then subjected to a heating process under inert atmosphere.

[Claim 2] The method of claim 1, wherein in step (b), the urea is added in such an amount that the concentration of the urea in the solution is in the range of from 1 to 3 g/mL.

[Claim 3] The method of claim 1, wherein in step (c), the mixture is dried at 60 °C to 90 °C in an oil bath upon stirring for 5 to 10 hours.

[Claim 4] The method of claim 1, wherein in step (d), the heating process comprises:
the temperature is raised to a temperature of 520 °C to 580 °C at a programming rate of from 0.4 to 0.6 °C/min and maintained at that temperature;
the temperature is further raised to 650 °C to 750 °C and maintained at that temperature.

[Claim 5] The method of claim 1, wherein in step (b), after adding urea, the solution is subjected to ultrasonic treatment for 4 to 8 minutes.

[Claim 6] The method of claim 1, wherein the nickel source compound in step (a) is selected from the group consisting of nickel acetate, nickel chloride, nickel nitrate, nickel sulfate and the combination thereof.

[Claim 7] The method of claim 1, wherein the ferric iron source compound in step (a) is selected from the group consisting of ferric chloride, ferric nitrate, ferric sulfate and the combination thereof.

[Claim 8] A bifunctional electrocatalyst made by a method comprising:
(a) a nickel source compound and a ferric iron source compound being added into a solvent, wherein the molar ratio of the nickel ion to the iron ion in the obtained solution is in the range of from 93:7 to 85:15, and the total metal ion content in the obtained solution is in the range of from 0.3 to 0.5 mmol;

(b) a urea being added into the obtained solution to give a mixture;
(c) the mixture obtained in step (b) being dried;
(d) the dried mixture being ground into homogeneous powders and then subjected to a heating process under inert atmosphere to give a product.

[Claim 9] A water splitting cell comprising two electrodes, each of the electrodes comprising the bifunctional electrocatalyst of claim 8.

[Claim 10] water splitting cell of claim 9, wherein the bifunctional electrocatalyst is loaded onto a carbon fiber paper or nickel foam.

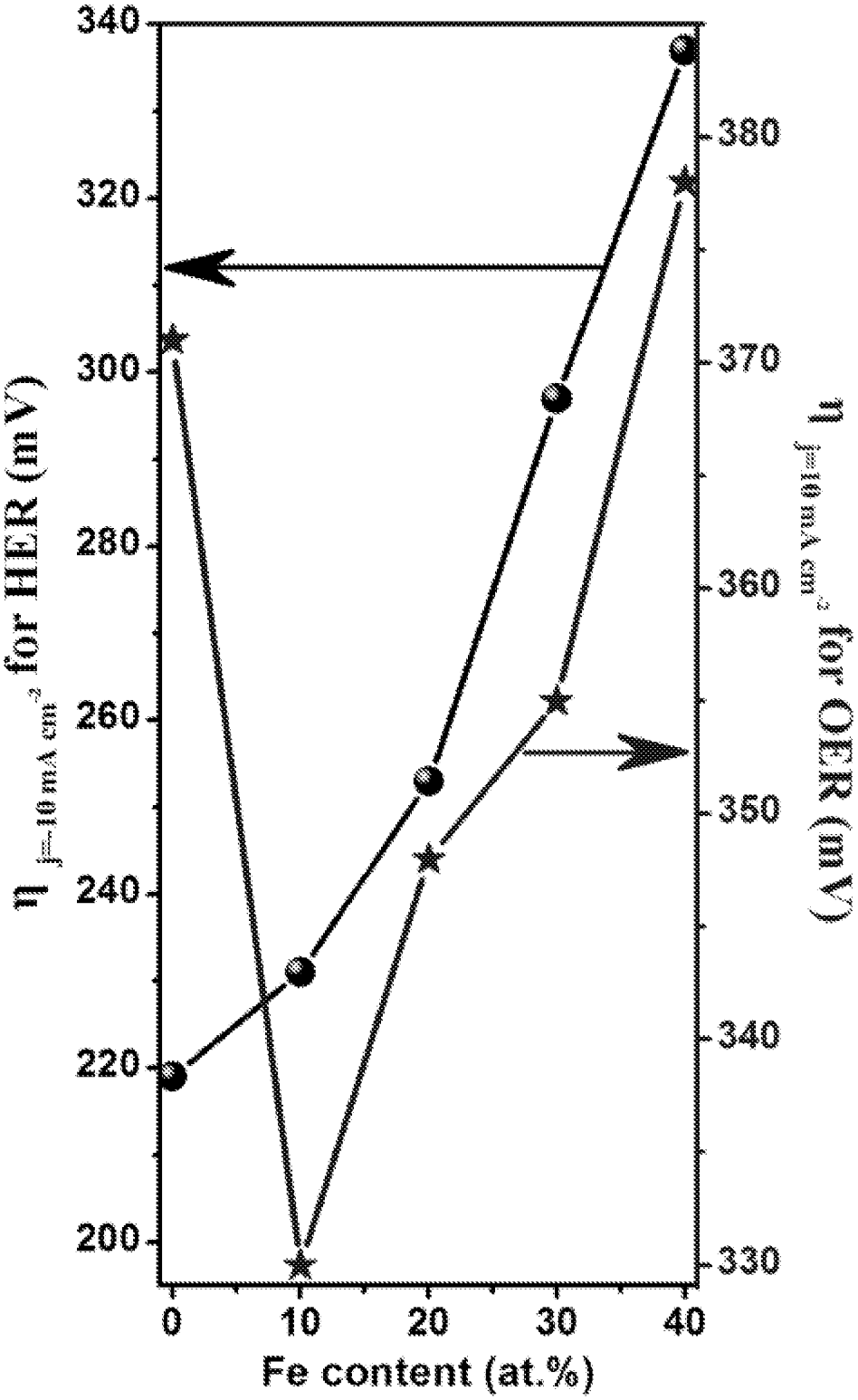

340
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340
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Fe content (at.%)
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η j=10 mA cm-2 for OER (mV)

Figure 1

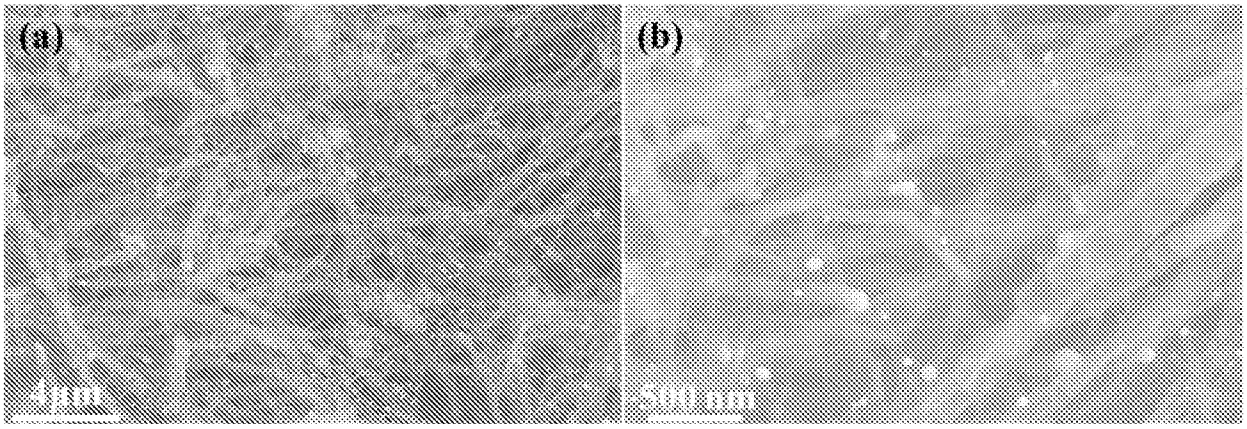


Figure 2

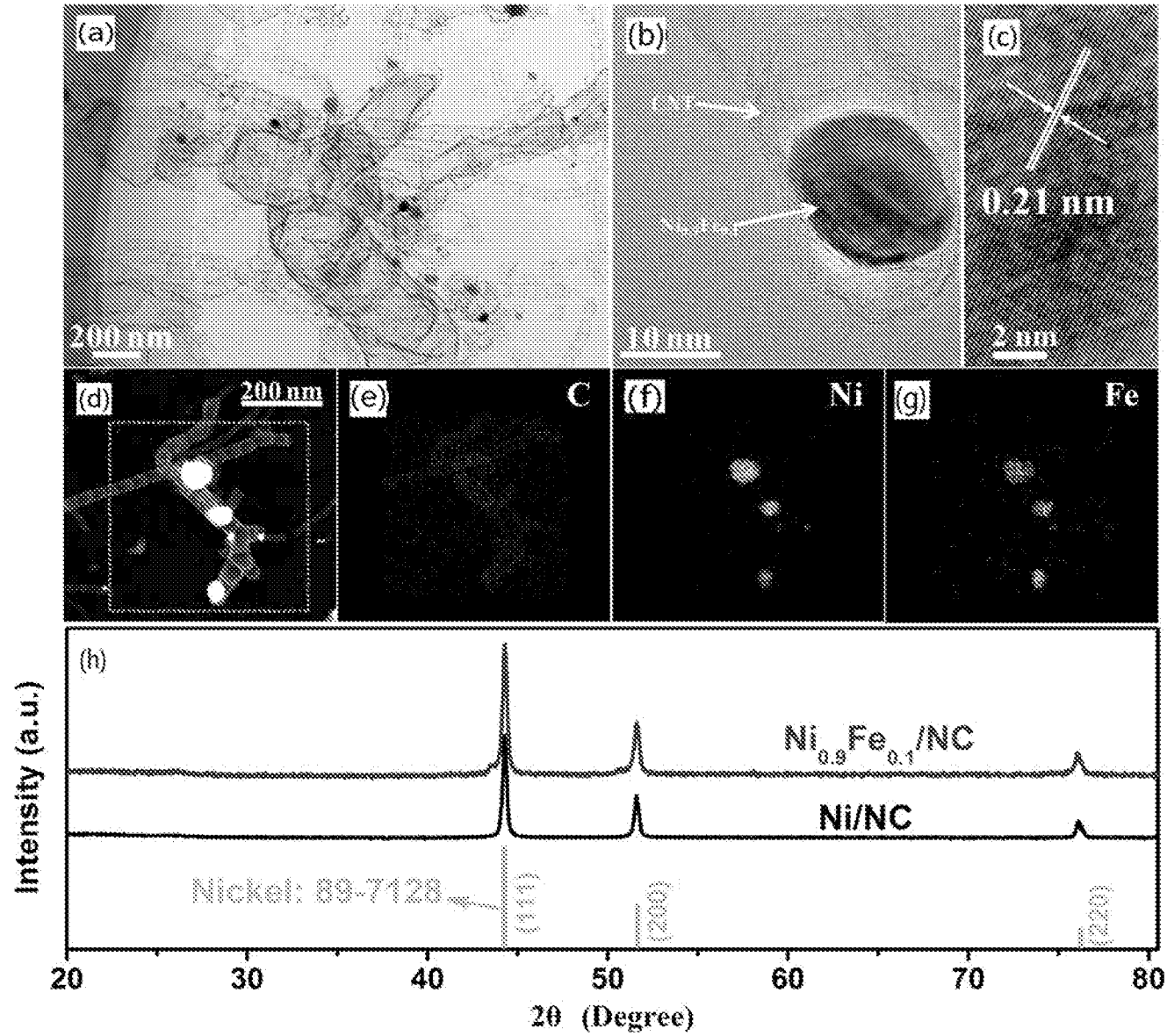


Figure 3

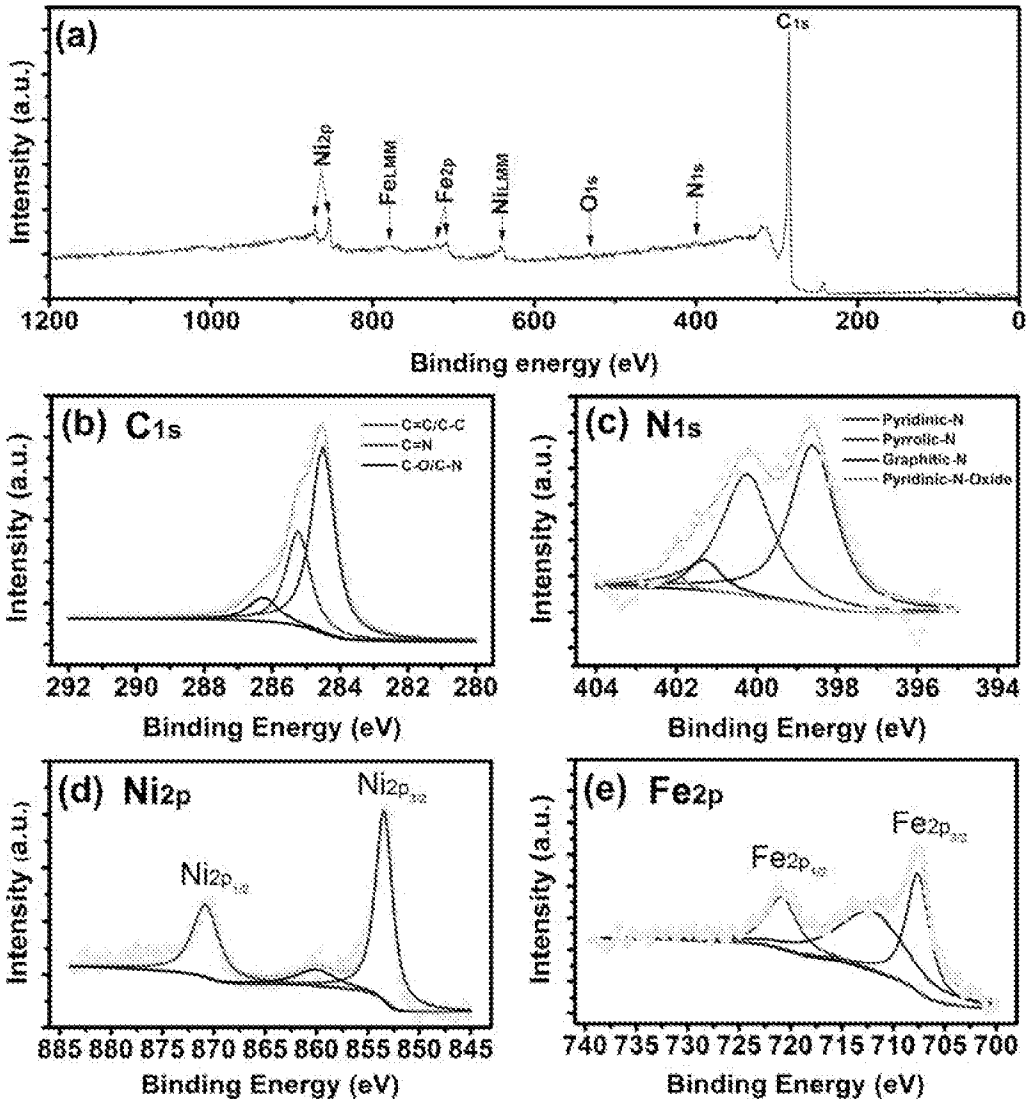

(a)
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Fe LMM
Fe2p
Ni LMM
O1s
N1s
C1s
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C=C/C-C
C=N
C-O/C-N
Intensity (a.u.)
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Graphitic-N
Pyridinic-N-Oxide
Intensity (a.u.)
404 402 400 398 396 394
Binding Energy (eV)
(d) Ni2p
Ni2p3/2
Ni2p1/2
Intensity (a.u.)
885 880 875 870 865 860 855 850 845
Binding Energy (eV)
(e) Fe2p
Fe2p3/2
Fe2p1/2
Intensity (a.u.)
740 735 730 725 720 715 710 705 700
Binding Energy (eV)

Figure 4

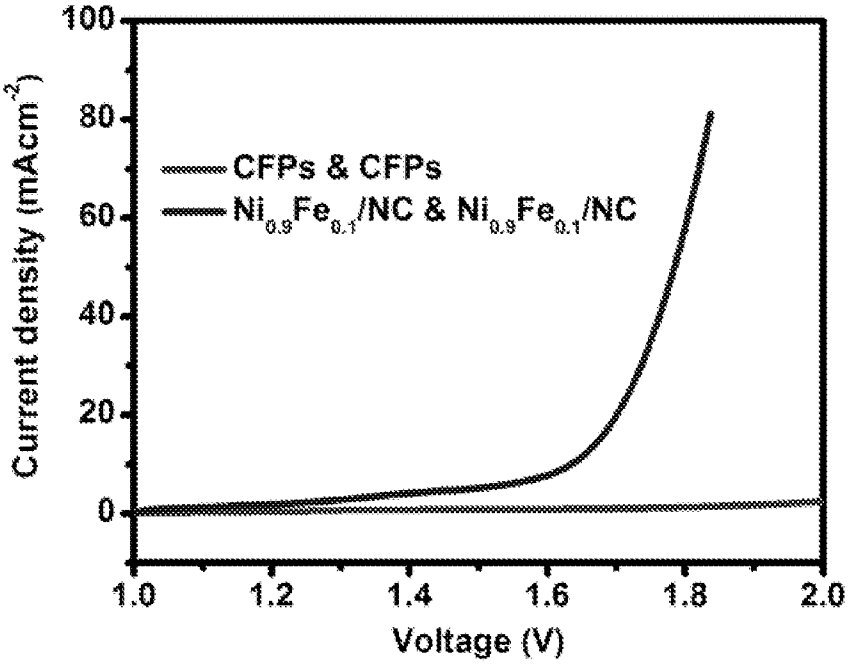


Figure 5

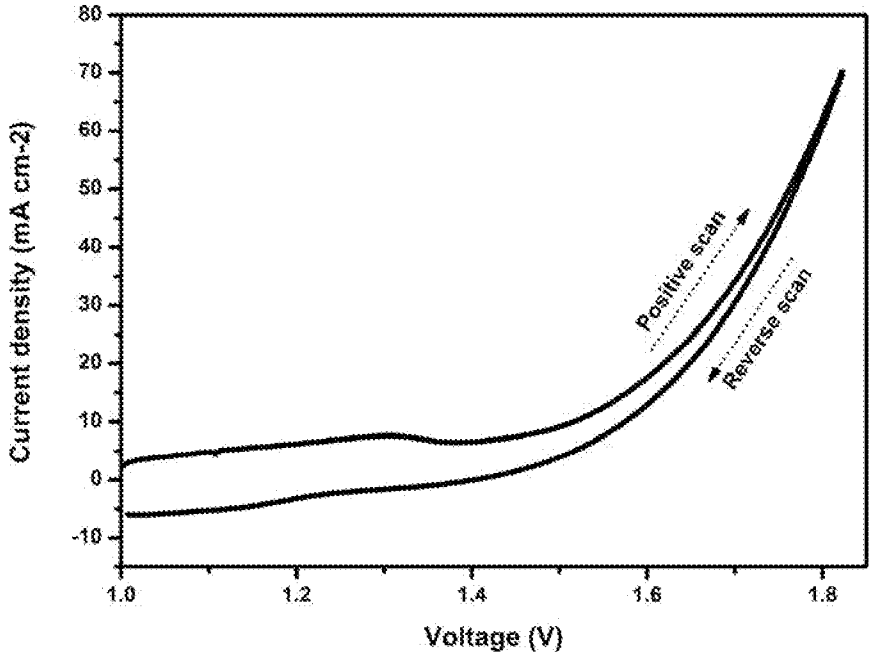


Figure 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/096020

A. CLASSIFICATION OF SUBJECT MATTER

B01J 23/755(2006.01)i; B01J 37/16(2006.01)i; C25B 1/04(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J23/-, B01J37/-, C25B1/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS; CNTXT; EPODOC; DWPI; CNKI: nickel, Ni, iron, ferric, Fe, urea, alloy, metallic, catalyst?, electro?, hydrogen, water, split+, oxides, mixed, composite, reduc+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101575713 A (ENN TECHNOLOGY DEV CO LTD) 11 November 2009 (2009-11-11) description, page 2, line 9 – page 3, line 4, and examples 1-3	8-10
A	CN 103952719 A (CHINESE ACAD SCI PHYSICS INST) 30 July 2014 (2014-07-30) the whole document	1-10
A	WO 2015087168 A2 (NANU NANU LTD) 18 June 2015 (2015-06-18) the whole document	1-10
A	JP 2015112501 A (GREEN CHEMY INC) 22 June 2015 (2015-06-22) the whole document	1-10

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 August 2016	**08 September 2016**

Name and mailing address of the ISA/CN	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/096020

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 101575713 A	11 November 2009	CN 101575713 B	13 October 2010
CN 103952719 A	30 July 2014	None	
WO 2015087168 A2	18 June 2015	None	
JP 2015112501 A	22 June 2015	None	