Electronic Supplementary Information

Hybrid-metal hydroxyl fluoride nanosheet arrays as a bifunctional electrocatalyst for efficient overall water splitting

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Electrochemical measurements.

Tafel slopes were calculated from the polarization curves using the Tafel equation

$$\eta = a + b \times \log[j] \tag{1}$$

where η is the overpotential, j is the current density, and b is the objective Tafel slope.

The value of turnover frequency (TOF) is obtained as follows

$$TOF = mol\ (O_2)\ s^{-1} / (mol\ active\ sites) = current \times A / (4F \times mol\ active\ sites) \tag{2}$$

$$TOF = mol\ (H_2)\ s^{-1} / (mol\ active\ sites) = current \times A / (2F \times mol\ active\ sites) \tag{3}$$

where current is the current density (mA cm^{-2}) at different overpotentials, A represents the surface area of as-prepared electrode, the number 4 (or 2) means a four- (or two-) electron reaction for OER and HER, respectively. F is the Faraday's constant (96485.3 C mol^{-1}), and the active sites is the number of moles of the active components that are deposited on the substrate of nickel foam.

Experimental Methods.

Materials.

Iron (III) nitrate nonahydrate (98.5%, AR) was purchased from Macklin Biochemical Co., Ltd (Shanghai), Cobalt (II) nitrate hexahydrate (99.0%, AR) and urea (99.0%, AR) were provided by Aladdin Biochemical Technology Development Co., Ltd (Shanghai), ammonium fluoride (98.0%, AR) was bought from Tianjin Chemical Co., Ltd, nickel foam (1.5 mm in thickness) was purchased from Lizhiyuan Intelligent

Technology Co., Ltd (Taiyuan), All chemicals were used without any purification. Ultrapure water (18.25 MX cm) was used throughout.

Pretreated nickel foam.

Nickel foam (NF) ultrasonically for 30 minutes in acetone solution, 1M HCl solution, alcohol and ultrapure water, successively. The pretreated NF was dried in vacuum at 80℃ for the whole night.
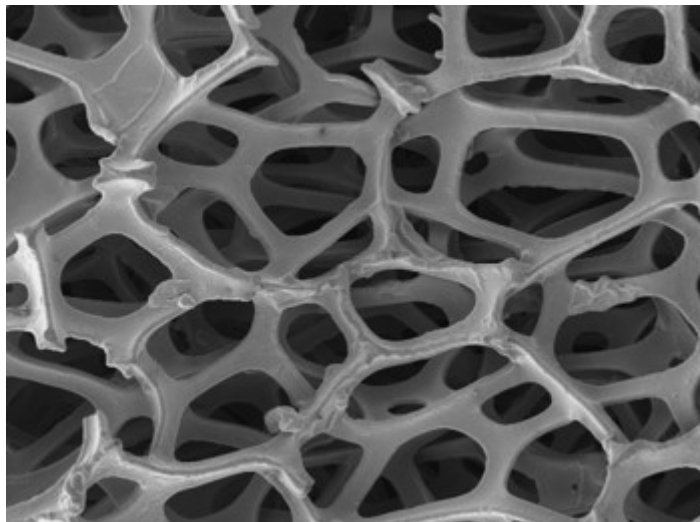
Supplementary Notes.
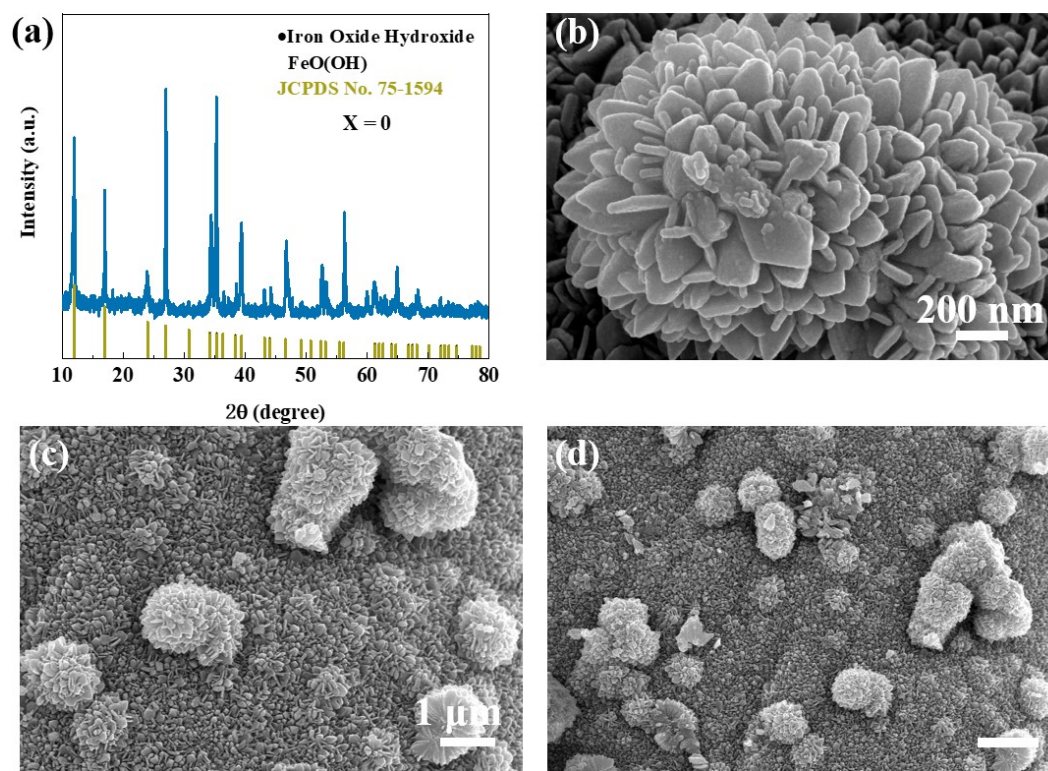

Figure S1. SEM patten of NF.

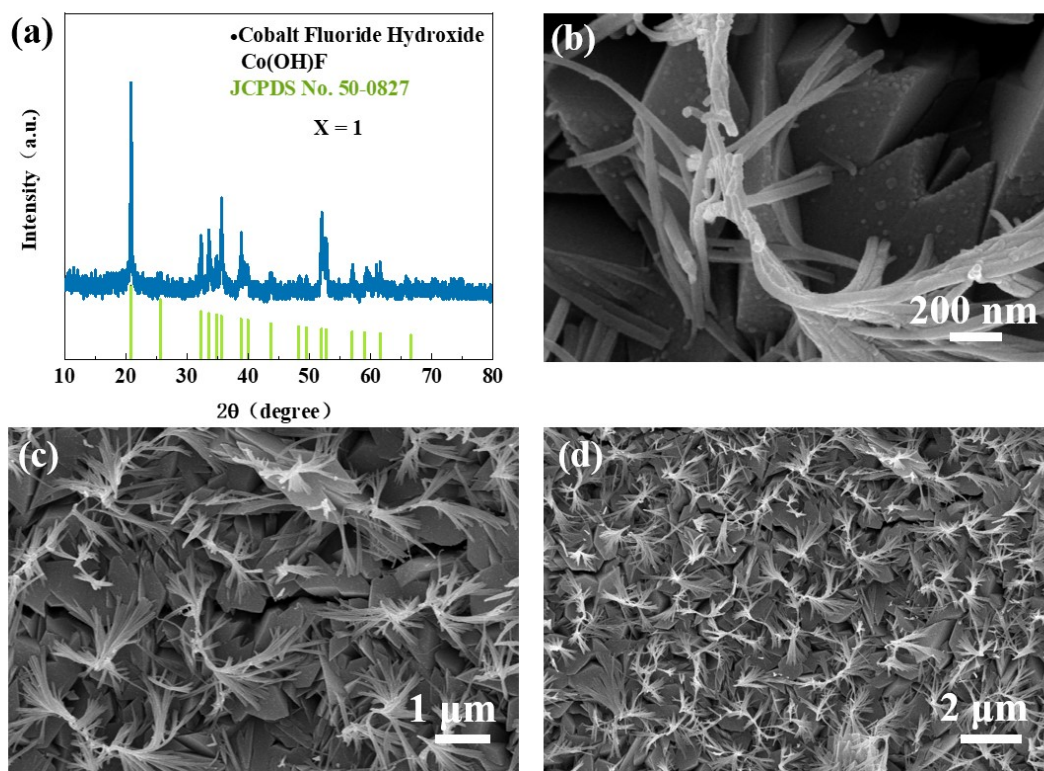**Figure S2.** (a) XRD patten and (b-d) SEM images of FeO(OH).

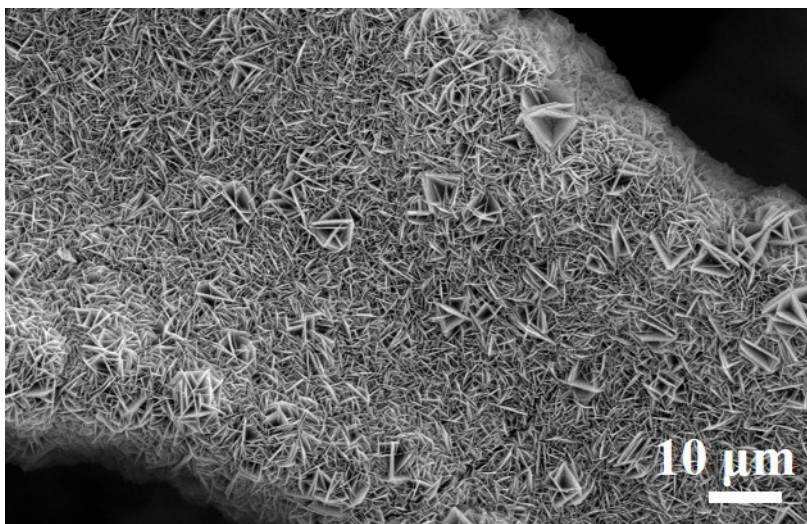**Figure S3.** (a) XRD patten and (b-d) SEM images of Co(OH)F.

Figure S4. SEM patten of $Co_{0.21}Fe_{0.28}(OH)F$.

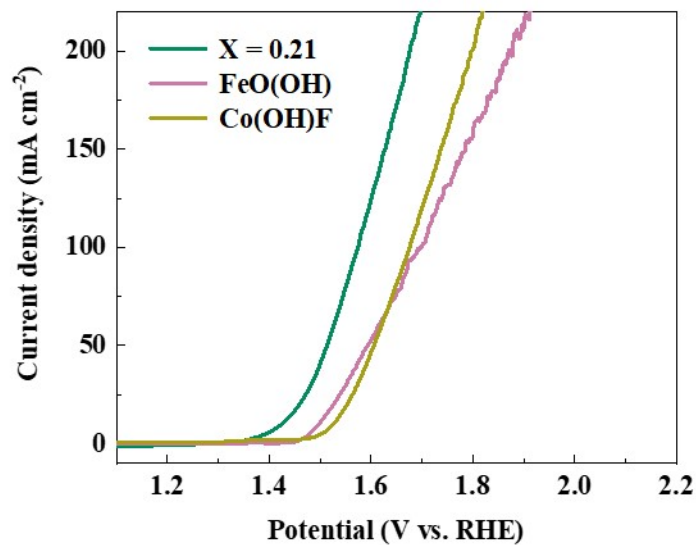**Figure S5.** OER LSV curves of $Co_xFe_y(OH)F$, FeO(OH), and Co(OH)F electrocatalysts 1 M KOH electrolyte.
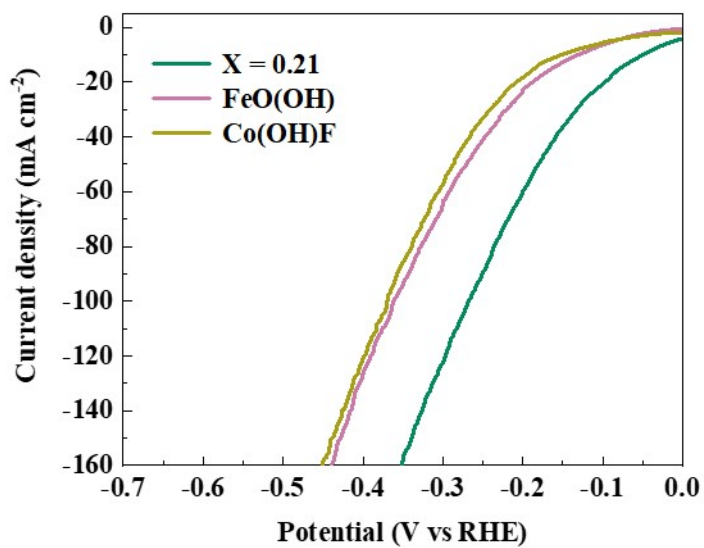
Figure S6. HER LSV curves of $Co_xFe_y(OH)F$, FeO(OH), and Co(OH)F electrocatalysts 1 M KOH electrolyte.

Figure S7. (a) XRD patten and (b-d) SEM images of x = 0.41.

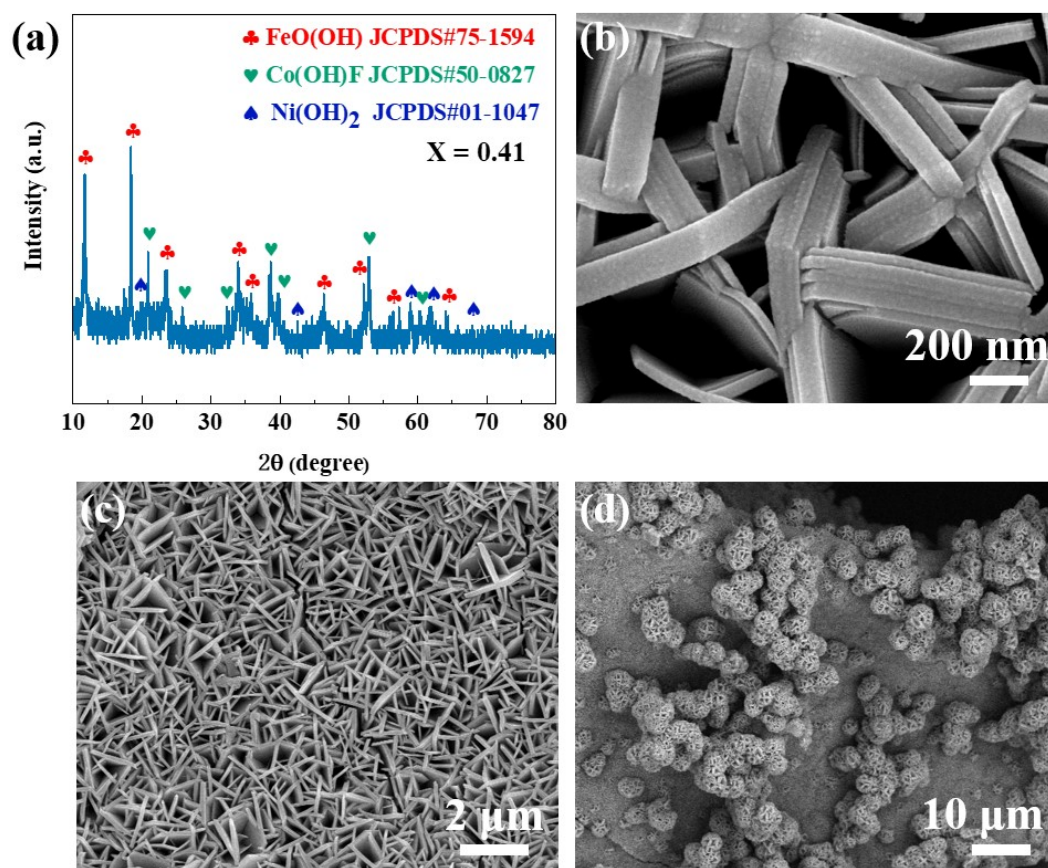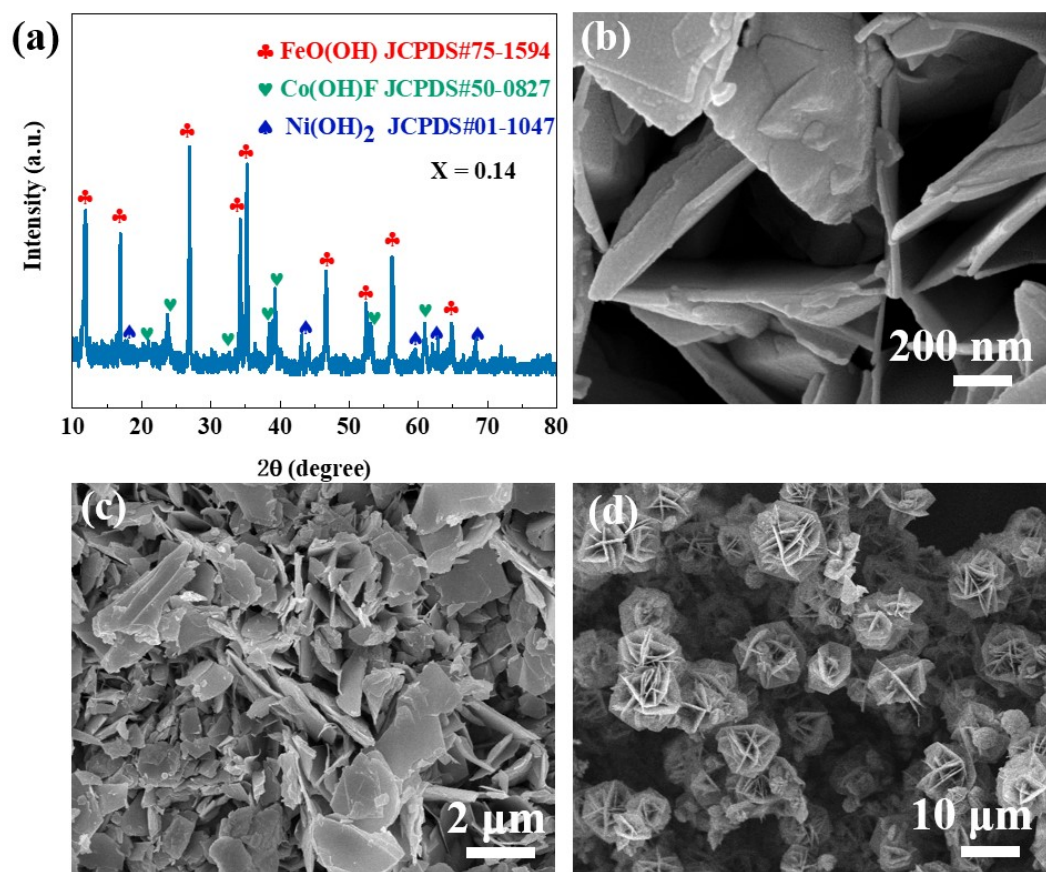**Figure S8.** (a) XRD patten and (b-d) SEM images of x = 0.14.

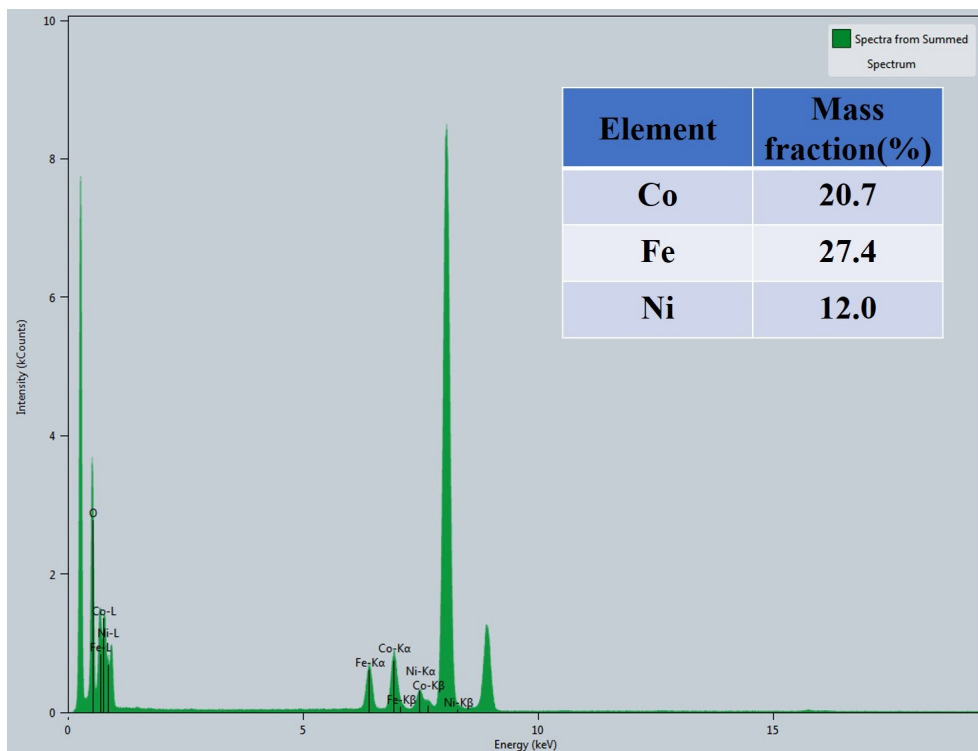**Figure S9.** EDS patten of x = 0.21.
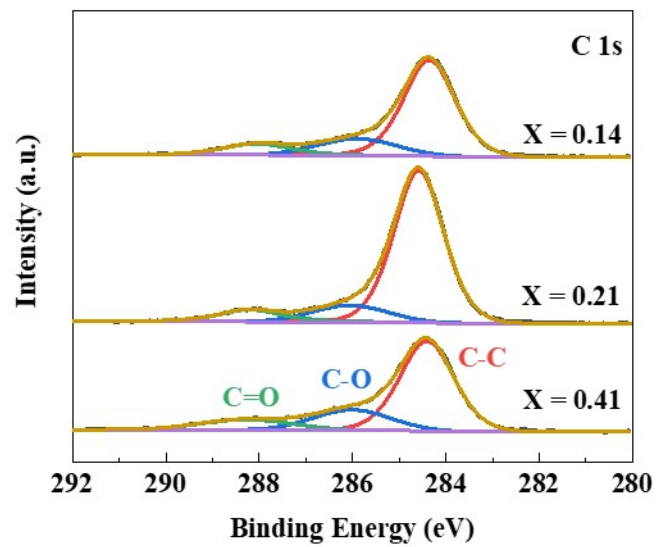
Figure S10. High-resolution XPS spectra of C in x = 0.41, 0.21, and 0.14.
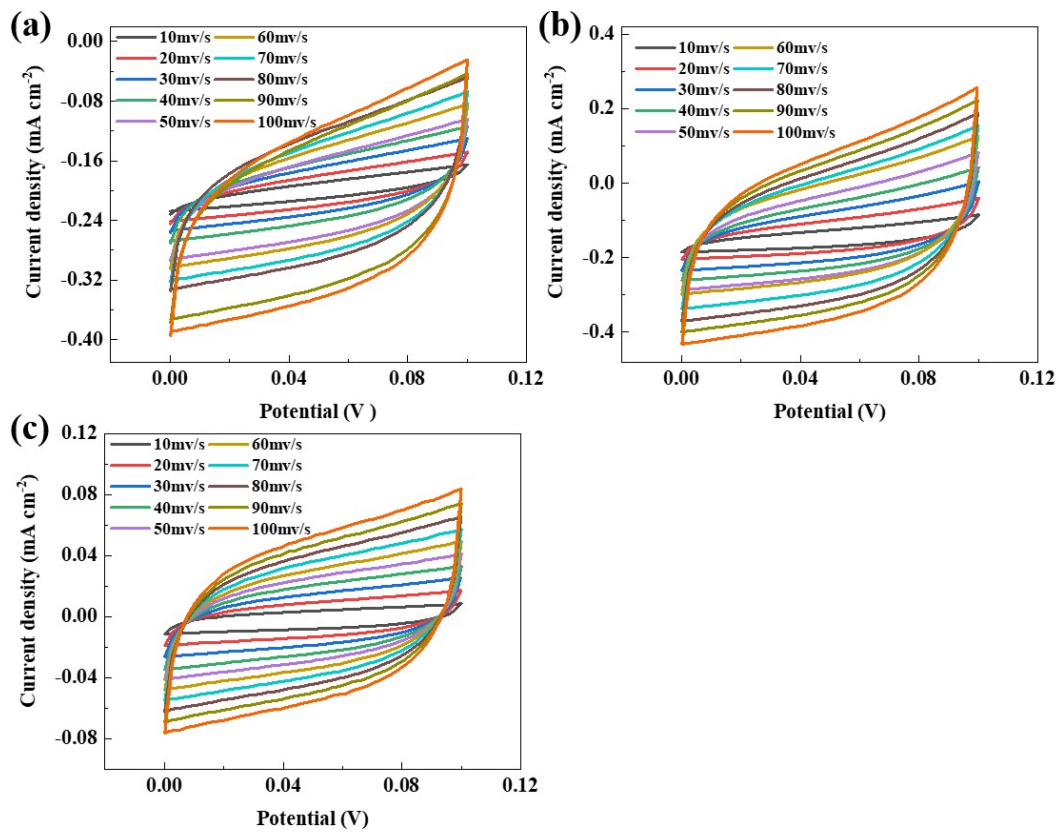
Figure S11. CV curves of $Co_xFe_y(OH)F$ (a) x = 0.41, (b) x = 0.21 and (c) x = 0.14 electrocatalysts at different scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s^{-1} in a non-faradaic region.
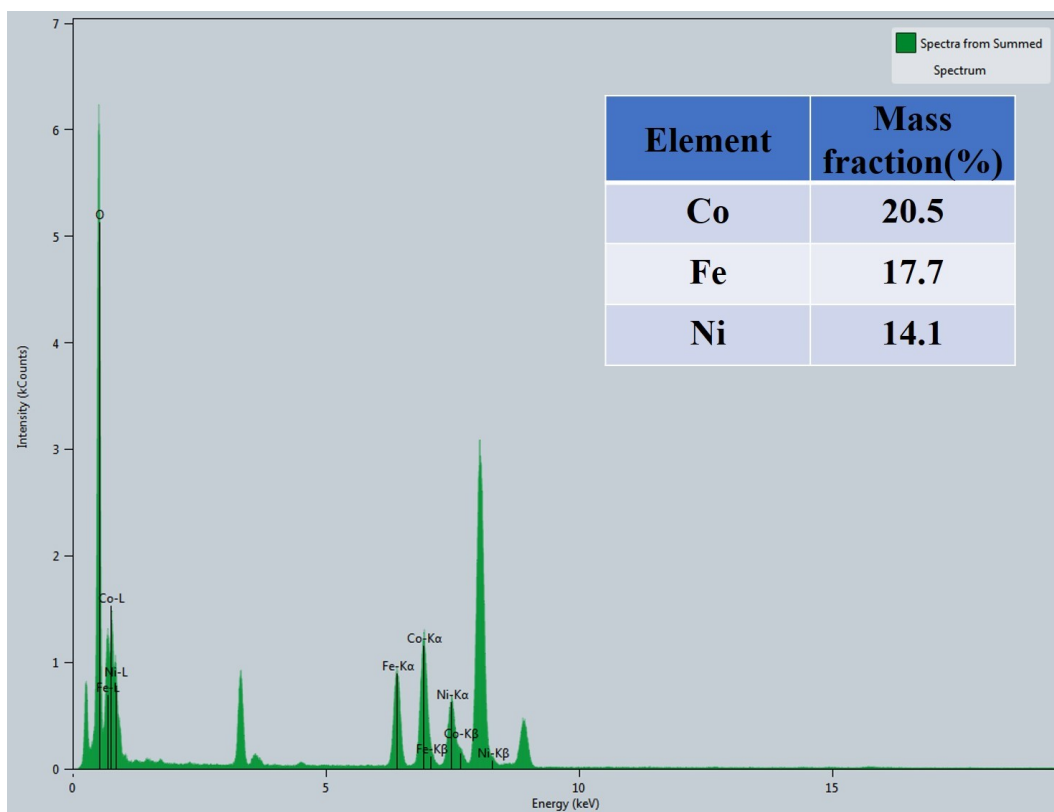
Figure S12. EDS patten of x = 0.21 after 10h OER reaction.
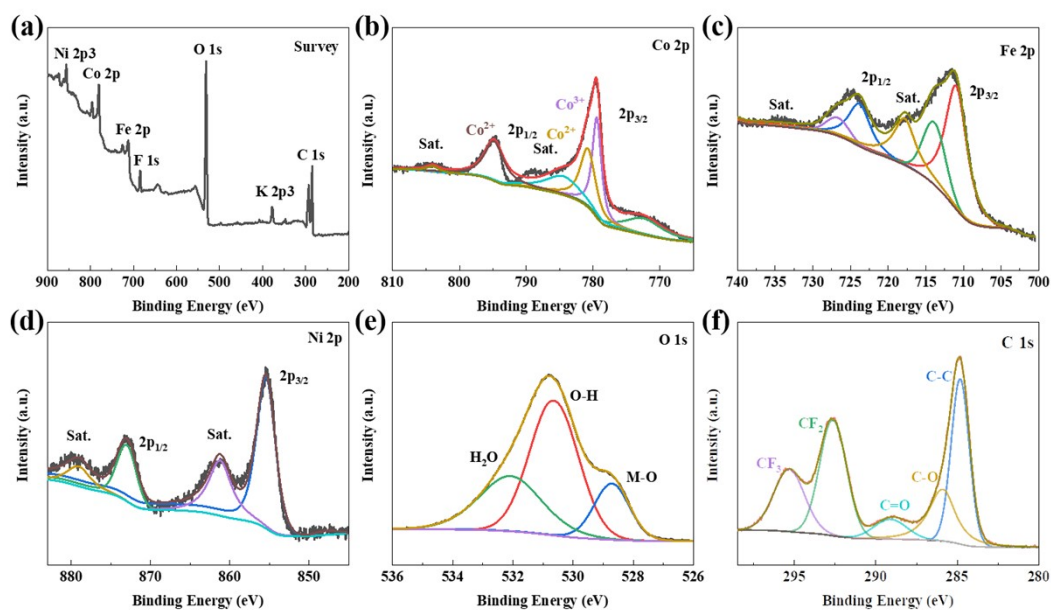
Figure S13. (a) the survey XPS spectra of x = 0.21 after 10h OER reaction. High-resolution XPS spectra of (b) Co, (c) Fe, (d) Ni, (e) O, and (f) C in x = 0.21 after 10h OER reaction.
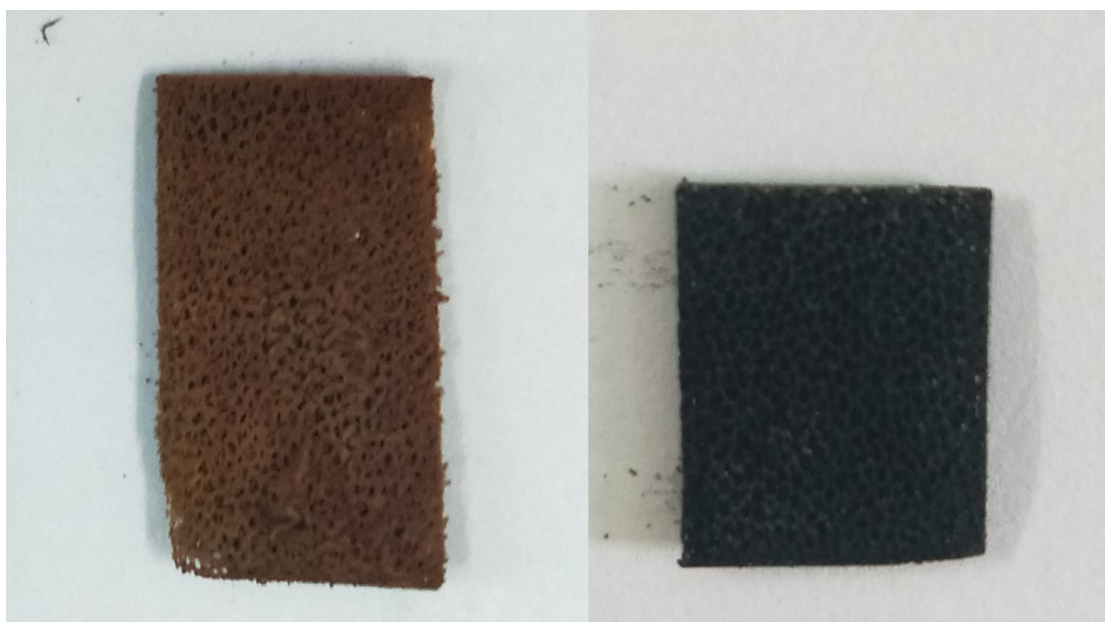
Initial   **After 120h**

Figure S14. Digital photograph of x = 0.21.
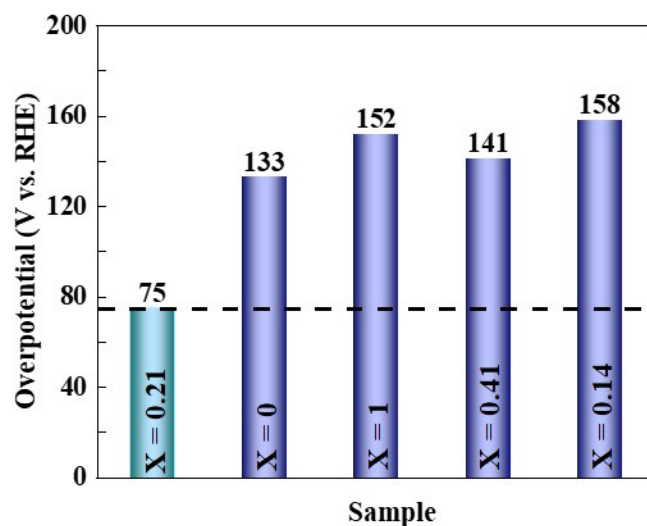
Figure S15. Overpotential derived from the LSV curves the x = 1, 0.41, 0.21, 0.14 and

0 electrocatalysts.
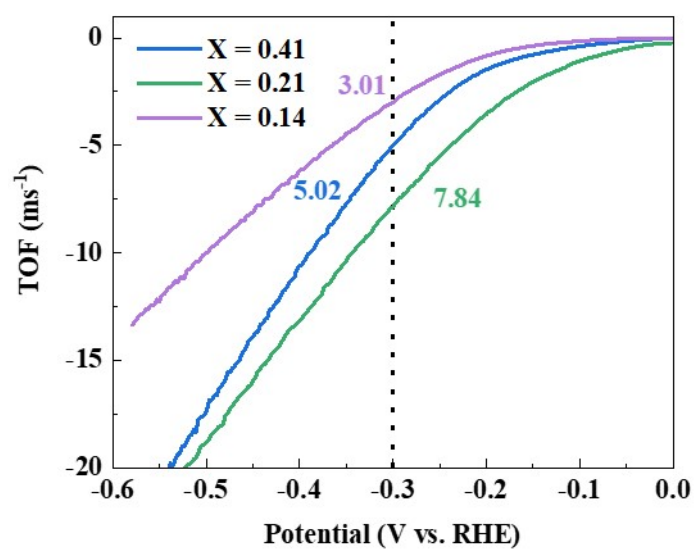
Figure S16. TOF values of the x = 0.41, 0.21, and 0.14 electrocatalysts.
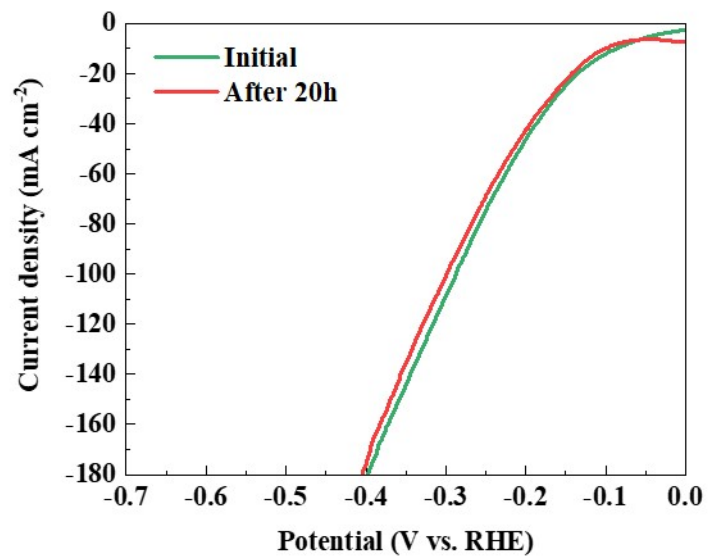
Figure S17. HER LSV of x = 0.21 in 1 M KOH electrolyte before and after running stability measurement.
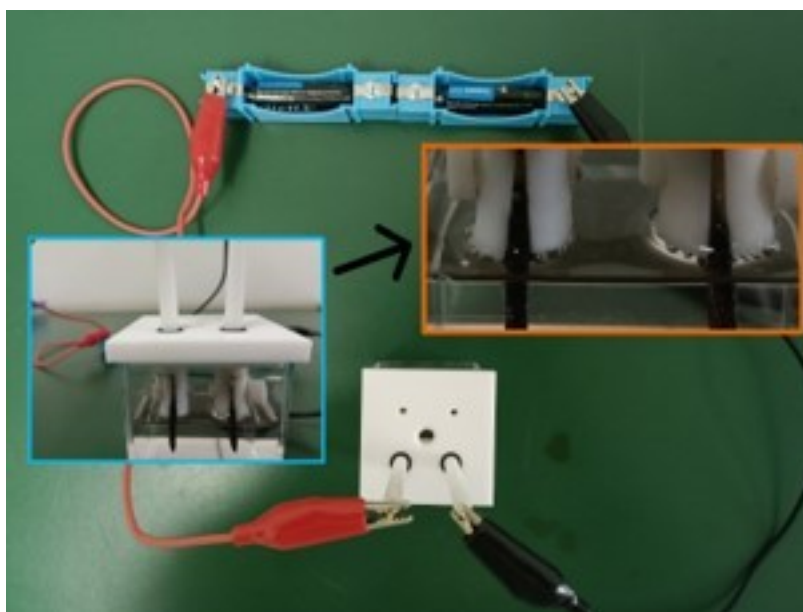
Figure S18. Digital photograph of the x = 0.21‖x = 0.21 cell for driven by two dry batteries.
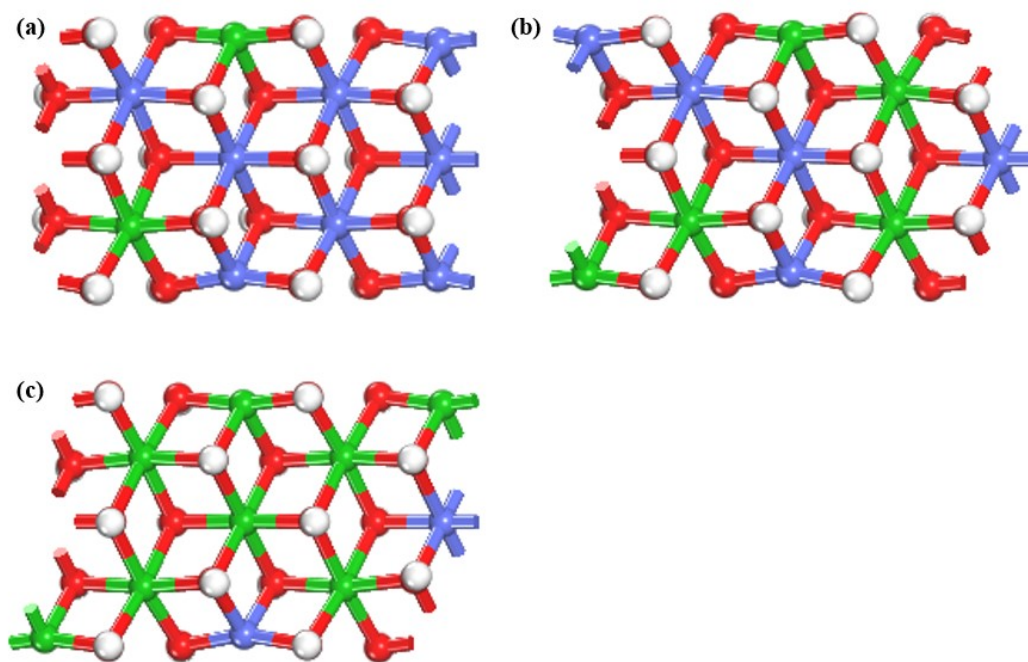
Figure S19. The physical model of CoFe hydroxide with different value of Co/Fe (a) 4:1, (b) 1:1, and (c) 1:4.

(a)

$E_{ads} = -0.55$ $E_{ads} = -0.47$

(b)

$E_{ads} = -0.46$ $E_{ads} = 0.32$

(c)

- ● Co
- ● Fe
- ● O
- ● O_{ads}
- ○ H

- ◯ Co top site
- ◯ Fe top site

$E_{ads} = -1.25$
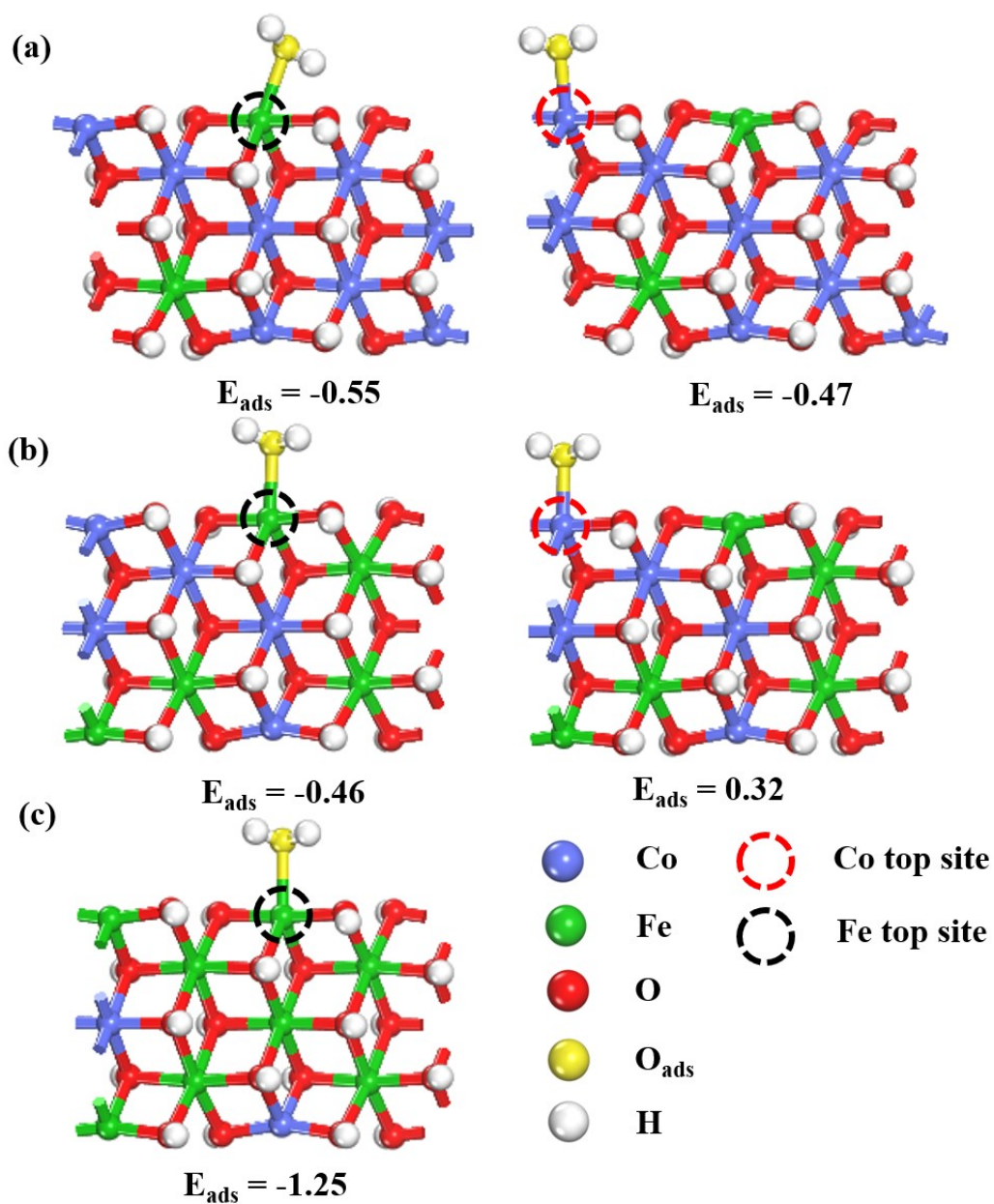
Figure S20. H_2O adsorption with different metal elements as active sites in CoFe hydroxide model on (a) 4:1, (b)1:1, and (c)4:1. In CoFe hydroxide, we calculated the H_2O adsorption of three samples with different metals as active sites, and the results shown that in CoFe hydroxide all Fe sites are favorable for H_2O adsorption, so Fe is selected as the active site.

Table S1. $Co_xFe_y(OH)F$ with different value of x and y load before and after mass (1*2 cm NF).

Sample name	Before the load (g)	After the load (g)	Charge number (g)
X = 0.41	0.0648	0.0808	0.0160
X = 0.21	0.0640	0.0802	0.0162
X = 0.14	0.0698	0.0864	0.0166

Table S2. ICP-MS of $Co_xFe_y(OH)F$ with different value of x and y.

Instrument model		ICP-MS:Aglient 7800									
Instrument parameters	Pump Rate	29r/min									
	Nebulizer Flow	0.86L/min									
	Auxiliary Gas	0.7L/min									
	Sample Flush Time	40s									
	RF Power	1300w									
Molar ratio of input	The sample quality m_0 (g)	The volume of constant volume V_0 (mL)	Test element	Test solution element concentration C_0 (mg/L)	Diluted multiples f	The elemental concentration of the sample digestion solution C_1 (mg/L)	Sample element content C_x (mg/kg)	Sample element content W (%)	Average element content of samples W (%)	Element content ratio of samples	Total average content of Fe and Co in samples (%)
X = 0.41	0.0453	25	Co	0.073	10000	730	402869.8	40.29%	40.84%	2.88	54.99%
	0.0453	25	Co	0.075	10000	750	413907.3	41.39%			
	0.0453	25	Fe	0.255	1000	255	140728.5	14.07%	14.16%		
	0.0453	25	Fe	0.258	1000	258	142384.1	14.24%			
X = 0.21	0.0358	25	Co	0.305	1000	305	212988.8	21.30%	21.33%	0.77	49.06%
	0.0358	25	Co	0.306	1000	306	213687.2	21.37%			
	0.0358	25	Fe	0.395	1000	395	275838.0	27.58%	27.72%		
	0.0358	25	Fe	0.399	1000	399	278631.3	27.86%			
X = 0.14	0.0314	25	Co	0.174	1000	174	138535.0	13.85%	13.77%	0.19	84.63%
	0.0314	25	Co	0.172	1000	172	136942.7	13.69%			
	0.0314	25	Fe	0.088	10000	880	700636.9	70.06%	70.86%		
	0.0314	25	Fe	0.090	10000	900	716560.5	71.66%			

$$Cx(mg/kg) = \frac{C_0(mg/L)*f*V_0*10^{-3}}{m(g)*10^{-3}} = \frac{C_1(mg/L)*V_0(mL)*10^{-3}}{m(g)*10^{-3}} \tag{4}$$

$$W(\%) = \frac{Cx(mg/kg)}{10^6}*100\% \tag{5}$$

M_o: The mass of the sample taken, g, is recorded by the analytical balance;

V_o: After sample digestion, the volume of constant volume, mL;

f: Diluted multiples;

C_o: Measurement of the concentration of elements in a solution, mg/L;

C_1: The elemental concentration of the sample digestion solution, mg/L, $C_1(mg/L) = C_o(mg/L)*f$;

Cx: The final test result of the element under test, mg/kg.

Calculated by the above formula (4); W(%): the final test result of the test element is expressed in the form of percentage and calculated by the above formula (5).

Table S3. ICP-MS and XPS analysis of with different value of x and y.

		ICP-MS		XPS	
		Average element content		Area ratio of sample	
Molar ratio of input	The sample quality(g)	Co	Fe	Co^{2+}	Co^{3+}
X = 0.41	0.0453	40.84%	14.16%	21.50%	14.89%
X = 0.21	0.0358	21.33%	27.72%	38.99%	14.47%
X = 0.14	0.0314	13.77%	70.96%	34.29%	14.91%

Table S4. Comparison of OER catalytic activity in 1 M KOH electrolyte between $Co_{0.21}Fe_{0.28}(OH)F/NF$ and recently reported self-supported oxyhydroxide, layered double hydroxide and other catalysts.

Catalyst	η_{10}* (mV)	η_{100}* (mV)	Reference
$Co_{0.21}Fe_{0.28}(OH)F/NF$	195	341	This work
NiFeCr LDH/CP	225 (η_{25}*)	N/A	Adv. Energy Mater. 2018, 8, 1703189.
$FeOOH/Ni_3N/CC$	244	~320	Appl. Catal. B. 2020, 269, 118600.
$NiFeO_x(OH)_y@MoS_2/rGO$	250 (η_{20}*)	N/A	Chem. Eng. J. 2020, 397, 125454.
FeNiOOH/FNF	252	~290	Chem. Eng. J. 2020, 395, 125180.
NCS/NS-rGO	253	~370	Nano Res. 2022, 15, 950-958.
CoOOH/Cu/NF	260	~357	ACS Sustain. Chem. Eng. 2021, 9, 12300-12310.
δ-FeOOH NSs/NF	265	~370	Adv. Mater. 2018, 30, 1803144.
Ni_xB/f-MWCNT	286	N/A	J. Mater. Chem. A 2019, 7, 764-774.
$NF/H-CoMoO_4$	295	~343	J. Catal. 2020, 381, 44-52.
Fe–NiO/NF	305	~390	Nano Energy 2019, 66, 104118.
Pc-Ni-B@NB	302	N/A	Angew. Chem. Int. Ed. 2017, 56, 6572
$Co-Ni_3N/CC$	307	N/A	Adv. Mater. 2018, 30, e1705516.
Co-Ni-B@NF	313	1.02(V)	J. Mater. Chem. A, 2017, 5, 12379.

*η_{10}, η_{20}, η_{25} and η_{100} represent the overpotentials required to attain current densities of 10, 20, 25, and 100 mA cm^{-2}, respectively. NF: nickel foam; CC: carbon cloth; CP: carbon paper; CF: carbon fiber; FNF: FeNi foam; rGO: reduced graphene oxide; CNTs: carbon nanotubes.