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(54) **METHOD OF MANUFACTURING
ELECTROCATALYST THROUGH ONE STEP
ELECTRODEPOSITION AND
ELECTROCATALYST MANUFACTURED
THEREFROM**

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CPC **C25B 11/0478** (2013.01); **C25B 1/04**
(2013.01)

(57) **ABSTRACT**

Disclosed is a method of manufacturing an electrocatalyst. The method may include forming a metal layer on a substrate, treating a substrate of the metal layer, and forming a catalyst layer on the metal layer by applying potential to an aqueous deposition solution including a nickel precursor, a copper precursor, a phosphorus precursor, and an additive, in which a molar ratio of the nickel precursor to the copper precursor may be greater than about 49:1. Accordingly, the present invention has an advantage in that the process of manufacturing the electrocatalyst may be simplified.

FIG 1

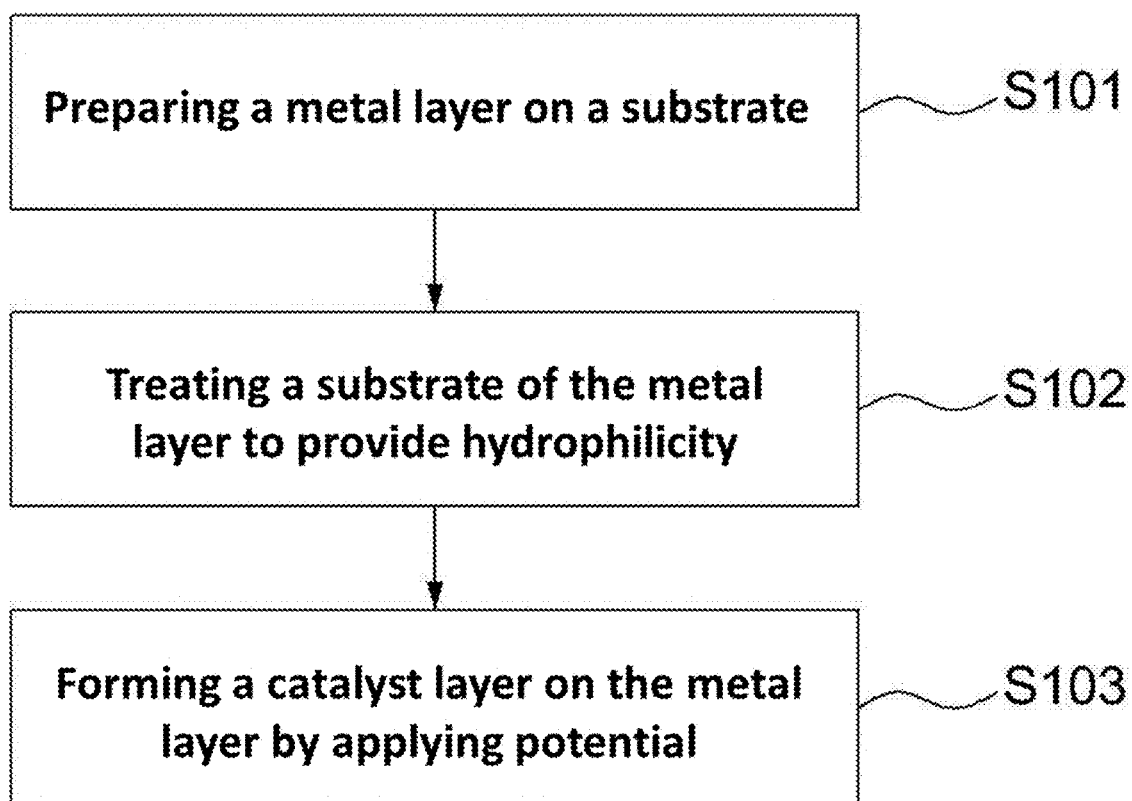


FIG 2

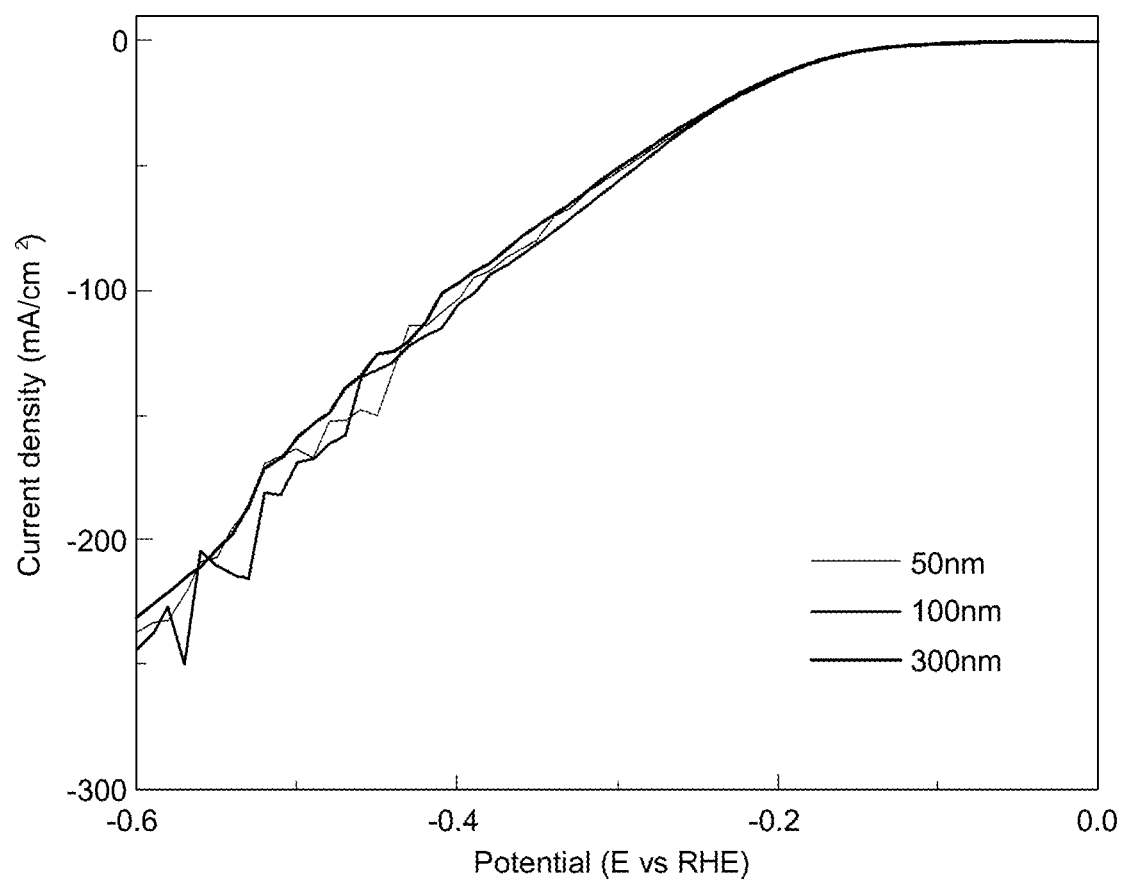


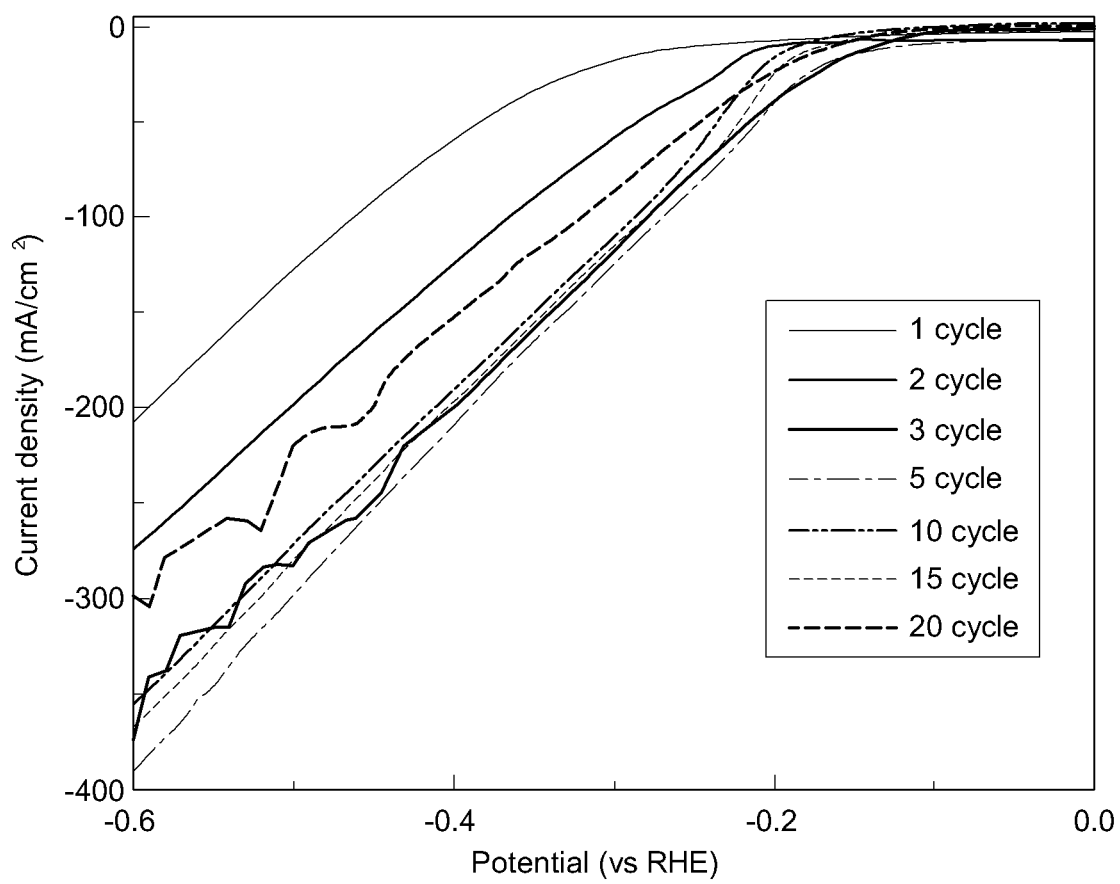
FIG 3

FIG 4

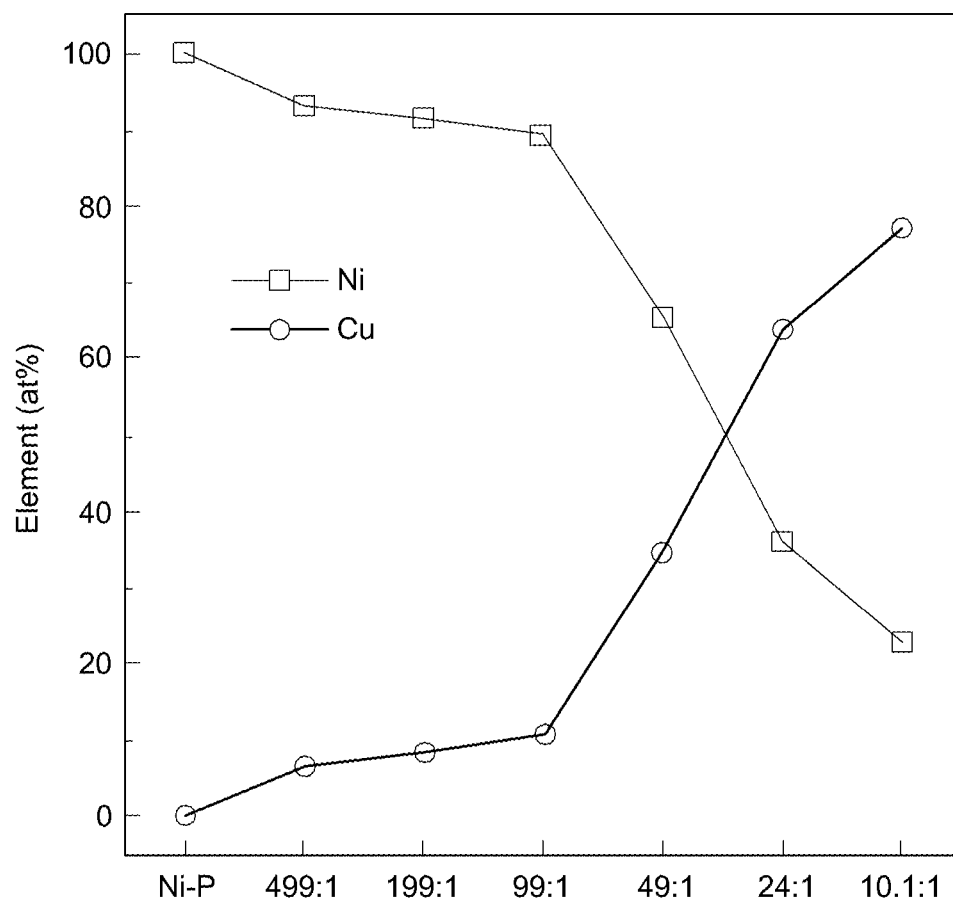


FIG 5

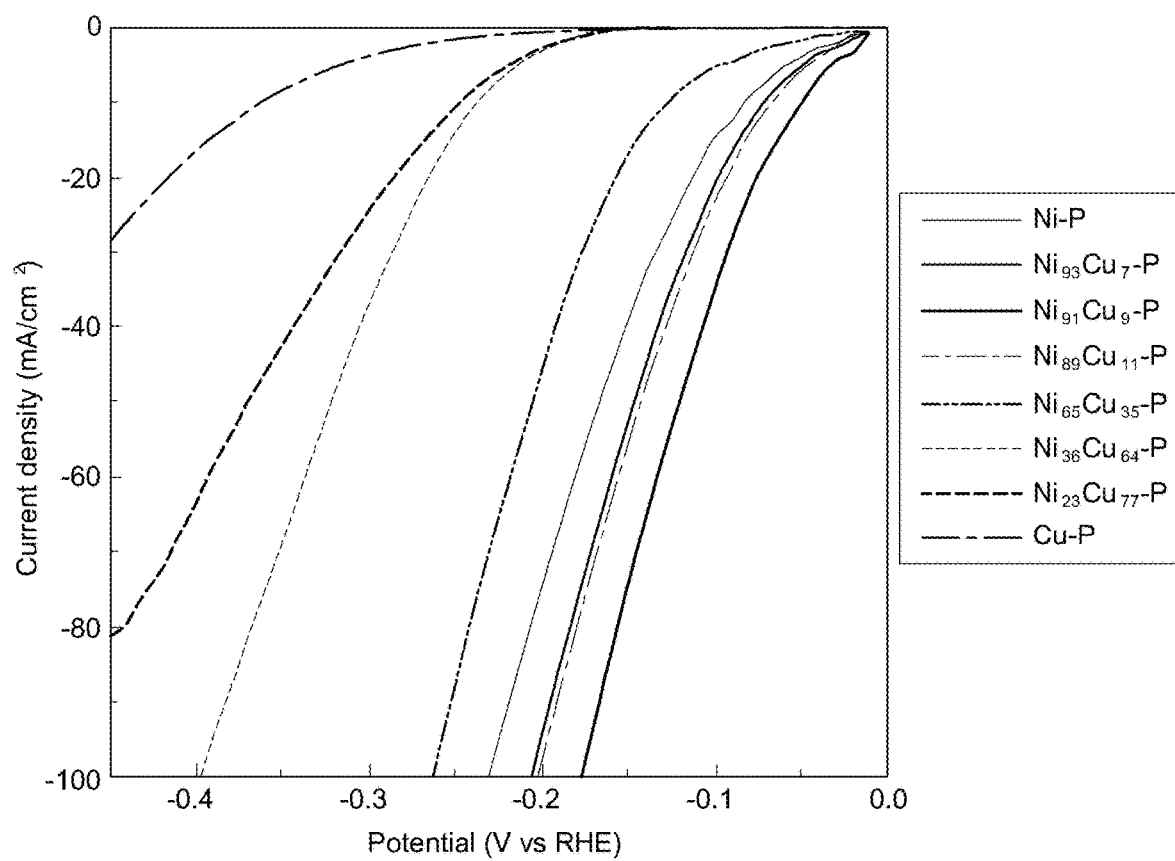


FIG 6A

FIG. 6B

FIG. 6C

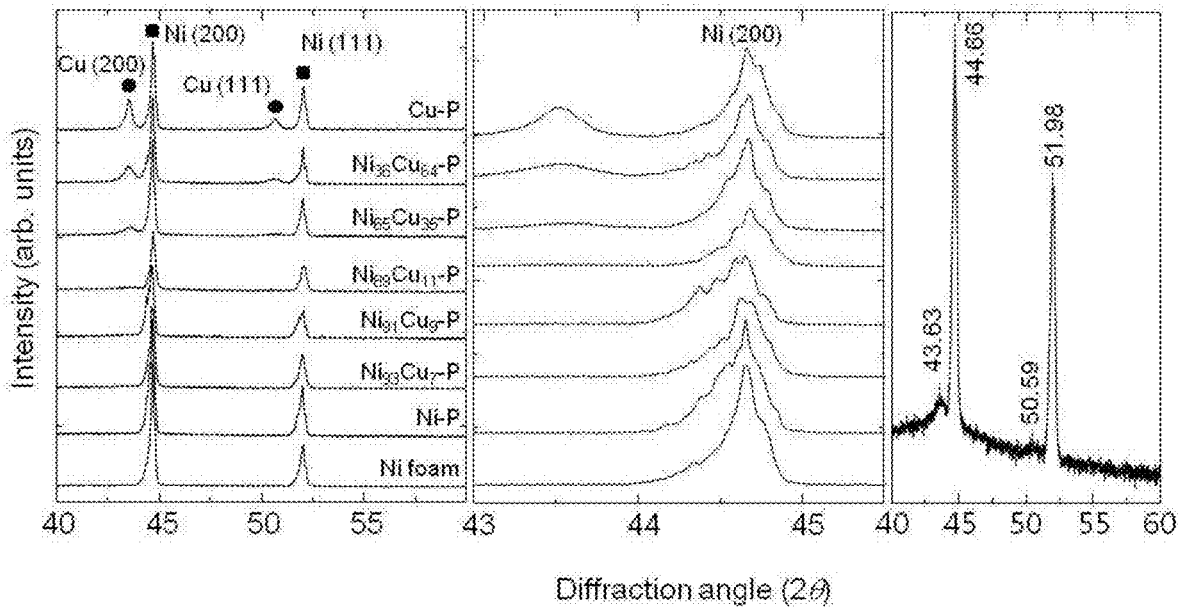


FIG 7A

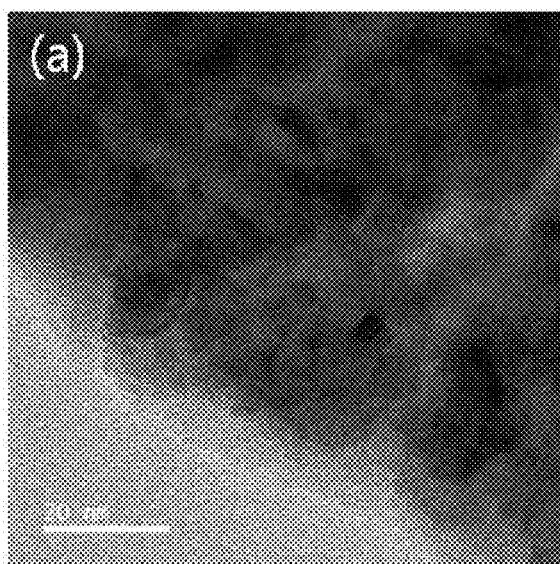


FIG. 7B

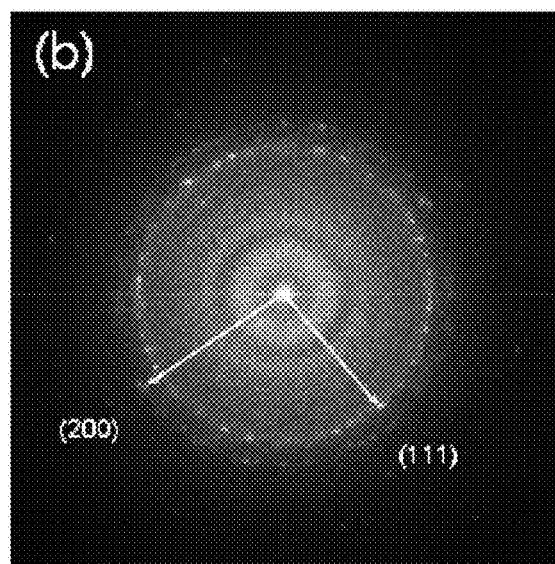


FIG 8A

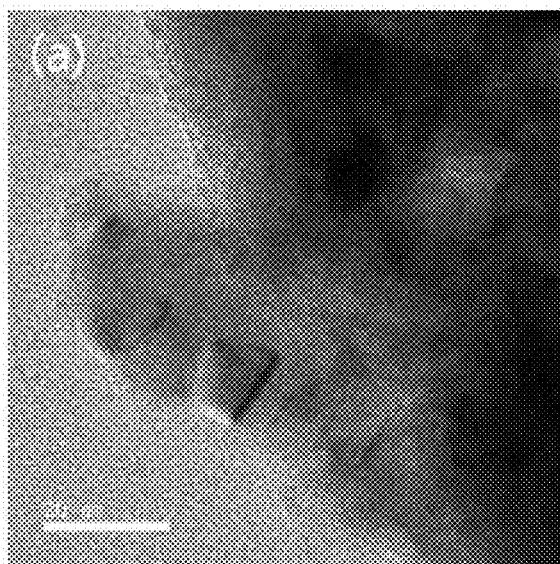


FIG. 8B

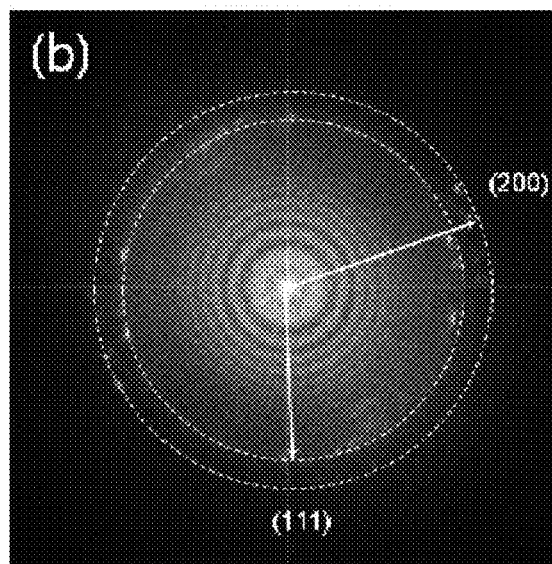


FIG 9A

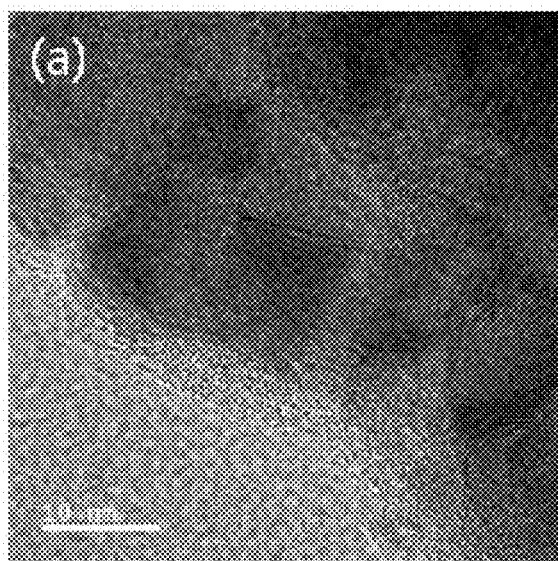


FIG. 9B

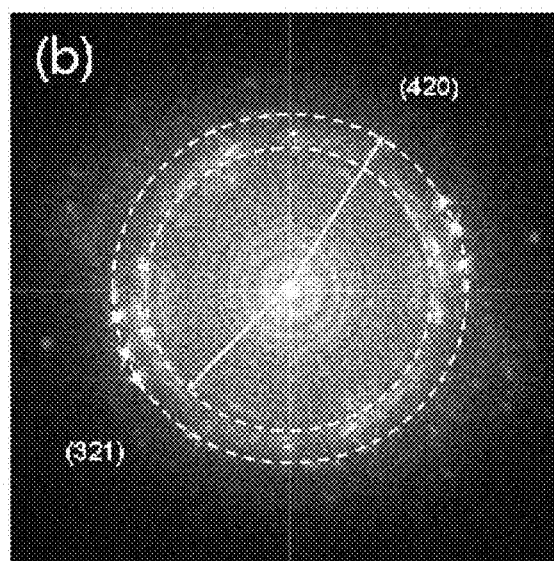


FIG 10A

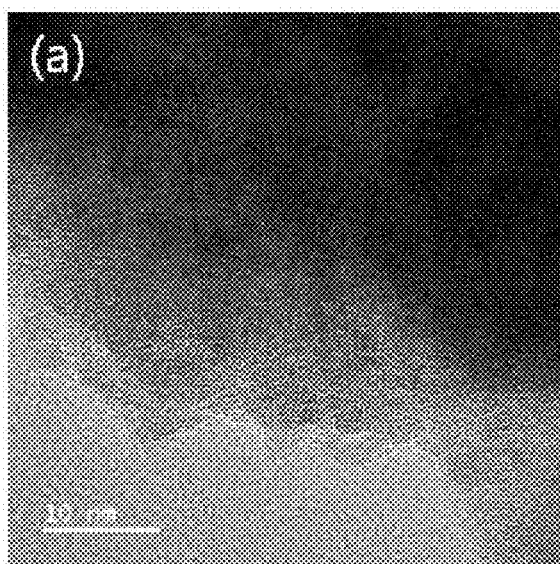


FIG. 10B

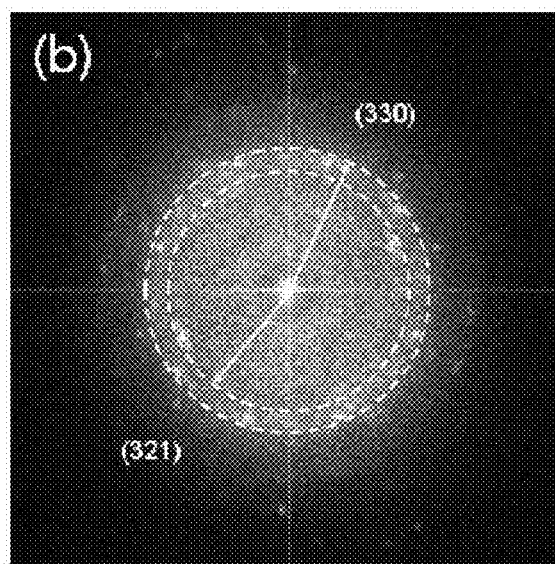


FIG 11

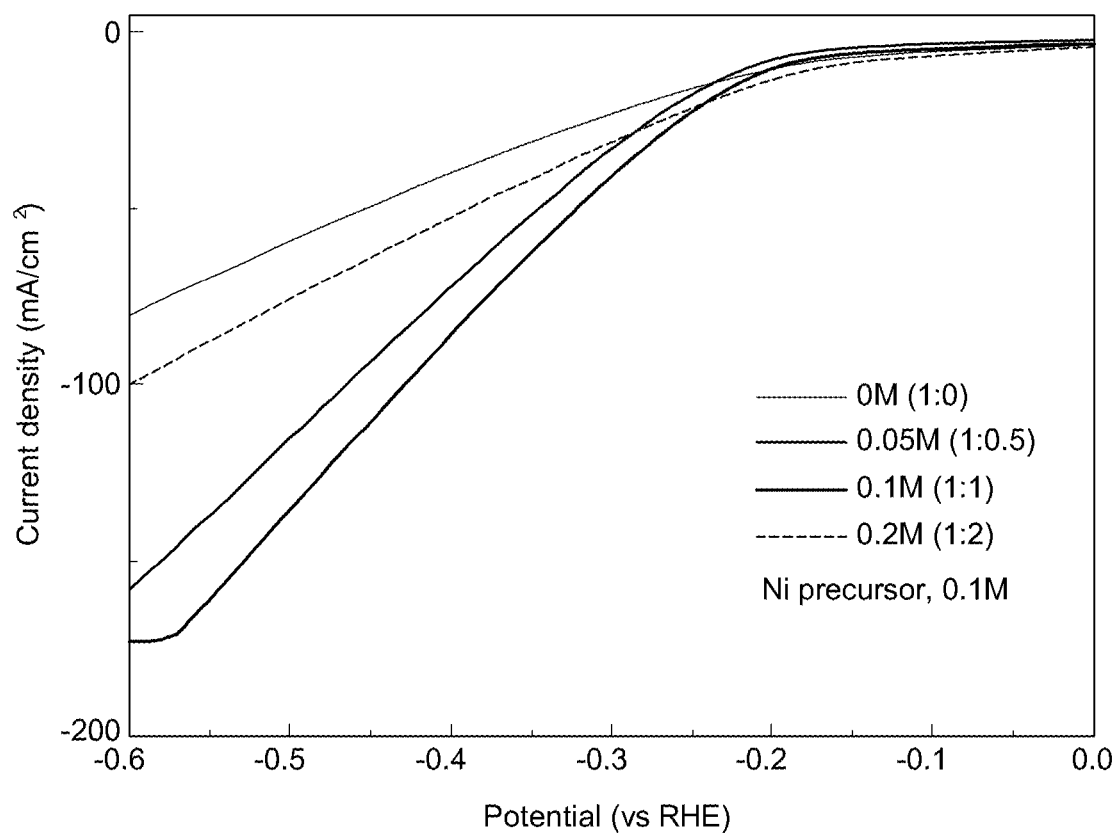


FIG 12

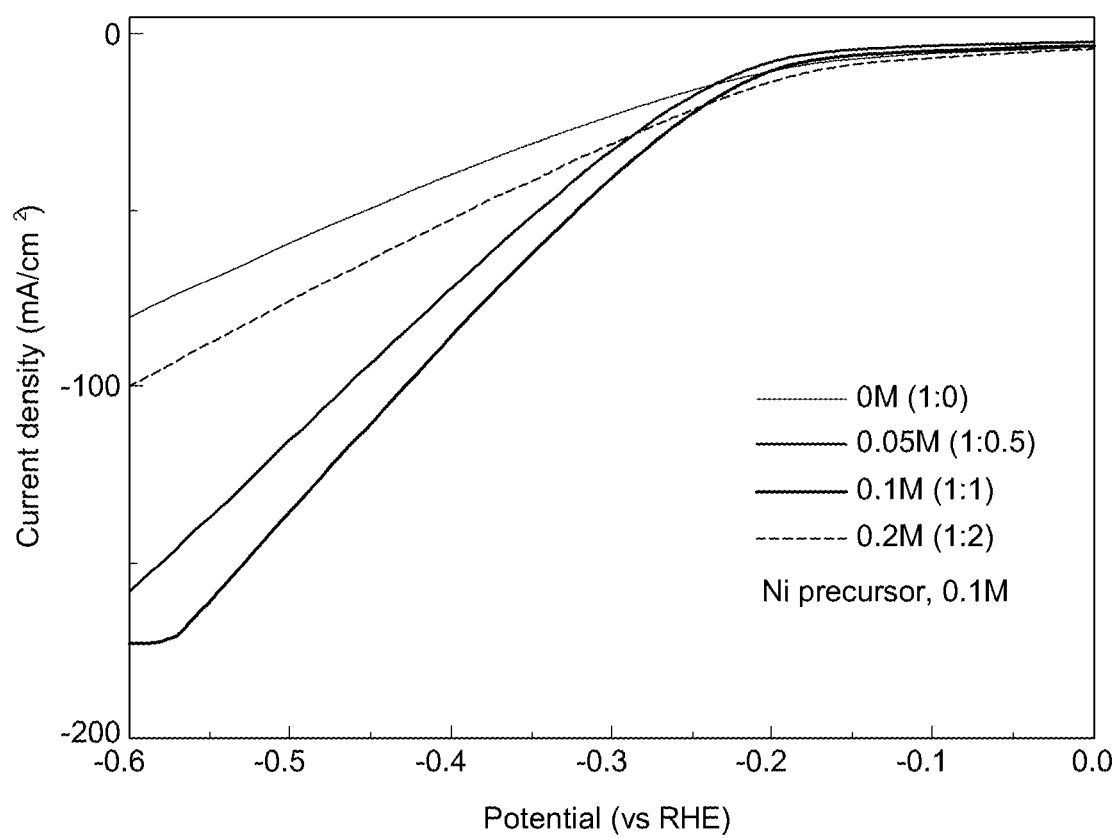


FIG 13

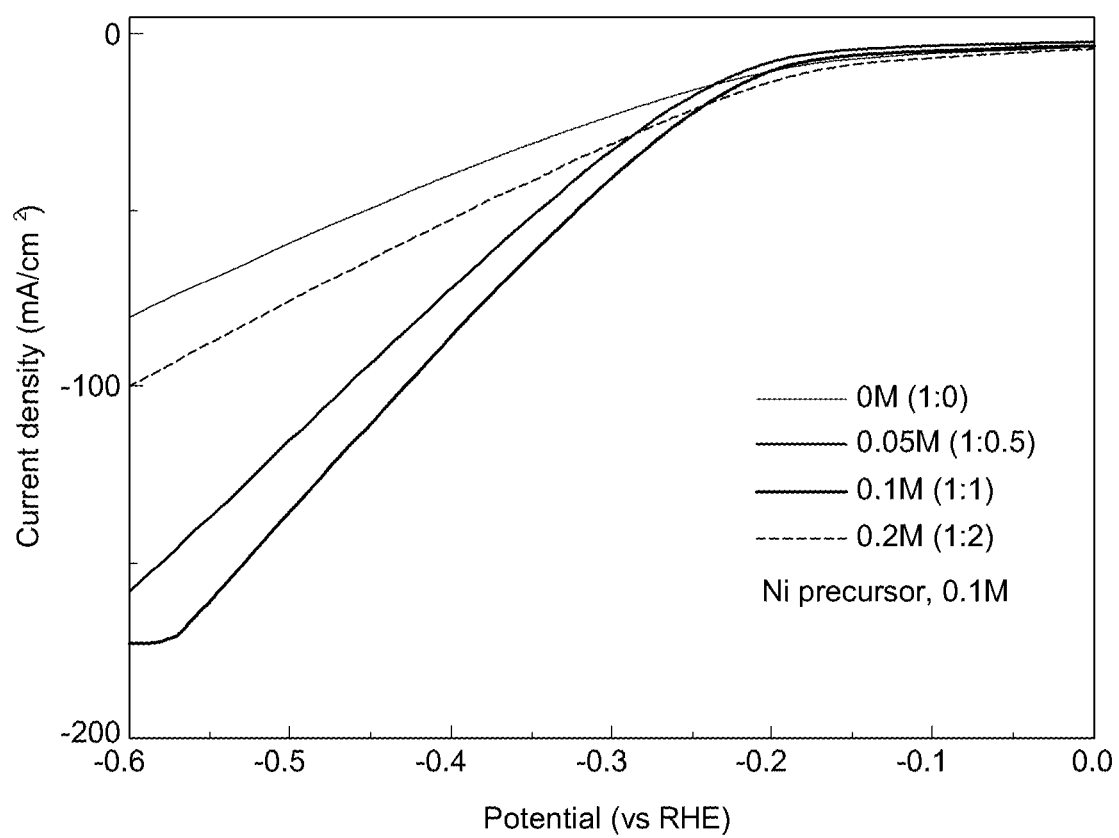


FIG 14

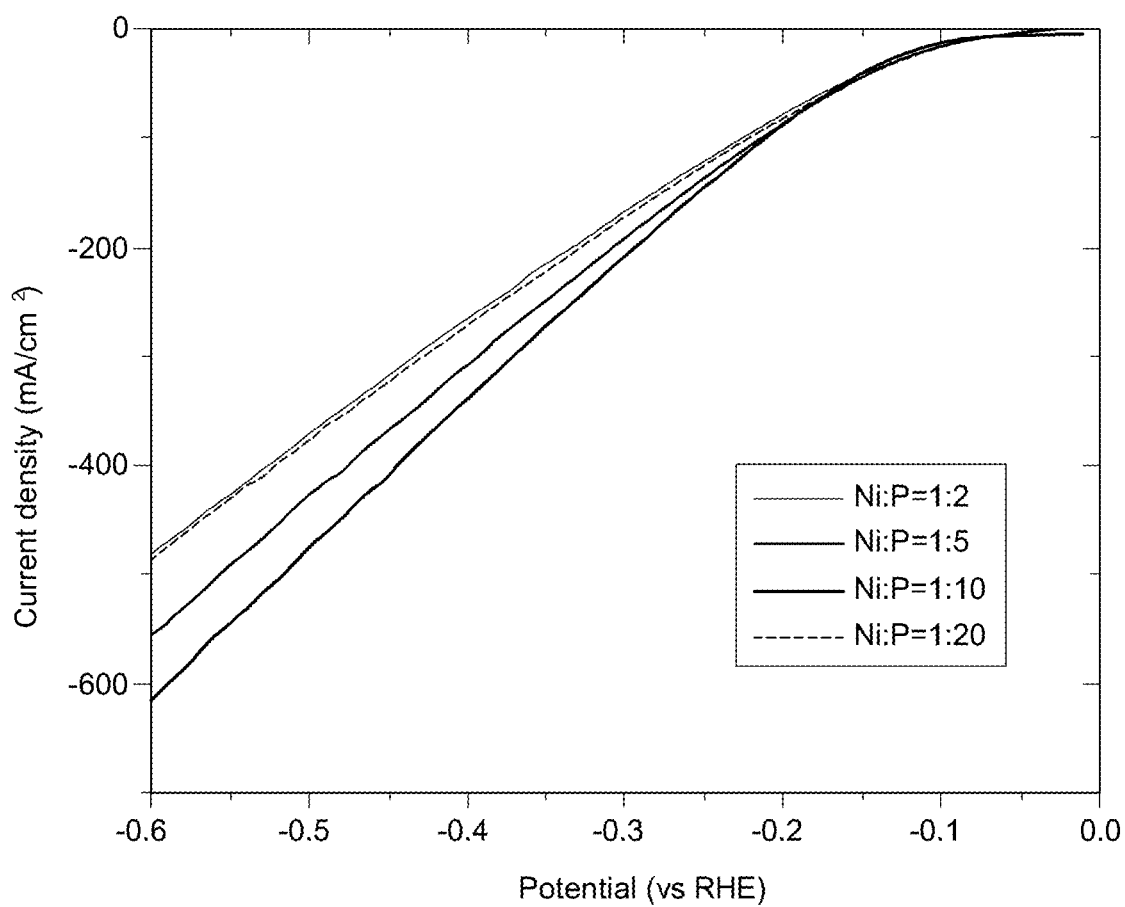


FIG 15A

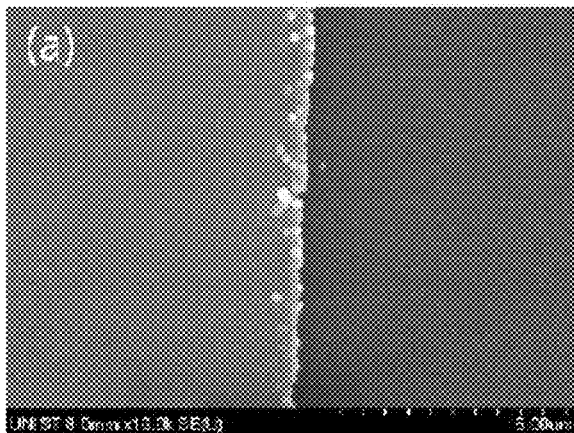


FIG. 15B

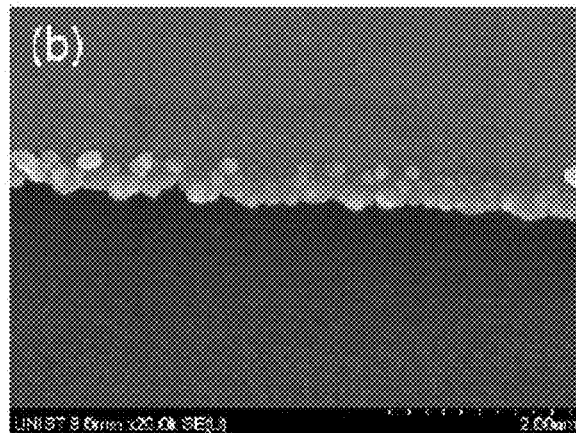


FIG 15C

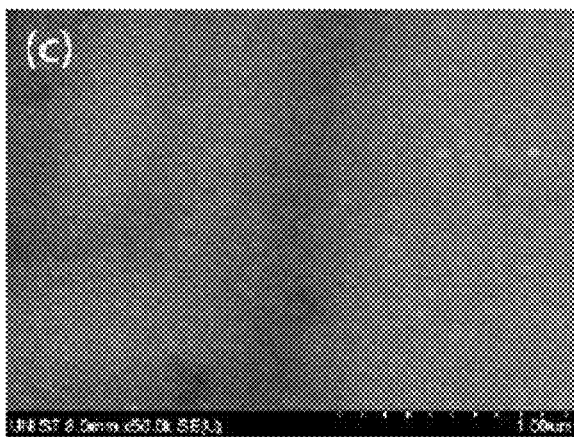


FIG. 15D

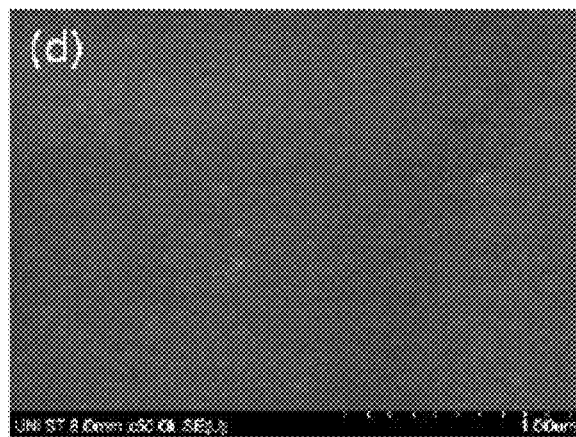


FIG 16A

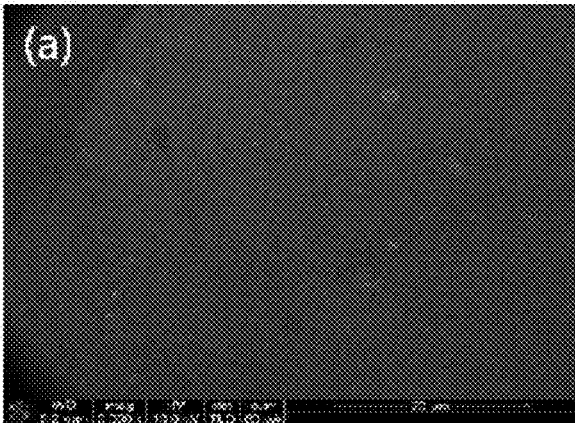


FIG. 16B

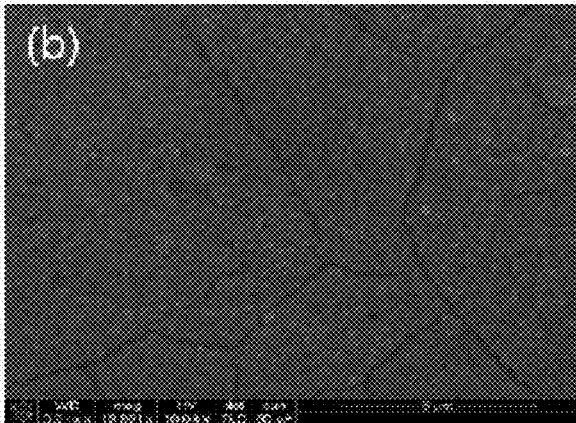


FIG 16C

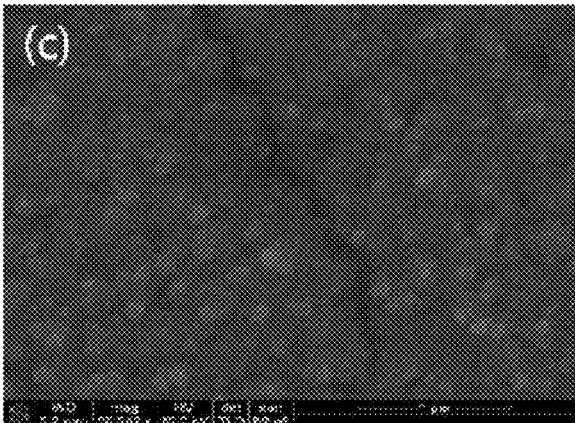


FIG. 16D

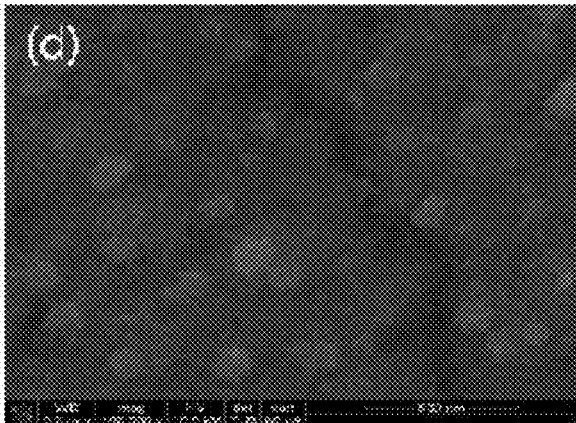


FIG 17

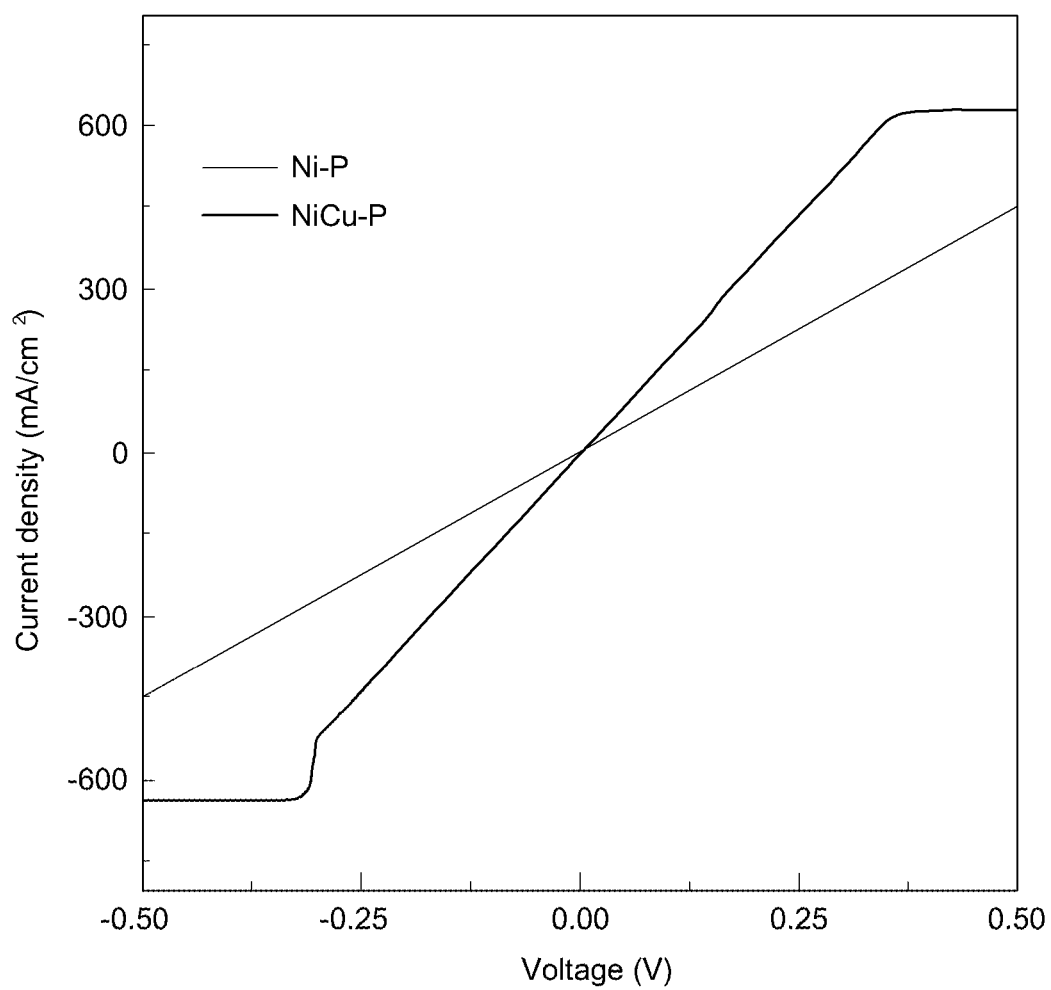


FIG 18

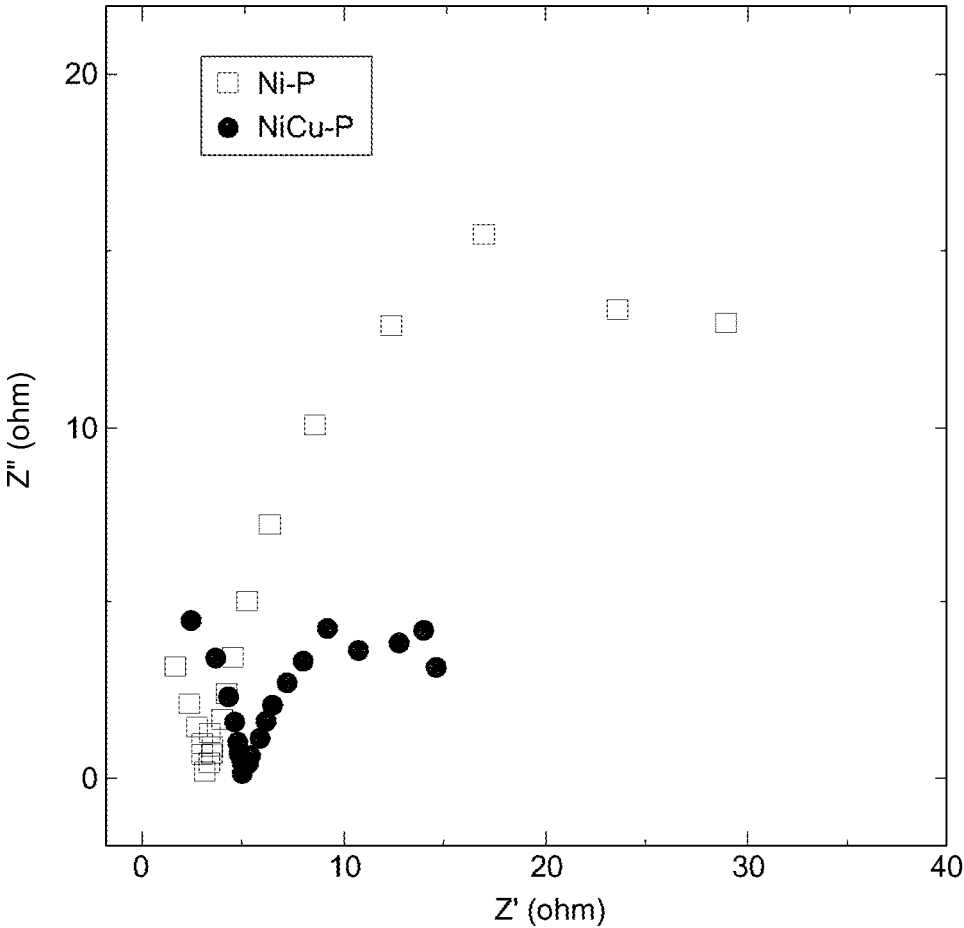


FIG 19

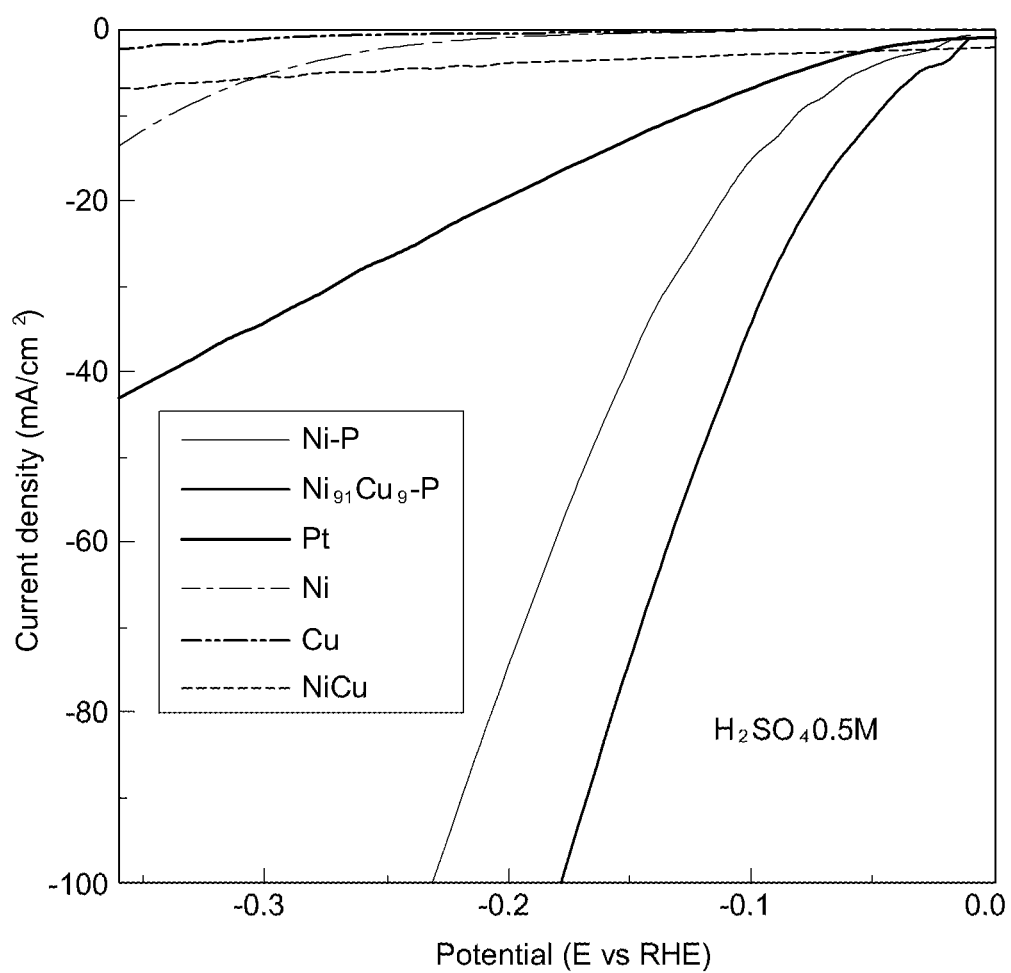


FIG 20

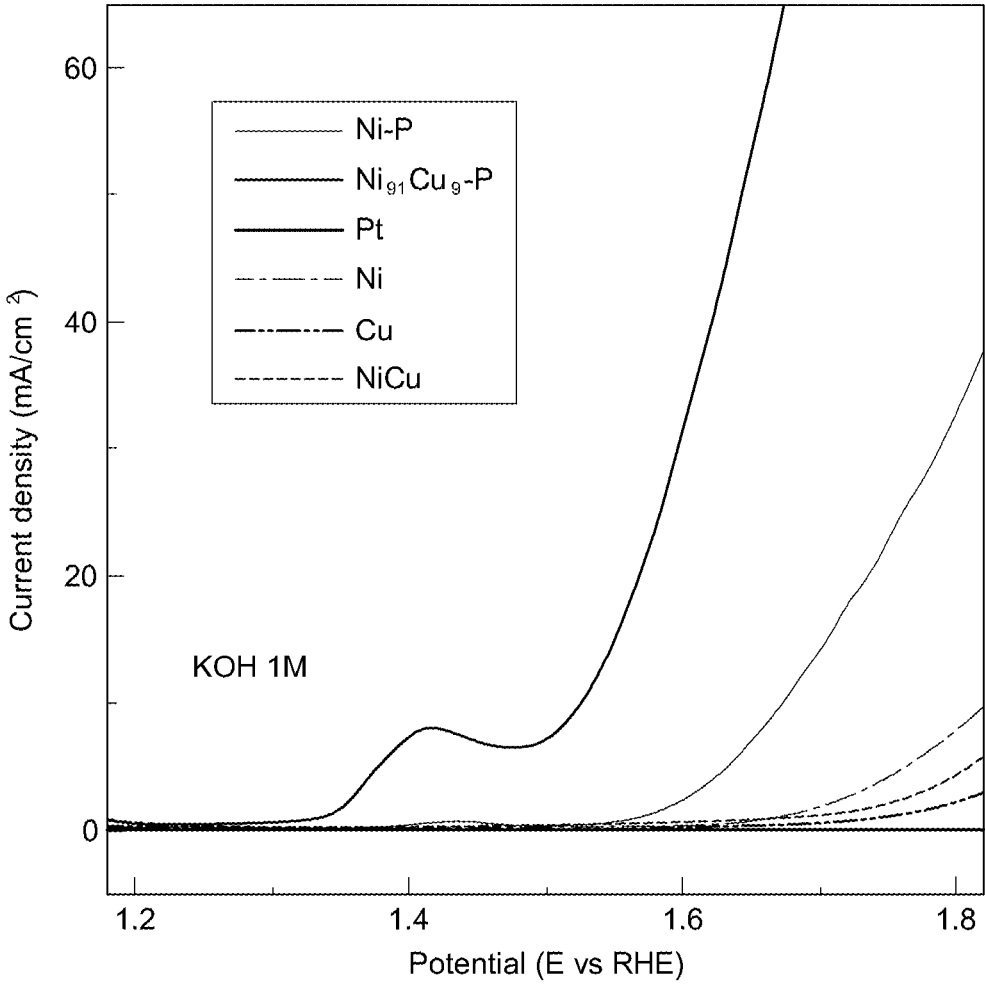


FIG 21A

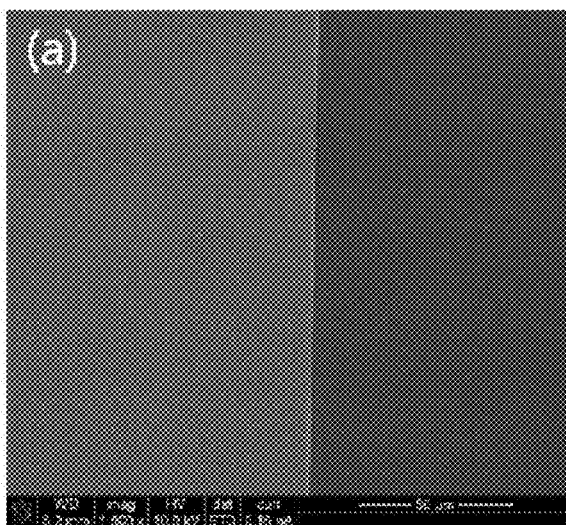


FIG. 21B

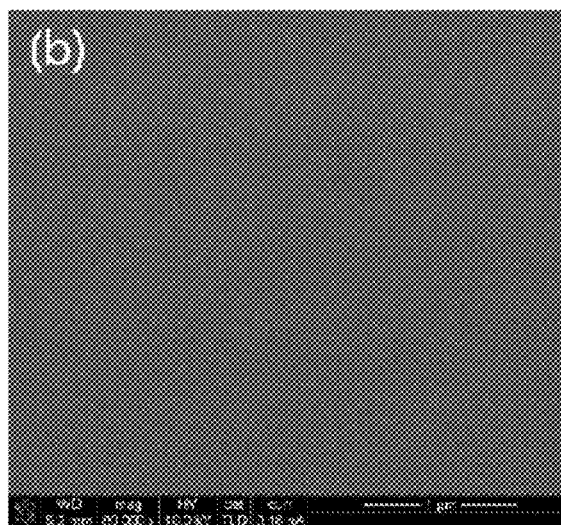


FIG 22A

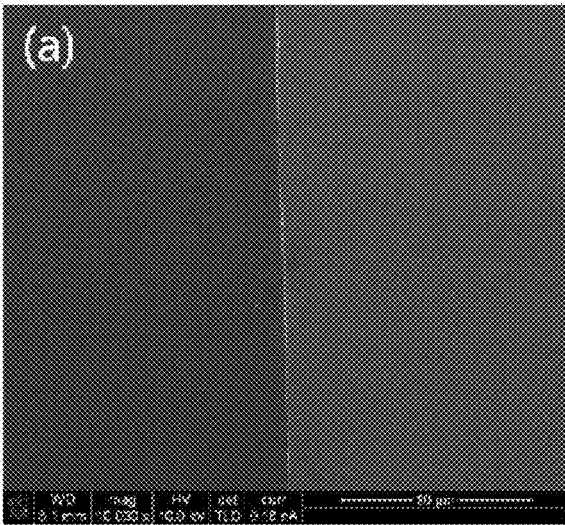


FIG. 22B

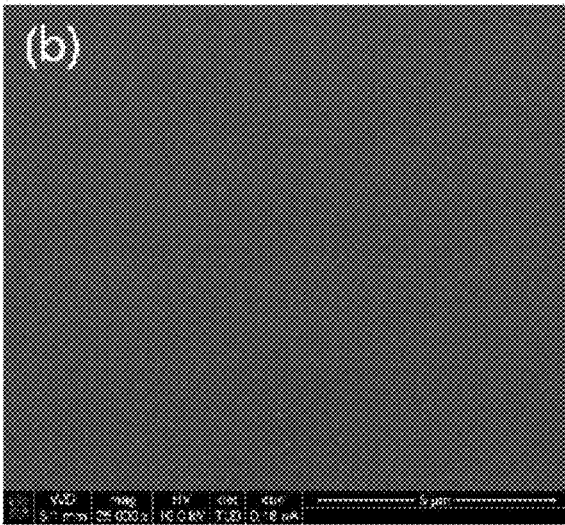


FIG 23

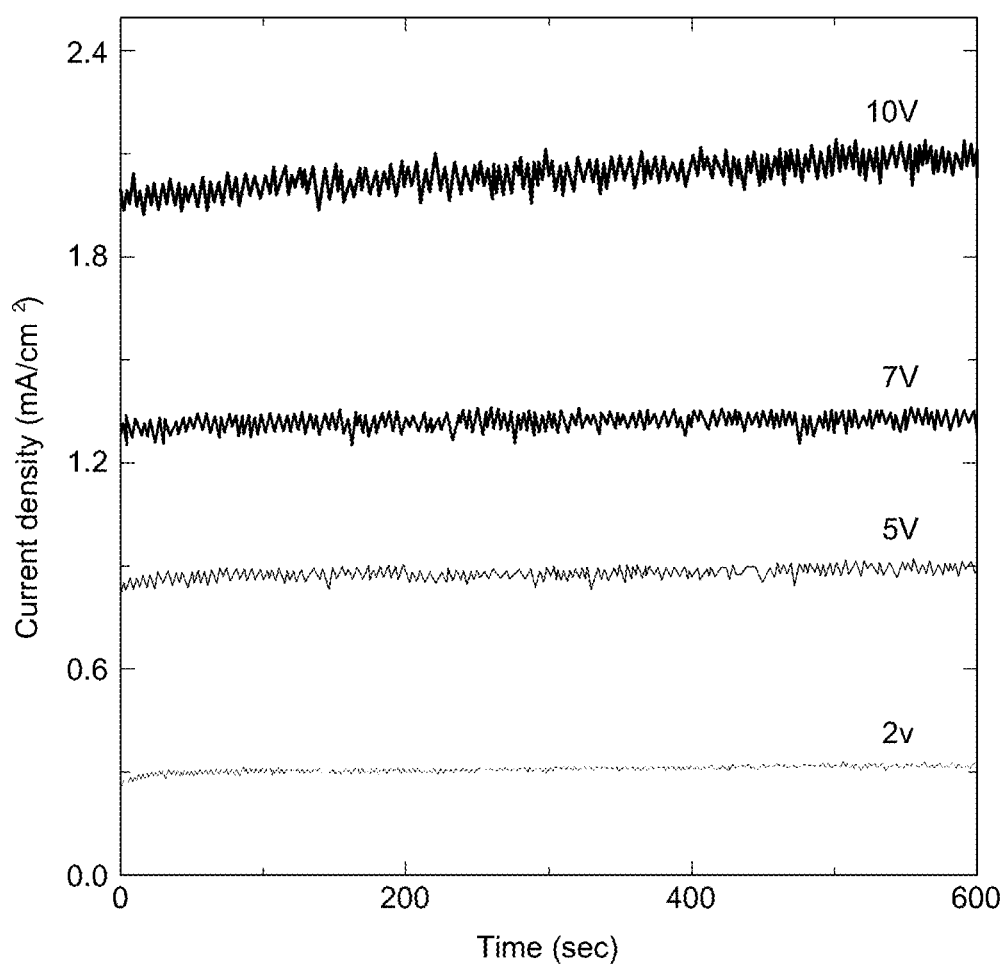
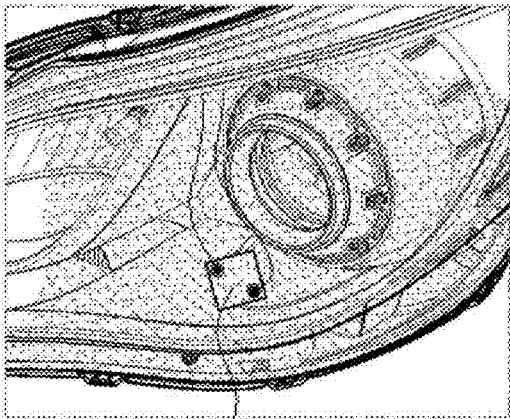


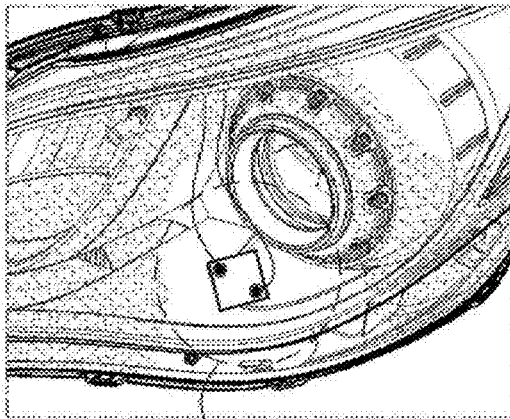
FIG 24A



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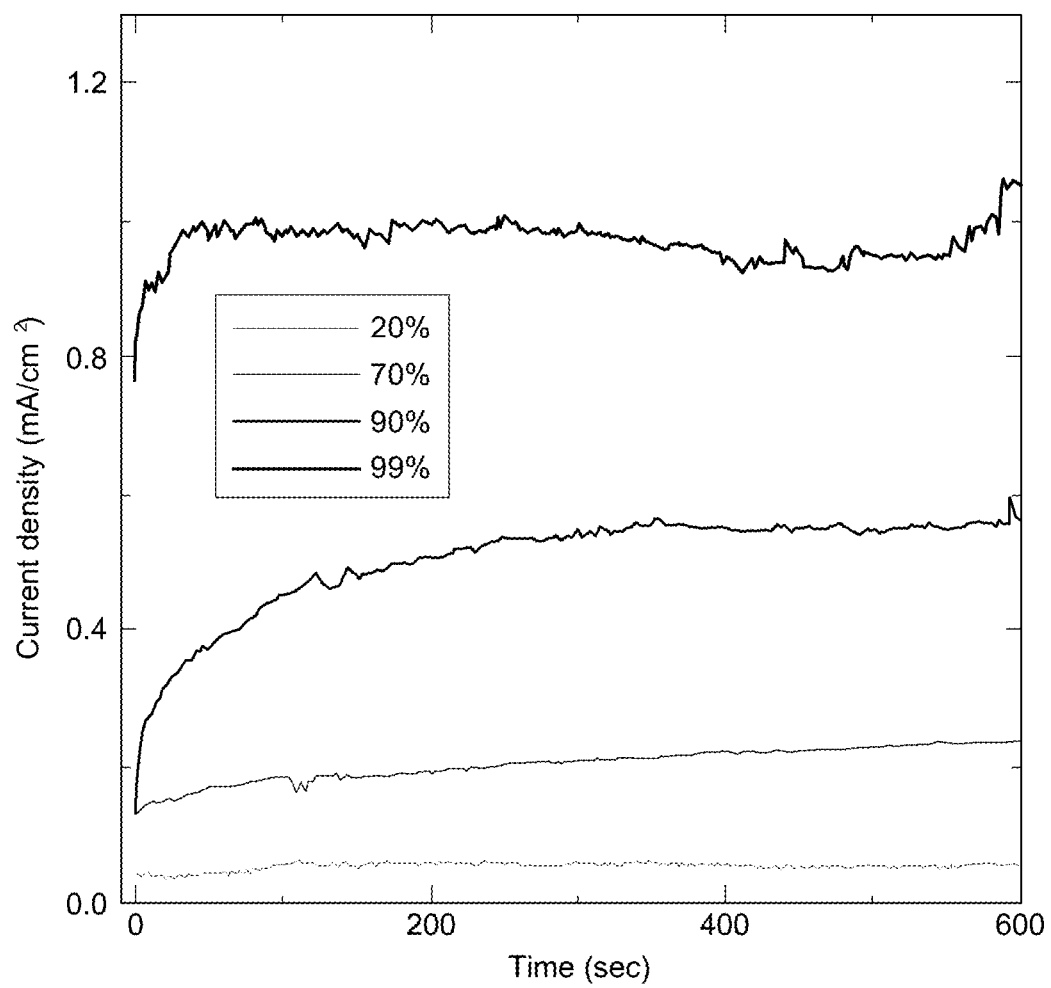


FIG. 24B



11

FIG 25



METHOD OF MANUFACTURING ELECTROCATALYST THROUGH ONE STEP ELECTRODEPOSITION AND ELECTROCATALYST MANUFACTURED THEREFROM

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. § 119 to Korean Patent Application No. 10-2018-0095514, filed on Aug. 16, 2018, in the Korean Intellectual Property Office, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a method of manufacturing an electrocatalyst by electrodeposition.

BACKGROUND OF THE INVENTION

[0003] Since the current hydrogen energy has received attention as an eco-friendly energy capable of replacing fossil fuels and the hydrogen energy can be produced only by electrolysis of water, interests in studies on an electrocatalyst that produces hydrogen energy by electrolyzing water have been increased.

[0004] Typically, the electrocatalyst is composed of a hydrogen evolution reaction (HER) electrode and an oxygen evolution reaction (OER) electrode. Platinum (Pt) has been the most widely known as a material for each electrode. However, since platinum corresponds to a noble metal and has a limitation on reserves, studies on using a metal rich in reserves, such as iron (Fe), nickel (Ni), copper (Cu), and cobalt (Co) as an element to replace platinum, particularly, studies on using a heterogeneous metal as a material for an electrocatalyst have been actively conducted.

[0005] For instance, in the related arts, a cobalt phosphide doped with copper has been used. However, a manufacturing process is complicated with being subjected to a carbonization process at 800° C. and a post-heat treatment process at 300° C. using a metal-organic framework (MOF) as a precursor and only the activity in a strong base (pH 13.5) electrolyte has been reported.

[0006] In addition, in the related arts, a material in which a nickel (Ni) foam has been doped with cobalt, which may involve a complicated process such as formation of a layered nanostructure (three-layered morphology) on the surface of the nickel foam using a sphere lithography process. Further, the material is amorphous and only the activity in a strong alkali (pH 13.5) electrolyte has been reported.

[0007] Moreover, in the related arts, a material has been prepared by electrodepositing nickel and copper on a stainless steel foil, and then applying a phosphide treatment thereto (so-called a two-step process). However, the addition of phosphorus requires a process at 300° C., and thus is not efficient in terms of costs.

[0008] Despite in the related art has introduced using a nickel precursor, a copper precursor, and a phosphorus precursor that can be electrodeposited, electrolyzing and removing liquid water or vapor water molecules (moisture) may be limited because the invention exhibits super hydrophobicity and is used for surface waterproof treatment. Further, because additives for various purposes are used, such as the use of SDS and Na₂SO₄ as an ion strengthening

agent and the use of aqueous ammonia as a pH adjusting agent, the process may not be simplified.

SUMMARY OF THE INVENTION

[0009] In preferred aspect, the present invention may provide simplified process of process of manufacturing an electrocatalyst and reduce an additive used in electrodeposition. In addition, the present invention may provide the process of manufacturing the electrocatalyst to remove moisture.

[0010] In an aspect, provided is a method of manufacturing an electrocatalyst. The method may include forming a metal layer on a substrate, treating a surface of the metal layer, and forming a catalyst layer on the metal layer by applying potential to an aqueous deposition solution including a nickel precursor, a copper precursor, a phosphorus precursor, and an additive. In particular, a molar ratio of the nickel precursor to the copper precursor may be greater than about 49:1 to 499:1, or more preferably between about 99:1 to about 499:1.

[0011] The “aqueous deposition solution” is meant by an admixture or a solution including water or water-based solvent for dispersing of other materials or components.

[0012] The metal layer may suitably include a nickel layer or a copper layer.

[0013] The treating the surface of the metal layer. Preferably, the treating may provide the hydrophilic surface, for example, the hydrophilic surface treatment may suitably include a UV-ozone cleaning treatment.

[0014] The potential may be applied by a cyclic voltammetry method.

[0015] Preferably, a range of the potential may be about -1.2 to 0.2 V, including from about -1.0 V to 0.2 V, -0.8 V to 0.2 V or -0.6 V to 0.2 V.

[0016] A frequency at which the range of the potential is applied may suitably be about 3 to 15 times.

[0017] A molar concentration of the nickel precursor may be of about 0.02 to 0.5 M, including 0.05 to 0.2 M or 0.1 to 0.15 M.

[0018] The nickel precursor may suitably include one or more selected from nickel sulfate, nickel nitrate, and nickel acetate.

[0019] A concentration of the copper precursor may be of about 0.001 to 0.02 M.

[0020] The copper precursor may suitably include one or more selected from copper sulfate, copper nitrate, copper acetate, and copper acetylacetonate.

[0021] The additive may suitably include sodium acetate, and may further include glycine or citric acid.

[0022] A molar ratio of the nickel precursor to sodium acetate, glycine, or citric acid may be about 1:about 0.5 or greater and about 1:less than about 2.

[0023] A molar concentration of each of sodium acetate, glycine, and citric acid may be of about 0.05 or greater and less than about 0.2 M.

[0024] A molar ratio of the nickel precursor to the phosphorus precursor may be of about 1:about 5 to about 1:about 20, more preferably, of about 1:about 5 to about 1:about 10.

[0025] A molar concentration of the phosphorus precursor may be of about 0.01 M to about 2.0 M, about 0.05 to about 1.5 M, or more preferably, of about 0.1 to 1.25 M.

[0026] The phosphorus precursor may suitably include sodium hypophosphite.

[0027] A substrate on which the nickel copper-phosphide catalyst layer is deposited may be pretreated. The pretreatment may be an oxygen plasma etching process.

[0028] In another aspect, provided is an electrocatalyst including an oxygen generation electrode and a hydrogen generation electrode which may be manufactured by the method described herein. At least one of the electrodes may include a substrate and a catalyst layer electrodeposited onto the substrate, and the catalyst layer may include greater than about 65 at % of nickel; and less than about 35 at % of copper, based on 100 at % of metal atoms. In preferred aspect, the catalyst layer may include Ni greater than about 66, 70, 75, 80, 85, 90, or 95 at % and include Cu less than about 34, 30, 25, 20, 15, 10 or 5 at %, based on 100 at % of total metal atom. In all the catalyst layer will contain copper, i.e. the amount of copper will be greater than 0 at % or preferably will be at least about 0.5 wt % or greater based on 100 at % of metal atoms.

[0029] The electrocatalyst may include a metal layer between the substrate and the catalyst layer. The metal layer may suitably include a nickel layer or a copper layer.

[0030] According to the various exemplary embodiments, the present invention may provide a simplified process of manufacturing an electrocatalyst and an additive used during an electrodeposition. Further, the method disclosed herein may remove moisture.

[0031] Still further provided is a vehicle part that may include the electrocatalyst as described herein. Exemplary vehicle part may include a headlamp. Also provided is a vehicle including the vehicle part as disclosed herein.

[0032] Other aspects of the invention are disclosed infra.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] FIG. 1 is a flowchart of an exemplary process for manufacturing an exemplary electrocatalyst by a single-step electrodeposition according to an exemplary embodiment of the present invention.

[0034] FIG. 2 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5M) according to the thickness of a nickel layer when the nickel layer is formed on a conductive substrate.

[0035] FIG. 3 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5M) according to the circulation frequency when the range of the potential and the scan rate are -1.2 to 0.2 V and 10 mV/s, respectively.

[0036] FIG. 4 is a graph showing a ratio (at %) of nickel and copper atoms in an exemplary catalyst layer according to the molar ratio of the nickel precursor to the copper precursor in an exemplary embodiment of the present invention.

[0037] FIG. 5 is a linear sweep voltammetry (LSV) graph according to the ratio (at %) of nickel and copper atoms.

[0038] FIG. 6A illustrates XRD patterns and crystal analyses according to the ratio (at %) of nickel and copper atoms in an exemplary embodiment of the present invention, and FIG. 6B enlarges XRD patterns at about 43° to about 45.5° among the diffraction angles in FIG. 6A. FIG. 6C enlarges XRD patterns of $\text{Ni}_{89}\text{Cu}_{11}$ -P illustrated in FIG. 6A.

[0039] FIG. 7A is a transmission electron microscope (TEM) image of a portion in which Ni-rich nickel copper-phosphide in an exemplary $\text{Ni}_{65}\text{Cu}_{35}$ -P catalyst layer appears in an exemplary embodiment of the present invention, and FIG. 7B is a fast Fourier transformed image of FIG. 7A.

[0040] FIG. 8A is a transmission electron microscope image of a portion in which Cu-rich nickel copper-phosphide in an exemplary $\text{Ni}_{65}\text{Cu}_{35}$ -P catalyst layer appears in an exemplary embodiment of the present invention, and FIG. 8B is a fast Fourier transformed image of FIG. 8A.

[0041] FIG. 9A is a transmission electron microscope image of a portion in which Ni_{12}P_5 crystals in an exemplary $\text{Ni}_{65}\text{Cu}_{35}$ -P catalyst layer appear in an exemplary embodiment of the present invention, and FIG. 9B is a fast Fourier transformed image of FIG. 9A.

[0042] FIG. 10A is a transmission electron microscope image of a portion in which Ni_3P crystals in an exemplary $\text{Ni}_{65}\text{Cu}_{35}$ -P catalyst layer appear in an exemplary embodiment of the present invention, and FIG. 10B is a fast Fourier transformed image of FIG. 10A.

[0043] FIG. 11 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the concentration of sodium acetate when the concentration of the nickel precursor is 0.1 M.

[0044] FIG. 12 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the concentration of glycine when the concentration of the nickel precursor is 0.1 M.

[0045] FIG. 13 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the concentration of citric acid when the concentration of the nickel precursor is 0.1 M.

[0046] FIG. 14 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the molar ratio of the nickel precursor to the phosphorus precursor.

[0047] FIG. 15A is an image captured by a scanning electron microscope (SEM) after 10 V is applied to a pretreated OER electrode for 10 minutes, and FIGS. 15B, 15C and 15D are images captured by enlarging the image in FIG. 15A.

[0048] FIG. 16A is an image captured by a scanning electron microscope after 10 V is applied to a non-pretreated OER electrode for 10 minutes, and FIGS. 16B, 16C and 16D are images captured by enlarging the image in FIG. 16A.

[0049] FIG. 17 is a graph comparing the conductivity of an exemplary $\text{Ni}_{91}\text{Cu}_9$ -P electrocatalyst with that of a Ni-P electrocatalyst in an exemplary embodiment of the present invention.

[0050] FIG. 18 is a graph comparing the charge mobility of an exemplary $\text{Ni}_{91}\text{Cu}_9$ -P electrocatalyst with that of a Ni-P electrocatalyst in an exemplary embodiment of the present invention.

[0051] FIG. 19 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) of an exemplary $\text{Ni}_{91}\text{Cu}_9$ -P electrocatalyst in an exemplary embodiment of the present invention, a Pt electrocatalyst, a Ni-P electrocatalyst, a NiCu electrocatalyst, a Ni electrocatalyst, and a Cu electrocatalyst.

[0052] FIG. 20 is a graph measuring a hydrogen evolution reaction (KOH 1 M) of an exemplary $\text{Ni}_{91}\text{Cu}_9$ -P electrocatalyst in an exemplary embodiment of the present invention, a Pt electrocatalyst, a Ni-P electrocatalyst, a NiCu electrocatalyst, a Ni electrocatalyst, and a Cu electrocatalyst.

[0053] FIGS. 21A-21B are scanning electron microscope images when a potential of 10 V is applied to an exemplary HER electrode of an exemplary $\text{Ni}_{91}\text{Cu}_9$ -P electrocatalyst for 10 minutes in an exemplary embodiment of the present invention.

[0054] FIGS. 22A-22B are scanning electron microscope images when a potential of 10 V is applied to an exemplary OER electrode of an exemplary $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst for 10 minutes in an exemplary embodiment of the present invention.

[0055] FIG. 23 illustrates a current density according to the potential applied to an exemplary $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst in an exemplary embodiment of the present invention.

[0056] FIG. 24A illustrates an exemplary $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst in an exemplary embodiment of the present invention mounted in a headlamp and moisture, and FIG. 24B illustrates a region in which moisture around the $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst is removed.

[0057] FIG. 25 is a graph measuring the current density according to the humidity of an exemplary $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst in an exemplary embodiment of the present invention.

DETAILED DESCRIPTION

[0058] Hereinafter, the present invention will be described in detail. However, the present invention is not limited or restricted by exemplary embodiments, objects and effects of the present invention will be naturally understood or become apparent from the following description, and the objects and effects of the present invention are not limited by only the following description. Further, in the description of the present invention, when it is determined that the detailed description for the publicly-known technology related to the present invention can unnecessarily obscure the gist of the present invention, the detailed description thereof will be omitted.

[0059] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. As used herein, the singular forms “a,” “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprise,” “include,” “have,” etc. when used in this specification, specify the presence of stated features, regions, integers, steps, operations, elements and/or components but do not preclude the presence or addition of one or more other features, regions, integers, steps, operations, elements, components, and/or combinations thereof.

[0060] It is understood that the term “vehicle” or “vehicular” or other similar term as used herein is inclusive of motor vehicles in general such as passenger automobiles including sports utility vehicles (SUV), buses, trucks, various commercial vehicles, watercraft including a variety of boats and ships, aircraft, and the like, and includes hybrid vehicles, electric vehicles, plug-in hybrid electric vehicles, hydrogen-powered vehicles and other alternative fuel vehicles (e.g. fuels derived from resources other than petroleum). As referred to herein, a hybrid vehicle is a vehicle that has two or more sources of power, for example both gasoline-powered and electric-powered vehicles.

[0061] Further, unless specifically stated or obvious from context, as used herein, the term “about” is understood as within a range of normal tolerance in the art, for example within 2 standard deviations of the mean. “About” can be understood as within 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, 0.5%, 0.1%, 0.05%, or 0.01% of the stated value. Unless otherwise clear from the context, all numerical values provided herein are modified by the term “about.”

[0062] FIG. 1 is a flowchart of the present invention which manufactures an exemplary electrocatalyst by a single-step electrodeposition in an exemplary embodiment of the present invention. As shown in FIG. 1, the present invention may include forming a metal layer on a substrate (S101), treating the surface of the metal layer, for example, hydrophilic surface treatment (S102), and forming a catalyst layer, e.g., nickel copper-phosphide catalyst layer, on the metal layer by applying potential to an aqueous deposition solution including a nickel precursor, a copper precursor, a phosphorus precursor, and an additive (S103).

[0063] The single-step electrodeposition may suitably include forming a nickel copper-phosphide catalyst layer with single electrodeposition, and the nickel copper-phosphide catalyst layer may suitably include a catalyst layer having a crystal structure in which phosphorus may be deposited into an interstitial site of nickel and copper ions may be deposited by substituting nickel atoms located in the nickel interstices with copper ions.

[0064] As the substrate, a glass or silicon wafer may suitably be used, and a metal layer formed on the substrate may suitably include a nickel layer or a copper layer. Moreover, the metal layer may be formed by sputtering or electron beam. However, the deposition method may not be limited thereto as long as the deposition method does not affect the electrodeposition of an aqueous deposition solution.

[0065] FIG. 2 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the thickness of a nickel layer when the nickel layer is formed on a conductive substrate. As shown in FIG. 2, the nickel layer may suitably have a thickness of about 50 to 300 nm. Since a metal layer such as a nickel layer serves as a channel to transfer electric charges during an electrodeposition, the thickness thereof is not necessarily limited to 50 to 300 nm.

[0066] The treating of the metal layer such as hydrophilic surface treatment may be a UV-ozone cleaning treatment. The hydrophilic surface treatment may increase the bonding strength between the surface of a substrate and an aqueous deposition solution including a precursor by surface modification, for example, forming a hydroxyl group (—OH). In addition, the hydrophilic surface treatment may prevent bubbles from being generated on the surface of the substrate during the electrodeposition. However, the hydrophilic surface treatment is not limited thereto, and a surface treatment using plasma and the like may suitably be used.

[0067] When a nickel copper-phosphide catalyst layer is formed, the potential may be applied by a cyclic voltammetry method. The potential applied may be set as to be less than reduction potentials of nickel, copper, and phosphorus (e.g., +0.272 V, +0.859 V, and 0.348 V, respectively vs Ag/AgCl), and preferably, the range of the potential may be about -1.2 to 0.2 V.

[0068] The frequency (circulation frequency) at which about -1.2 to 0.2 V is applied may be about 3 to 15 times. When the circulation frequency is less than 3 times, the nucleation followed by the growth of the ion catalyst layer may not uniformly occur over the entire region of the metal layer, and when the circulation frequency is greater than 15 times, catalyst characteristics may deteriorate.

[0069] FIG. 3 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the circulation frequency when the range of the potential and the scan rate are -1.2 to 0.2 V and 10 mV/s, respectively. As shown in FIG.

3, the hydrogen generation effects of electrocatalysts manufactured by setting the circulation frequency to 3 times to 15 times may be better than those of electrocatalysts manufactured by setting the circulation frequency to 1 time, 2 times, and 20 times.

[0070] When the circulation frequency is set to 3 times to 15 times, the catalyst layer may be formed uniformly over the entire region of the metal layer, and catalyst characteristics may not deteriorate. However, the nickel copper-phosphide catalyst layer may also be formed by using a constant current method (10 to 20 mA/cm²) instead of a cyclic voltammetry method.

[0071] The molar ratio of the nickel precursor to the copper precursor included in the aqueous deposition solution of the present invention may be greater than about 49:1. The molar ratio will be described below in detail.

[0072] FIG. 4 is a graph showing a ratio (at %) of nickel and copper atoms in the catalyst layer according to the molar ratio of the nickel precursor to the copper precursor, and FIG. 5 is a linear sweep voltammetry graph according to the ratio (at %) of nickel and copper atoms. Tables 1 and 2 show the results of measuring the ratio of nickel and copper atoms in the catalyst layer according to the molar ratio of nickel and copper precursors by EDX, and over voltages at 10 mA/cm² when each catalyst layer is used as a catalyst layer of a hydrogen generation electrode, respectively.

TABLE 1

	Molar ratio of nickel and copper precursors				
	100:0	499:1	199:1	99:1	49:1
	Composition of catalyst layer				
	Ni—P	Ni ₉₃ Cu ₇ —P	Ni ₉₁ Cu ₉ —P	Ni ₈₉ Cu ₁₁ —P	Ni ₆₅ Cu ₃₅ —P
Overvoltage (mV)	-82	-69	-48	-66	-126

TABLE 2

	Molar ratio of nickel and copper precursors		
	24:1	10.1:1	0:100
	Composition of catalyst layer		
	Ni ₃₆ Cu ₆₄ —P	Ni ₂₃ Cu ₇₇ —P	Cu—P
Overvoltage (mV)	-259	-247	-359

[0073] As shown in FIGS. 4 and 5 and Tables 1 and 2, the nickel precursor and the copper precursor may suitably be included at a molar ratio of about 199:1 in the aqueous deposition solution, and when the nickel copper-phosphide catalyst layer is composed of about 91 at % of nickel and about 9 at % of copper based on 100 at % of metal atoms, that is, the Ni₉₁Cu₉—P catalyst layer is used as a catalyst layer of a hydrogen generation electrode, the overvoltage measured at a current density of 10 mA/cm² is -48 mV, which is the lowest value.

[0074] The over voltages measured from the Ni₉₃Cu₇—P catalyst layer, the Ni₉₁Cu₉—P catalyst layer or the Ni₈₉Cu₁₁—P catalyst layer formed from aqueous deposition solutions in which the molar ratio of the nickel precursor to the copper precursor was 499:1, 199:1, or 99:1 were lower

than the overvoltage measured from the Ni—P catalyst layer formed from the aqueous deposition solution including no copper precursor.

[0075] These results are shown because electric charges accumulated between nickel and phosphorus are decreased by doping the nickel-phosphorus catalyst layer with copper. In other words, free electrons may be increased, and the hydrogen adsorption energy may converge to 0.

[0076] Meanwhile, when the molar ratio of the nickel precursor to the copper precursor in the aqueous deposition solution is equal to or less than about 49:1, that is, the ratio of copper atoms is about 35 at % or greater, catalyst characteristics rapidly may deteriorate. For example, because a nickel copper-phosphide layer with a uniform composition is not formed as the copper-phosphide is first deposited onto the metal layer as described below, the phase separation occurs.

[0077] Accordingly, the nickel precursor and the copper precursor may be included at a ratio greater than a molar ratio of the nickel precursor and the copper precursor included in the aqueous deposition solution of the present invention of about 49:1 where catalyst characteristics rapidly deteriorate.

[0078] FIG. 6A illustrates XRD patterns and crystal analyses according to the ratio (at %) of nickel and copper atoms, and FIG. 6B enlarges XRD patterns at about 43° to about

45.5° among the diffraction angles in FIG. 6A. FIG. 6C enlarges XRD patterns of the Ni₈₉Cu₁₁—P catalyst layer illustrated in FIG. 6A. Table 3 shows the crystals where the peaks appear and the positions of the peaks.

TABLE 3

	Cu (200)	Ni (200)	Cu (111)	Ni (111)
Peak angle	43.63°	44.66°	50.95°	51.98°

[0079] As shown in FIGS. 6A to 6C and Table 3, when the catalyst layer includes 7 at % or greater of copper atoms, peaks appear at 44.66° and 51.98°, corresponding to a Ni (200) surface and a Ni (111) surface, and accordingly, the nickel copper-phosphide catalyst layer may be formed by the analysis of XRD patterns.

[0080] In the Ni₈₉Cu₁₁—P catalyst layer, peaks appeared at 44.66° and 51.98°, whereas peaks appeared very finely at 43.63° and 50.95° corresponding to the Cu (200) surface and the Cu (111) surface. For instance, as the copper-phosphide was first deposited onto the metal layer, the phase separation finely occurred with a copper-phosphide and a nickel-phosphide. However, since the Ni₈₉Cu₁₁—P catalyst layer exhibits an overvoltage lower than those of the Ni—P catalyst layer and the Ni₉₃Cu₇—P catalyst layer, the effect of increasing the electric conductivity according to the addition

(doping) of copper more significantly may act than the effect caused by the formation of a non-uniform catalyst layer.

[0081] In the $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer, the $\text{Ni}_{36}\text{Cu}_{64}$ —P catalyst layer, and the $\text{Ni}_{23}\text{Cu}_{77}$ —P catalyst layer, which had a copper atom ratio greater than about 11 at %, peaks clearly appeared at 43.63° and 50.95° . As a copper precursor at high concentration is included in the aqueous deposition solution, the phase separation of the copper phosphide remarkably appears. Since catalyst characteristics (overvoltage) of each catalyst layer rapidly deteriorate, the nickel precursor and the copper precursor may not be included at a copper atom ratio greater than a copper atom ratio of about 35 at % or at a molar ratio of the nickel precursor to the copper precursor in the aqueous deposition solution, which may be equal to or less than about 49:1. Hereinafter, the phase separation in the $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer will be described in detail.

[0082] FIG. 7A is a transmission electron microscope image of a portion in which Ni-rich nickel copper-phosphide in a $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer appears, and FIG. 7B is a fast Fourier transformed image of FIG. 7(A). As shown in FIG. 7A and FIG. 7B, Ni-rich nickel copper-phosphide may be formed in the $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer because the inverse number of the length of each of an arrow mark indicating a direction of about 8 o'clock and an arrow mark indicating a direction between about 4 o'clock and about 5 o'clock is the same as the (200) surface and the (111) surface corresponding to the crystal surface of the Ni-rich nickel copper-phosphide.

[0083] FIG. 8A is a transmission electron microscope image of a portion in which Cu-rich nickel copper-phosphide in a $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer appears, and FIG. 8B is a fast Fourier transformed image of FIG. 8A. As shown in FIGS. 8(A) and 8(B), Cu-rich nickel copper-phosphide may be formed in the $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer because the inverse number of the length of each of an arrow mark indicating a direction of about 6 o'clock and an arrow mark indicating a direction between about 2 o'clock and about 3 o'clock is the same as the (100) surface and the (200) surface corresponding to the crystal surface of the Cu-rich nickel copper-phosphide.

[0084] FIG. 9A is a transmission electron microscope image of a portion in which Ni_{12}P_5 crystals in a $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer appear, and FIG. 9B is a fast Fourier transformed image of FIG. 9A. As shown in FIGS. 9S-9B, Ni_{12}P_5 crystals are formed in the $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer because the inverse number of the length of each of an arrow mark indicating a direction of about 1 o'clock and an arrow mark indicating a direction between about 7 o'clock and about 8 o'clock is the same as the (420) surface and the (321) surface corresponding to the Ni_{12}P_5 crystal surface.

[0085] FIG. 10A is a transmission electron microscope image of a portion in which Ni_3P crystals in a $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer appear, and FIG. 10B is a fast Fourier transformed image of FIG. A. As shown in FIGS. 10A-10B, Ni_3P crystals may be formed in the $\text{Ni}_{65}\text{Cu}_{35}$ —P catalyst layer because the inverse number of the length of each of an arrow mark indicating a direction of about 1 o'clock and an arrow mark indicating a direction of about 7 o'clock is the same as the (330) surface and the (321) surface corresponding to the Ni_3P crystal surface.

[0086] Meanwhile, the molar concentration of the nickel precursor may be about 0.02 to 0.5 M, and the nickel

precursor may be at least one or more of nickel sulfate, nickel nitrate, or nickel acetate.

[0087] The concentration of the copper precursor may be about 0.001 to 0.02 M, and the copper precursor may suitably include one or more selected from copper sulfate, copper nitrate, copper acetate, and copper acetylacetonate.

[0088] The additive included in the aqueous deposition solution of the present invention includes sodium acetate, and may further include glycine or citric acid. Sodium acetate as used herein may regulate the reduction rate of metal ions by maintaining the pH and regulating the deposition reaction, and glycine and citric acid may be a so-called complexing agent which may inhibit metal ions from being bonded to oxygen, hydrogen, and the like which may be easily bonded and promotes the bonding of metal ions to phosphorus (P).

[0089] A molar ratio of the nickel precursor included in the aqueous deposition solution of the present invention to sodium acetate, glycine, or citric acid may be about 1:about 0.5 or greater and about 1:less than about 2. When the molar ratio is about 1:about 2 or greater, the bonding strength between the metal ions and the additive may be increased, so that uniform electrodeposition may not be achieved. Accordingly, catalyst characteristics may deteriorate.

[0090] FIG. 11 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the concentration of sodium acetate when the concentration of the nickel precursor is 0.1 M, FIG. 12 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the concentration of glycine when the concentration of the nickel precursor is 0.1 M, and FIG. 13 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the concentration of citric acid when the concentration of the nickel precursor is 0.1 M.

[0091] As shown in FIGS. 11 to 13, when the molar ratio of the nickel precursor to sodium acetate, glycine, or citric acid is about 1:0.5 and 1:1, the excellent hydrogen generation effect may be exhibited, but when the molar ratio is about 1:2, the hydrogen generation effect deteriorates.

[0092] Meanwhile, a molar concentration of each of sodium acetate, glycine, and citric acid may be about 0.05 to 0.1 M, and glycine or citric acid may be suitably used. However, glycine and citric acid may be used in mixture as long as the bonding and reaction between glycine and citric acid may not affect the role of the complexing agent.

[0093] The aqueous deposition solution of the present invention may be an aqueous solution with a molar ratio of the nickel precursor to the phosphorus precursor of about 1:about 5 or greater and about 1:less than about 20. When the molar ratio is 1:5 or greater, electrodeposition may be achieved without an ion strengthening agent (for example, SDS, Na_2SO_4 , and the like) and a pH adjusting agent (for example, aqueous ammonia) used for the electrodeposition, and when the molar ratio is 1:20 or greater, characteristics of the electrocatalyst may deteriorate.

[0094] FIG. 14 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) according to the molar ratio of the nickel precursor to the phosphorus precursor, and Table 4 shows over voltages measured at 10 mA/cm² when the molar ratio of the nickel precursor to the phosphorus precursor is varied.

TABLE 4

	Molar ratio of nickel and phosphorus precursors			
	1:2	1:5	1:10	1:20
Overvoltage (mV)	-85	-82	-74	-84

[0095] As shown in FIG. 14 and Table 4, when the molar ratio of the nickel precursor to the phosphorus precursor is 1:5 and 1:10, the hydrogen generation effect may be substantially improved, whereas when the molar ratio of the precursors is 1:2 or 1:20, the hydrogen generation effect may deteriorate. Meanwhile, the molar concentration of the phosphorus precursor may be about 0.1 to 1.25 M, and the phosphorus precursor may be sodium hypophosphite.

[0096] A substrate onto which the nickel copper-phosphide catalyst layer is deposited may be pretreated, for example, a substrate to be used as an OER electrode may be pretreated. When an electrocatalyst is etched at high potential, the electrocatalyst may be damaged due to the sharp increase of current, so that the electrocatalyst may be pretreated in order to improve the durability of the electrocatalyst. The pretreatment may be an oxygen plasma etching process, but is not limited thereto.

[0097] FIG. 15A is an image captured by a scanning electron microscope after 10 V is applied to a pretreated OER electrode for 10 minutes, and FIGS. 15B to 15D are images captured by enlarging the image in FIG. 15A. As shown in FIGS. 15A-15D, catalytic reactions were observed at the central longitudinal axis and the central horizontal axis in FIGS. 15A and 15B, but no desiccation crack was observed.

[0098] FIG. 16A is an image captured by a scanning electron microscope after 10 V is applied to a non-pretreated OER electrode for 10 minutes, and FIGS. 16B-16D are images captured by enlarging the image in FIG. 16A. As shown in FIGS. 16A-16D, a plurality of desiccation cracks was observed.

[0099] Thus, the durability of the electrocatalyst including the nickel-copper phosphide catalyst layer may be increased as a pretreatment, for example, an oxygen plasma etching is performed, and the durability against a potential of 10 V may be obtained.

Example

[0100] Hereinafter, a process of manufacturing a $\text{Ni}_{91}\text{Cu}_9\text{—P}$ catalyst layer as the Example of the present invention will be described in detail. However, the Examples described below are only provided for specifically exemplifying or explaining the present invention, and the present invention is not limited thereby.

[0101] A nickel layer was formed to have a thickness of 50 nm on a silicon wafer by using an electron beam deposition apparatus, and the substrate was subjected to hydrophilic surface treatment with a UV ozone cleaner (AC-6, 15 to 20 mW/cm^2) for 10 minutes.

[0102] An aqueous deposition solution was prepared by mixing nickel sulfate, copper sulfate, and sodium hypophosphite, which are a nickel precursor, a copper precursor, and a phosphorus precursor, respectively, and sodium acetate and citric acid, which are additives with distilled water. The molar ratio of the nickel precursor to the copper precursor was adjusted to 199:1, the molar ratio of the nickel precursor

to each additive was adjusted to 1:1, and the molar ratio of the nickel precursor to the phosphorus precursor was adjusted to 1:10.

[0103] After the aqueous deposition solution was purged with a nitrogen gas for 20 minutes, a $\text{Ni}_{91}\text{Cu}_9\text{—P}$ catalyst layer was formed by using an electroplating apparatus. In the formation of the catalyst layer, a three-electrode (counter electrode: graphite rod, reference electrode: Ag/AgCl) cyclic voltammetry method was used. The range of potential to be applied was -1.2 to 0.2 V, the cyclic frequency was set to three times, and the scan rate was set to 10 mV/s .

[0104] A substrate on which the catalyst layer was formed after electrodeposition was washed with ethanol and distilled water in this order, and then dried at room temperature. Among the manufactured substrates, a substrate to be used as an OER electrode was oxygen plasma etched under the conditions of 100 W, 20 Pa, and 100 sccm of O_2 for 30 minutes by using a reactive ion etcher (RIE) apparatus.

[0105] A $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst to be mentioned below refers to an electrocatalyst in which a $\text{Ni}_{91}\text{Cu}_9\text{—P}$ catalyst layer manufactured according to the aforementioned Example is used as a catalyst layer of a HER electrode and/or an OER electrode of the electrocatalyst.

[0106] FIGS. 17 and 18 are graphs comparing the conductivity and charge mobility of a $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst with those of a Ni—P electrocatalyst. As shown in FIGS. 17 and 18, the $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst had greater conductivity over the entire regions of potential than that of the Ni—P electrocatalyst, and the $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst had low resistance because the $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst draws a circle with a relatively smaller diameter toward the x-axis than the Ni—P electrocatalyst.

[0107] FIG. 19 is a graph measuring a hydrogen evolution reaction (H_2SO_4 0.5 M) of a $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst, a Pt electrocatalyst, a Ni—P electrocatalyst, a NiCu electrocatalyst, a Ni electrocatalyst, and a Cu electrocatalyst. Table 5 shows over voltages measured when the current density of each electrocatalyst is 10 mA/cm^2 .

TABLE 5

	Composition of electrocatalyst					
	$\text{Ni}_{91}\text{Cu}_9\text{—P}$	Pt	Ni—P	NiCu	Ni	Cu
Overvoltage (mV)	-48	-129	-82	-406	-338	-439

[0108] As shown in FIG. 19 and Table 5, the $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst had an overvoltage measured at a lower level than the overvoltage of a Pt electrocatalyst, which may be a representative electrocatalyst, and had an overvoltage measured at a lower level than the overvoltage of the Ni—P electrocatalyst. Through FIG. 19 and Table 5, the $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst had an excellent effect in the hydrogen evolution reaction.

[0109] FIG. 20 is a graph measuring an oxygen evolution reaction (KOH 1 M) of a $\text{Ni}_{91}\text{Cu}_9\text{—P}$ electrocatalyst, a Pt electrocatalyst, a Ni—P electrocatalyst, a NiCu electrocatalyst, a Ni electrocatalyst, and a Cu electrocatalyst. Table 6 shows over voltages measured when the current density of each electrocatalyst is 10 mA/cm^2 .

TABLE 6

	Composition of electrocatalyst					
	Ni ₉₁ Cu ₉ —P	Pt	Ni—P	NiCu	Ni	Cu
Overvoltage (mV)	290	>1,000	450	650	590	620

[0110] As shown in FIG. 20 and Table 6, the Ni₉₁Cu₉—P electrocatalyst also had an overvoltage measured at a lower level in the oxygen evolution reaction than the overvoltage of a Pt electrocatalyst, and had an overvoltage measured at a lower level than the overvoltage of the Ni—P electrocatalyst. Through FIG. 20 and Table 6, the Ni₉₁Cu₉—P electrocatalyst also had an excellent effect in the oxygen evolution reaction.

[0111] FIGS. 21A-21B and 22A-22B are scanning electron microscope images when a potential of 10 V is applied to a HER electrode and an OER electrode of a Ni₉₁Cu₉—P electrocatalyst for 10 minutes. As shown in FIGS. 21A-21B and 22A-22B, the HER electrode and the OER electrode may be durable at high potential because no desiccation crack was observed on the surface of the HER electrode and the surface of the OER electrode.

[0112] FIG. 23 illustrates a current density according to the potential applied to a Ni₉₁Cu₉—P electrocatalyst. Table 7 shows the current density when the potential is 2 V, 5 V, 7 V, and 10 V.

TABLE 7

Potential (V)	2	5	7	10
Current density (mA/cm ²)	0.31	0.88	1.33	2.06

[0113] As shown in FIG. 23 and Table 7, because the Ni₉₁Cu₉P-electrocatalyst exhibited a predetermined current density at a potential of 10 V or less, the electrocatalyst was stably operated even though high potential was applied to the electrocatalyst.

[0114] FIG. 24A illustrates a Ni₉₁Cu₉—P electrocatalyst 10 mounted in a headlamp, and FIG. 24B illustrates a region 11 in which moisture around the Ni₉₁Cu₉—P electrocatalyst is removed. As shown in FIGS. 24A-24B, the Ni₉₁Cu₉—P electrocatalyst 10 may be mounted at a lower portion of the inner side surface of a headlamp lens, preferably at a lower end portion of the inner side surface of the lens. Since moisture may remain at the end portion of the headlamp when the lamp is lit, the electrocatalyst may be mounted at a lower portion of the inner side surface of the headlamp lens because moisture produced on the surface of the electrocatalyst device can be removed, and water drops flowing down at the inner side surface of the lens can be broken down. However, the position of the electrocatalyst is not limited as long as the operation of the headlamp and the driver's view are not obstructed.

[0115] FIG. 25 is a graph measuring the current density according to the humidity of the Ni₉₁Cu₉—P electrocatalyst. Table 8 shows the current density when a potential of 10 V is applied and the humidity is 20%, 70%, 90%, and 99%.

TABLE 8

Humidity (%)	20	70	90	99
Current density (mA/cm ²)	0.06	0.3	0.6	1.08

[0116] As shown in FIG. 25 and Table 8, as the humidity is increased, the current density may be increased, and the current density at each humidity may be constantly shown. Moreover, the ability to remove moisture may be constantly maintained while the Ni₉₁Cu₉—P electrocatalyst is stably operated at a potential of 10 V. Meanwhile, in the Ni₉₁Cu₉—P electrocatalyst, 0.1 μ l of water per hour was removed at a humidity of 99%.

[0117] The present invention has been described in detail through representative Examples, but it is to be understood by a person with ordinary skill in the art to which the present invention pertains that various modifications are possible in the above-described Examples within the range not departing from the scope of the present invention. Therefore, the scope of the present invention should not be limited to the above-described Examples but should be determined by not only the claims to be described below but also all the changes or modified forms derived from the claims and the equivalent concept thereof.

EXPLANATION OF REFERENCE NUMERALS AND SYMBOLS

[0118] 10: Ni₉₁Cu₉—P Electrocatalyst

[0119] 11: Region in which moisture is remove

What is claimed is:

1. A method of manufacturing an electrocatalyst, comprising:

forming a metal layer on a substrate;

treating a surface of the metal layer; and

forming a catalyst layer on the surface-treated metal layer by applying potential to an aqueous deposition solution comprising a nickel precursor, a copper precursor, a phosphorus precursor, and an additive,

wherein a molar ratio of the nickel precursor to the copper precursor is greater than about 49:1.

2. The method of claim 1, wherein the metal layer comprises a nickel layer or a copper layer.

3. The method of claim 1, wherein the treating the surface comprises treating the surface using a UV-ozone cleaning treatment.

4. The method of claim 1, wherein the potential is applied by a cyclic voltammetry method.

5. The method of claim 4, wherein a range of the potential is of about -1.2 to 0.2 V.

6. The method of claim 5, wherein a frequency at which the range of the potential is applied is of about 3 to 15 times.

7. The method of claim 1, wherein a molar concentration of the nickel precursor is of about 0.02 to 0.5 M.

8. The method of claim 1, wherein the nickel precursor comprises one or more of nickel sulfate, nickel nitrate, and nickel acetate.

9. The method of claim 1, wherein a molar concentration of the copper precursor is of about 0.001 to 0.02 M.

10. The method of claim 1, wherein the copper precursor comprises one or more of copper sulfate, copper nitrate, copper acetate, and copper acetylacetonate.

11. The method of claim **1**, wherein the additive comprises sodium acetate, and further comprises glycine or citric acid.

12. The method of claim **11**, wherein a molar ratio of the nickel precursor to sodium acetate, glycine, or citric acid is about 1:about 0.5 or greater and about 1:less than about 2.

13. The method of claim **11**, wherein a molar concentration of each of sodium acetate, glycine, and citric acid is of about 0.05 or greater and less than about 0.2 M.

14. The method of claim **1**, wherein a molar ratio of the nickel precursor to the phosphorus precursor is of about 1:5 to 1:20.

15. The method of claim **1**, wherein a molar concentration of the phosphorus precursor is of about 0.1 to 1.25 M.

16. The method of claim **1**, wherein the phosphorus precursor comprises sodium hypophosphite.

17. The method of claim **1**, wherein the substrate is pretreated using an oxygen plasma etching process.

18. An electrocatalyst comprising an oxygen generation electrode and a hydrogen generation electrode,

wherein at least one of the electrodes comprises a substrate and a catalyst layer electrodeposited onto the substrate, and the catalyst layer comprises greater than about 65 at % of nickel; and less than about 35 at % of copper, based on 100 at % of metal atoms.

19. The electrocatalyst of claim **18**, further comprising a metal layer between the substrate and the catalyst layer.

20. The electrocatalyst of claim **19**, wherein the metal layer comprises a nickel layer or a copper layer.

21. A vehicle part comprising an electrocatalyst of claim **19**.

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