Amorphous Ni-Fe Double Hydroxides Hollow Nanocubes Enriched with Oxygen Vacancies as Efficient Electrocatalytic Water Oxidation Catalyst

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Experimental section

Materials.

All chemicals used in this study were of analytical grade and used without further purification. Purified water (18.25 M Ω ·cm) for the experiments was attained from a Molecular Lab Water Purifier.

Synthesis of Cu₂O nanocubes.

Cu₂O nanocubes were synthesized using a similar method with previously reported work.¹ Briefly speaking, 0.34 g CuCl₂·2H₂O was dissolved in 200 mL deionized water. Then 20 mL 2 M NaOH was dropwisely into the solution at the temperature of 30°C. After 30 min stirring, 20 mL 0.6 M ascorbic acid added to the above solution with another 30 min agitation. The resulting precipitate was collected and washed with deionized water and absolute ethanol for several times by centrifugation, dried at 40°C in air for 12 h.

Preparation of Ni-Fe amorphous double hydroxides.

The Ni-Fe amorphous double hydroxides were prepared according to Pearson's hard and soft acid-base (HSAB) principle by using Cu₂O nanocubes as soft template.² 20 mg of obtained Cu₂O was dispersed into 40 mL deionized water and absolute ethanol mixed solvent (volume ratio = 1:1); Then 10 mg of different molar ratios FeCl₂·4H₂O, and NiCl₂·6H₂O were dissolved in this solution with the present of 0.3333 g PVP (Mw = 30,000). After magnetic stirring 15 min, Na₂S₂O₃ solution (1 mol/L, 16 mL) was added dropwise into the above solution for another 30 min. Finally, the resulting products were washed with deionized water and anhydrous ethanol, dried in an electric oven at 40 °C for 12 h. The as-synthesized Cu₂O nanocubes are regradually removed by forming a soluble $[Cu_2(S_2O_3)_x]^{2-2x}$ complex when reacting with Na₂S₂O₃ solution, and then abundant amount of OH⁻ ions are released at the etching interface. Simultaneously, Ni²⁺ and Fe²⁺ species can coprecipitate with these OH⁻ ions at the etching interface to generate Ni-Fe double hydroxides hollow nanocubes by inheriting the geometries of Cu₂O templates. The general chemical route could be described as

$$Cu_2O + x S_2O_3^{2-} + H_2O \rightarrow [Cu_2(S_2O_3)_x]^{2-2x} + 2OH^{-}$$
(1)

$$xS_2O_3^{2-}+H_2O\rightleftharpoons HS_2O_3^{2-}+OH^-$$
(2)

$$Fe^{2+} Ni^{2+} + yOH^{-} + O_2^{+} H_2O \rightarrow Ni_xFe_{1-x}(OH)_y$$
(3)

Materials characterization.

Powder X-ray diffraction (PXRD) data were conducted on a PANalytical X'Pert Pro Diffractometer operating at a voltage of 40 kV and a current of 40 mA with Cu Ka radiation (λ = 1.5418 A) from 10 to 80 degrees (2 θ). Field emission scanning electron microscopy (FESEM) observations were gathered on a Hitachi S-4800 microscope performing at an accelerating voltage of 20.0 kV. Transmission electron microscopy (TEM) images were collected with a JEOLJEM-2010 instrument operating at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were acquired using an ESCALab220i-XL electron spectrometer.

2.5. Electrochemical measurements.

5 mg of Ni-Fe powder was dispersed in mixture of distilled water and ethanol (3:1 v/v, 1 mL). Then, 10 μ L 5 wt% Nafion was added to the above solution. The mixed

solution was under sonication condition at least 30 min to form a homogeneous ink. 5 μ L of the mixed solution was drop-casted onto the glassy carbon electrode with the diameter of 3 mm for the electrochemical measurements. All the electrochemical experiments were performed on an electrochemical workstation (CHI760D, CH Instruments Inc., Shanghai) in a typical three-electrode setup with an electrolyte solution of 1 M KOH, using a Pt wire as the counter electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and a modified glassy carbon electrodes as the working electrode. All potentials measured were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059$ pH. AC impedance measurements were carried out at potential of 1.673 V (vs. the RHE) in 1 M KOH from 10⁻¹ to 10⁵ Hz with an AC amplitude of 5 mV. Chronoamperometric responses were obtained at 1.664 V (vs. the RHE) in 1 M KOH. The current density was calculated by the geometric area (0.071 cm²) of the glassy carbon electrode. All data were corrected for ohmic drop.

Calculation of electrochemically active surface area (ECSA).

The calculation of ECSA is based on the measured double layer capacitance of Ni-Fe amorphous double hydroxides in 1 M KOH according to previous report.³ Briefly, a potential range where no apparent Faradic process happened was determined firstly using the static CV. The charging current i_c was measured from CVs at different scan rates. The relation between i_c , scan rate (v) and the double layer capacitance (C_{DL}) was given as below

$$i_c = vC_{DL}$$

Thus, the ECSA can be calculated with C_{DL} and $C_s=0.040$ mF cm⁻² in 1 M KOH adopted from previous reports^{3, 4}.

The roughness factor (RF) can be obtained of geometric surface area (GSA) of the glassy carbon and ECSA by following equation.

$$RF = \frac{ECSA}{GSA}$$

Calculation of Turnover Frequency (TOF).

The TOFs of catalysts were calculated according to the previous report,⁵

$$TOF = \frac{JA}{4Fm}$$

In this equation, J is the current density at a given potential (in our study at the overpotential of 400 mV), A is the surface area of the glassy carbon electrode (0.071 cm²), F is Faraday constant (96485 s A mol⁻¹) and m is the moles number of the metal on the electrodes. In our cases, all the metal sites were actively involved in the electrochemical reaction.



Fig. S1 The powder XRD patterns of fresh Cu₂O.



Fig. S2 XRD patterns of Ni-Fe amorphous double hydroxides.



Fig. S3 SEM image of of Cu_2O .



Fig. S4 SEM images of (a)Ni_{0.88}Fe_{0.12}(OH)_x, (b) Ni_{0.66}Fe_{0.34}(OH)_x and (c) Ni_{0.5}Fe_{0.5}(OH)_x.



Fig. S5 SEM images of $Ni(OH)_2$ (a) and $Fe(OH)_3$ (b).



Fig. S6 XPS spectra of Ni-Fe amorphous double hydroxides: O 1s (a)Ni_{0.88}Fe_{0.12}(OH)_x, (b) Ni_{0.75}Fe_{0.25}(OH)_x, (c) Ni_{0.66}Fe_{0.34}(OH)_x and (d) Ni_{0.5}Fe_{0.5}(OH)_x.



Fig. S7 Cyclic voltammograms of Ni-Fe amorphous double hydroxides on glassy carbon electrodes recorded at a potential sweep rate of 5 mV \cdot s⁻¹ in 1 M KOH.



Fig. S8 LSVs curve compared with different catalysts.



Fig. S9. (a) Mass activity as a function of the overpotential for the Ni-Fe amorphous double hydroxides. (b) Capacitive currents at 1.223 V as a function of scan rate for the Ni-Fe amorphous double hydroxides.



Fig. S10 CVs of different samples measured at different scan rates from 2 to 14 mV s⁻¹: (a)Ni_{0.88}Fe_{0.12}(OH)_x, (b)Ni_{0.75}Fe_{0.25}(OH)_x, (c) Ni_{0.66}Fe_{0.34}(OH)_x, (d) Ni_{0.5}Fe_{0.5}(OH)_x.



Fig. S11 (a) The overpotential of $Ni_{0.88}Fe_{0.12}(OH)_x$, $Ni_{0.75}Fe_{0.25}(OH)_x$, $Ni_{0.66}Fe_{0.34}(OH)_x$ and $Ni_{0.5}Fe_{0.5}(OH)_x$ at 10 mA cm⁻²; (b) The overpotential of $Ni_{0.88}Fe_{0.12}(OH)_x$, $Ni_{0.75}Fe_{0.25}(OH)_x$, $Ni_{0.66}Fe_{0.34}(OH)_x$ and $Ni_{0.5}Fe_{0.5}(OH)_x$ at 20 mA cm⁻².



Fig. S12 Generated oxygen monitored by a Clark electrode in the OER experiment: (a) $Ni_{0.5}Fe_{0.5}(OH)_x$, (b) $Ni_{0.66}Fe_{0.34}(OH)_x$, (c) $Ni_{0.75}Fe_{0.25}(OH)_x$ and (d) $Ni_{0.88}Fe_{0.12}(OH)_x$ at an applied potential of 1.55 V.



Fig. S13 LSVs of the Ni(OH)₂ (a) and Ni_{0.75}Fe_{0.25}(OH)_x (b) at different KOH concentrations.



Fig. S14 (a) Nyquist plots of the Ni(OH)₂ at potential of 1.803 V in different electrolyte pHs, (b) Nyquist plots of the $Ni_{0.75}Fe_{0.25}(OH)_x$ at potential of 1.673 V in different electrolyte pHs.



Fig. S15 Ni2p (a) and Fe 2p (b) XPS spectra of the $Ni_{0.75}Fe_{0.25}(OH)_x$ after electrocatalytic water oxidation.

nanocubes obtained by ICF-AES.	
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Samples	Ni to Fe ratio	Ni to Fe ratio	
	(Theory)	(ICP-AES)	
Ni _{0.88} Fe _{0.12} (OH) _x	7.3:1	7.26:1	
Ni _{0.75} Fe _{0.25} (OH) _x	3:1	3.06:1	
Ni _{0.66} Fe _{0.34} (OH) _x	2:1	2.03:1	
$Ni_{0.5}Fe_{0.5}(OH)_x$	1:1	1.06:1	

Table S2. O 1s peaks area for different samples.

Catalyst	Peak 1	Peak 2	Peak 3	Peak 4	O _{voc} %
Ni _{0.5} Fe _{0.5} (OH) _x	26524.77	29643.18	22142.44	17213.45	27.0
Ni _{0.66} Fe _{0.34} (OH) _x	24391.14	30141.21	30159.56	-	28.7
Ni _{0.75} Fe _{0.25} (OH) _x	35365.11	40404.27	23768.75	-	35.5
Ni _{0.88} Fe _{0.12} (OH) _x	26184.32	41098.61	31597.62	-	26.4

Table S3. EIS fitting results of the components of the circuit.

Catalyst	$R_s(\Omega)$	CPE ₁ (10 ⁻	$R_{p}\left(\Omega\right)$	CPE ₂ (10 ⁻³)	$R_{ct}(\Omega)$
		⁶)			
Ni _{0.5} Fe _{0.5} (OH) _x	8.107	35.750	30.590	0.985	45.590
Ni _{0.66} Fe _{0.34} (OH) _x	9.643	38.985	29.820	0.756	43.930
Ni _{0.75} Fe _{0.25} (OH) _x	8.213	39.220	25.990	0.312	37.500
Ni _{0.88} Fe _{0.12} (OH) _x	9.123	40.230	30.230	0.599	64.420

Table S4. Comparison of OER activity data for different catlysts in 1 M KOH.

Catalyst	η at j =10 mA cm ⁻² (mV)	ECSA/cm ²	RF	TOF (s ⁻¹) at η =400 mV
Ni _{0.88} Fe _{0.12} (OH) _x	400	0.76	10.70	0.0075
Ni _{0.75} Fe _{0.25} (OH) _x	310	2.87	40.42	0.0292
Ni _{0.66} Fe _{0.34} (OH) _x	360	1.05	14.79	0.0133
Ni _{0.5} Fe _{0.5} (OH) _x	370	0.88	12.39	0.0110

Table S5. Summary of the electrochemical water oxidation activities of other OER electrocatalysts.

catalysts	electrolyte	η at	10 mA cm ⁻² (mV)	ref
Ni _{0.75} Mn _{0.25} (OH) _x	1 M KOH		310	This work
Co-P films	1 M KOH		345	6
Ni ₂ P nanoparticles	1 M KOH		290	7
Ni ₃ Fe-LDH	1 M KOH		472	8
NiCo-LDH	1 M KOH		334	9
CoCo-LDH	1 M KOH		393	9
NiFe-LDH/carbon	1 M KOH		247	9
nanotubes				
NiCo(OH) _x	1 M KOH		410	10
Graphene-CoO	1 M KOH		420	11
Hollow Co ₃ O ₄	1 M KOH		290	12
microtubes				
NiCo-LDH	1 M KOH		367	13
nanosheets				
Single-layer	1 M KOH		320	14
Ni(OH) ₂				
α -Ni(OH) ₂	1 M KOH		331	15
amorphous	0.1 M KOH		344	16
Ni(OH) ₂				
highly crystallized	1 M KOH	2	>500	17
α-FeOOH				
NiFe bulk	1 M KOH		347	9

Electrolyte	Rs (Ω)	CPE ₁ (10 ⁻⁶)	$R_{p}\left(\Omega\right)$	$CPE_2(10^{-3})$	$R_{ct}\left(\Omega\right)$
0.1 M	15.98	58.300	32.98	0.2006	55.100
0.5 M	11.05	17.020	30.85	0.3835	40.630
1 M	8.213	39.220	29.99	0.3120	37.500

Table S6. EIS fitting results of the components of the circuit shown in Fig. 14b.

Table S7. EIS fitting results of the components of the circuit shown in Fig. 14a.

Electrolyte	$R_s(\Omega)$	CPE(10 ⁻⁶)	$R_{ct}(\Omega)$
0.1 M	16.549	5.182	416.200
0.5 M	11.480	4.962	336.700
1 M	8.993	4.542	277.300

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