Supplementary Information

Boosting oxygen evolution electrocatalysis of high-entropy hydroxide by high-valence nickel species regulation

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1. Experiment section

1.1. Materials

Chemicals and Reagents include $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cr(NO)_3 \cdot 9H_2O$, $Na_2MoO_4 \cdot H_2O$, Hexamethylenetetramine (HMT), KOH (85%), Nafion solution (5wt%, Aldrich corporation). All the reagent were used as received without any further purification.

1.2. Materials Synthesis

In a typical synthesis of NiCoFeCrMo-based HEH, equimolar $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cr(NO)_3 \cdot 9H_2O$ and $Na_2MoO_4 \cdot H_2O$ (0.06 mmol each) were dissolved in H_2O (3 mL) to obtain solution A. HMT (1.2 mmol) was dissolved in H_2O (3 mL) to obtain solution B. Then, solution A was poured into solution B and continue stirring for ten minutes to obtain a homogeneous solution. Then the resulting homogeneous solution was transferred into an autoclave lined with polytetrafluoroethylene with a volumetric capacity of 10 mL. The autoclave was heated at 110 ℃ for 8 h. After cooling down naturally, the powder was obtained by centrifugation and washing twice with deionized water and once with ethanol. The powder product was finally dried at 60 ℃ for 8 hours. Other catalysts, including NiCoFeCr-LDH, NiCoFe-LDH, NiCo-LDH, α-$Ni(OH)_2$, were prepared by using the same method and the total moles of metal components were kept constant.

1.3 Characterizations

The crystalline structure of powder was characterized using XRD-7000S model X-ray diffractometer (Cu-Kα radiation source with a wavelength of 1.5406 Å) produced by Shimadzu Corporation. The Field emission scanning electron microscopy (FESEM) examinations were performed using a FEI Nova Nano SEM 450 field emission scanning electron. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS) were collected on a transmission electron microscope of Tecnai-G2 F30 produced by FEEI

Corporation. The surface chemistry was detected using X-ray photoelectron spectroscopy (XPS) with ESCALABTM 250Xi (Al Kα radiation source).

1.4 Electrochemical measurements

The OER catalytic performances test was conducted on CHI660E electrochemical workstation (Chenhua, Shanghai) with a typical three-electrode configuration. And KOH (1 M) was used as electrolyte. The glassy carbon electrode (area = 0.19625 cm^{-2}), Hg/HgO electrode and Pt plate were used as the working, reference, and counter electrode, respectively. To prepare the working electrode, each catalyst (4 mg) was firstly dispersed into a homogeneous solution consisting of 480 μL deionized water, 480 μL ethanol and 40 μL Nafion (5 wt%). Hereafter, the suspension was sonicated for 0.5 h to obtain a uniform catalyst ink. Then the catalyst ink was drop onto glassy carbon electrode with loading amount of 0.362 mg/cm^{-2}. The potential was calibrated to reversible hydrogen electrode (RHE) following the equation of $E_{RHE} = E_{Hg/HgO} + 0.0591*pH + 0.098$ V (pH = 13.99). The overpotential was calculated by $\eta = E_{RHE} - 1.23$ V. The Linear sweep voltammetry (LSV) was collected at a scan rate of 5 mV s^{-1} without iR-correction. Then the Tafel slope was obtained from the conversion from the LSV curves and subsequent fitting. Electrochemical impedance spectroscopy (EIS) was collected with a frequency ranged from 10^{-2} to 10^{5} Hz (AC amplitude: 5 mV). Cyclic voltammetry (CV) curves were recorded at a scan rate from 20 mV s^{-1} to 100 mV s^{-1} with a potential range of 0.2 – 0.3 V versus Hg/HgO to calculate the double layer capacitance (C_{dl}). The long-term stability of catalyst-loaded working electrode prepared by loading HEH on carbon paper (NiCoFeCrMo 1 mg cm^{-2}) was test catalyst with chronoamperometry. Turnover frequencies (TOFs) for the OER are calculated using the following equation:

$$TOF = jS/4Fn$$

Where j (A cm^{-2}) is the current density, S is the surface area (1.963 cm^{-2}), the number 4 means 4 electron transfer in the OER reaction, F is the Faraday constant of 96485 C mol^{-1}, and n is the molar number of Ni from EDS results of NiCo-LDH, NiCoFe-LDH, NiCoFeCr-LDH, HEH.

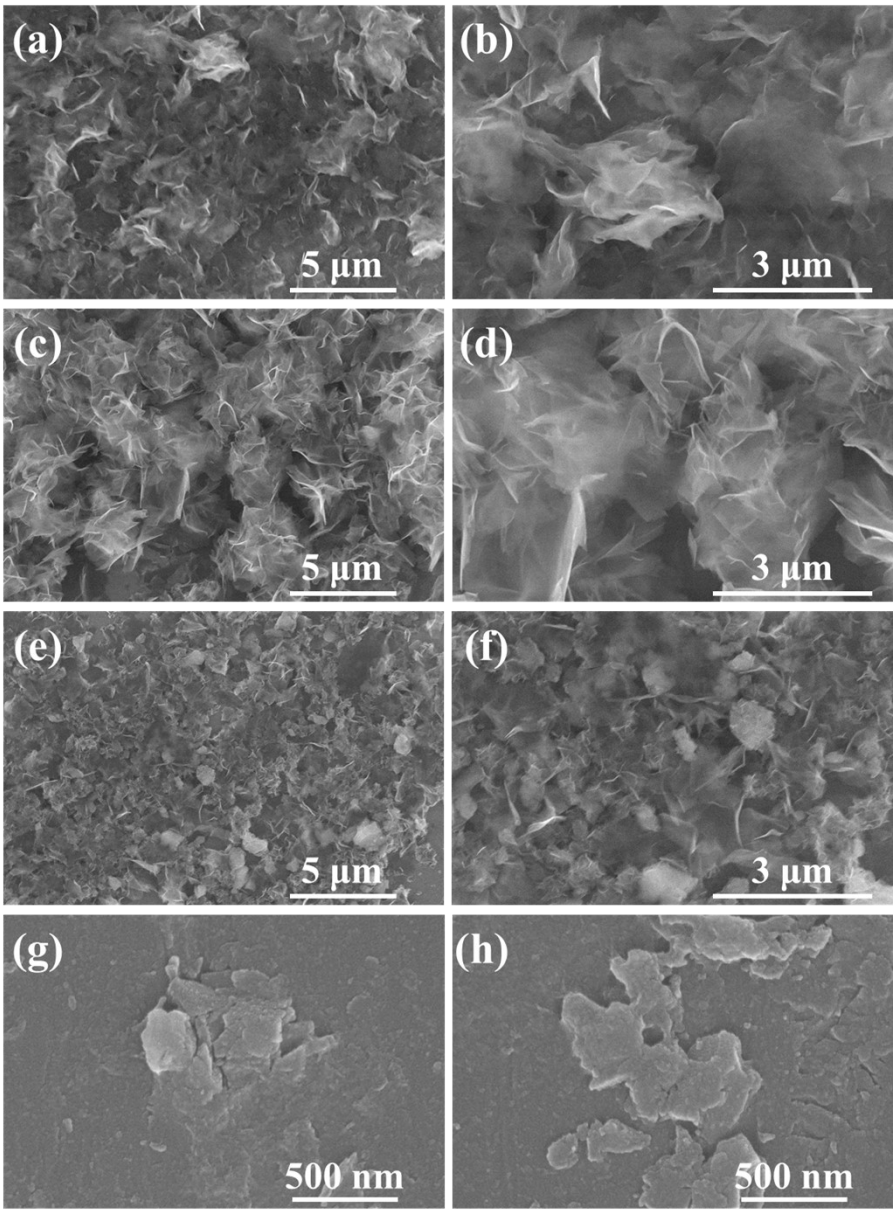

Figure S1. SEM images of α-$Ni(OH)_2$ (a) and (b), NiCo-LDH (c) and (d), NiCoFe-LDH (e) and (f), and NiCoFeCr-LDH (g) and (h).

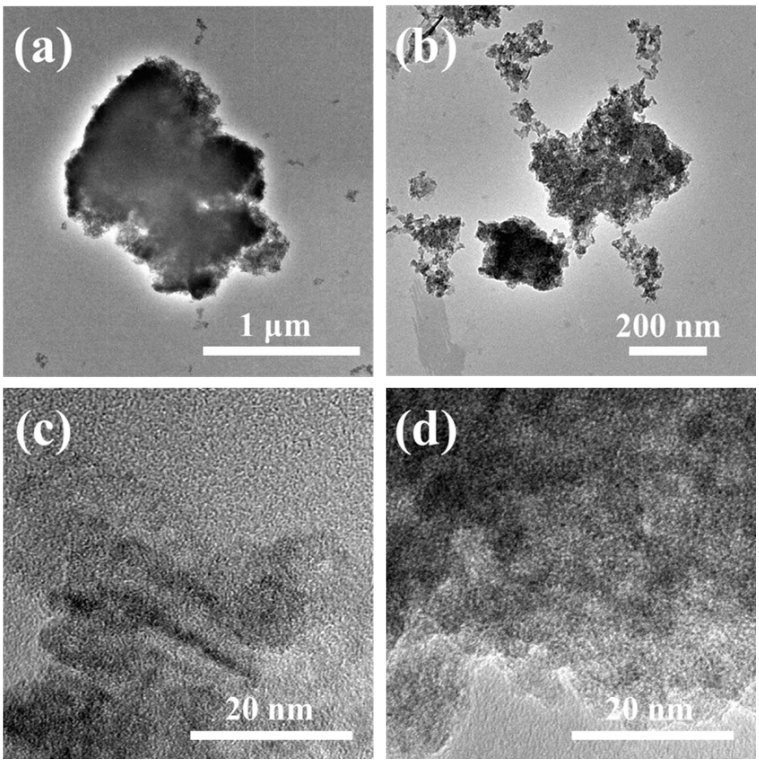

Figure S2. TEM images of HEH (a) and (b), HRTEM of HEH (c) and (d).

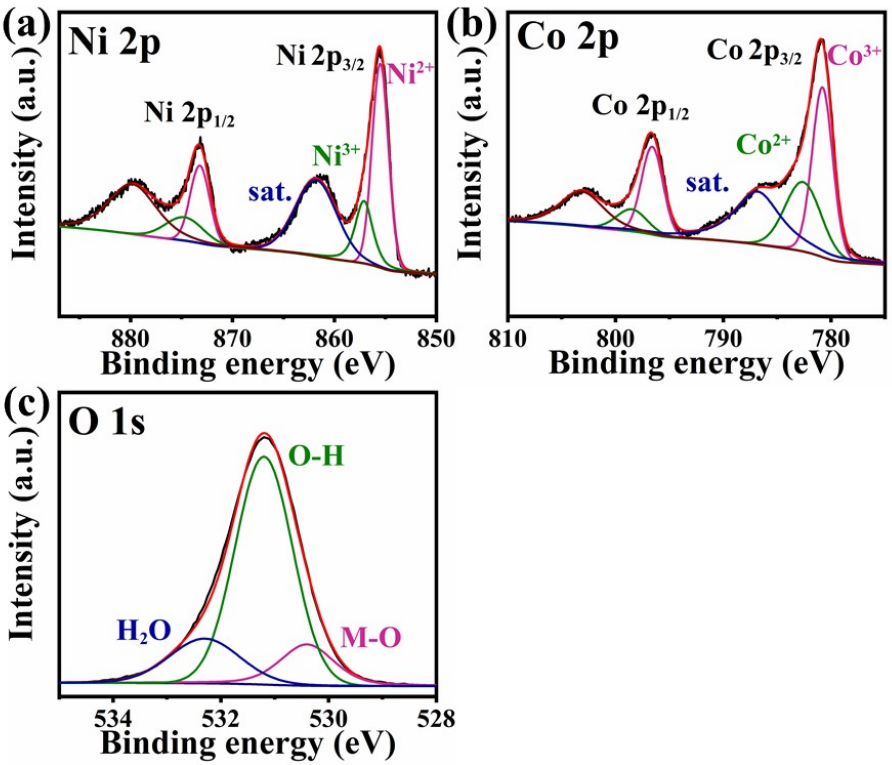

Figure S3. XPS spectra of NiCo-LDH (a) Ni 2p, (b) Co 2p, (c) O 1s.

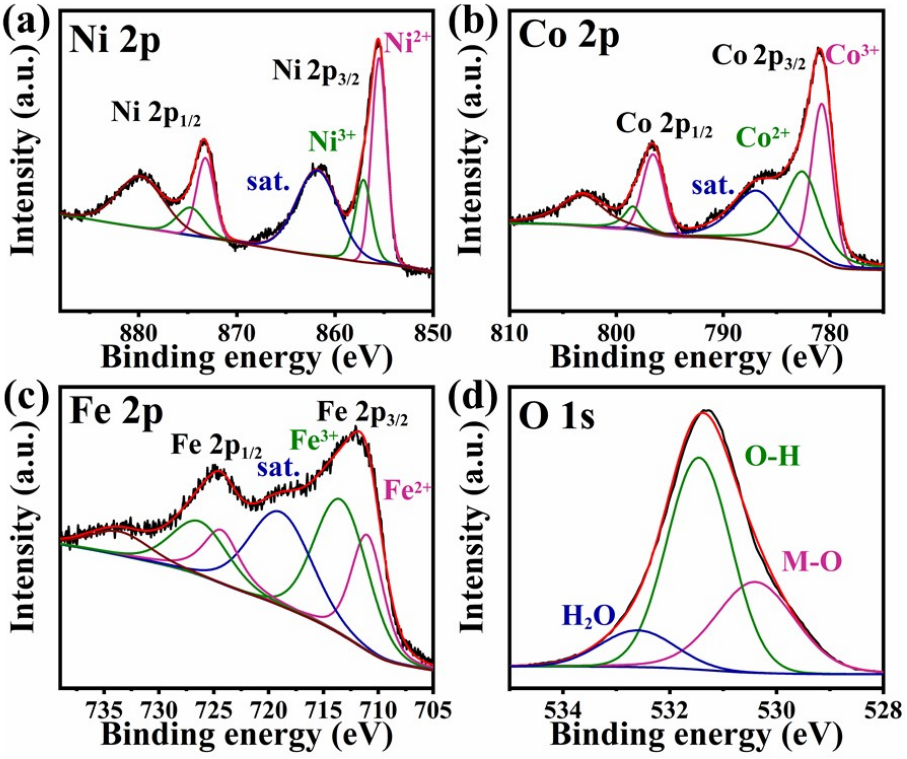

Figure S4. XPS spectra of NiCoFe-LDH, (a) Ni 2p, (b) Co 2p, (c) Fe 2p, (d) O 1s.

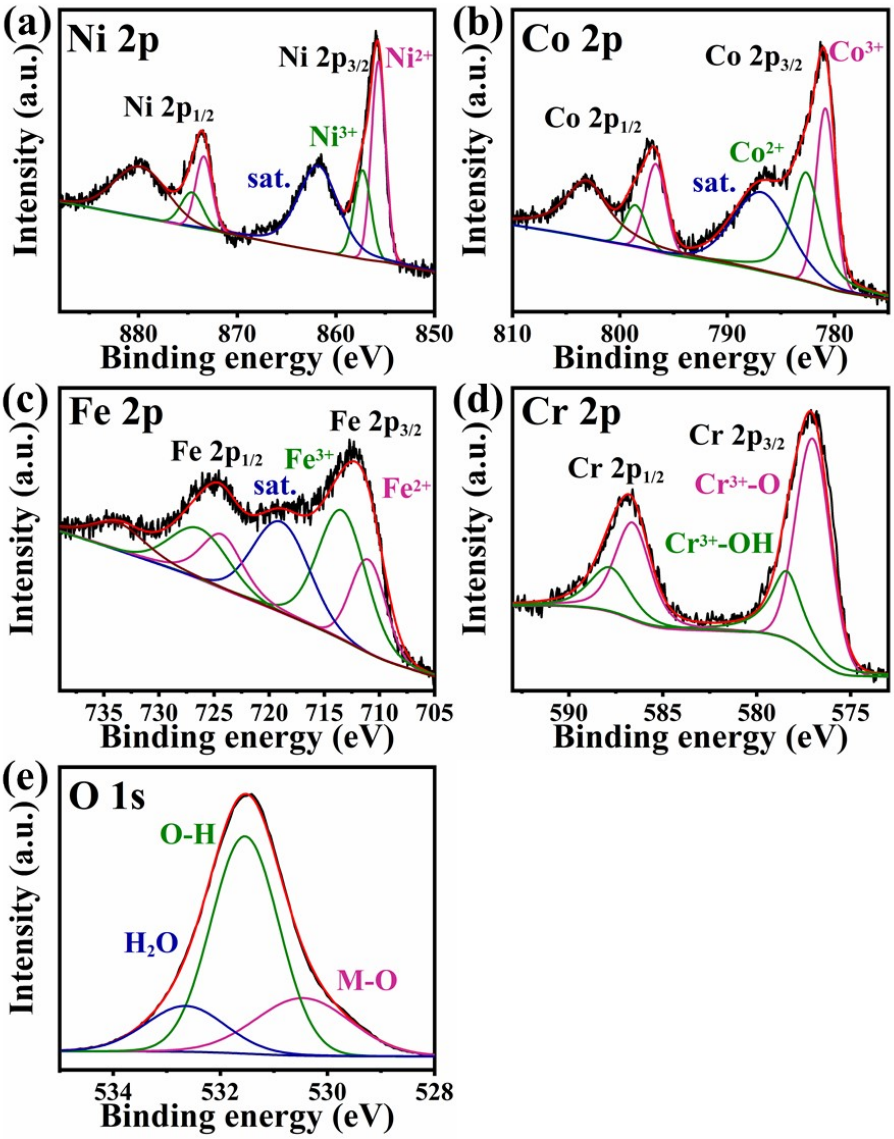

Figure S5. XPS spectra of NiCoFeCr-LDH, (a) Ni 2p, (b) Co 2p, (c) Fe 2p, (d) Cr 2p, (e) O 1s.

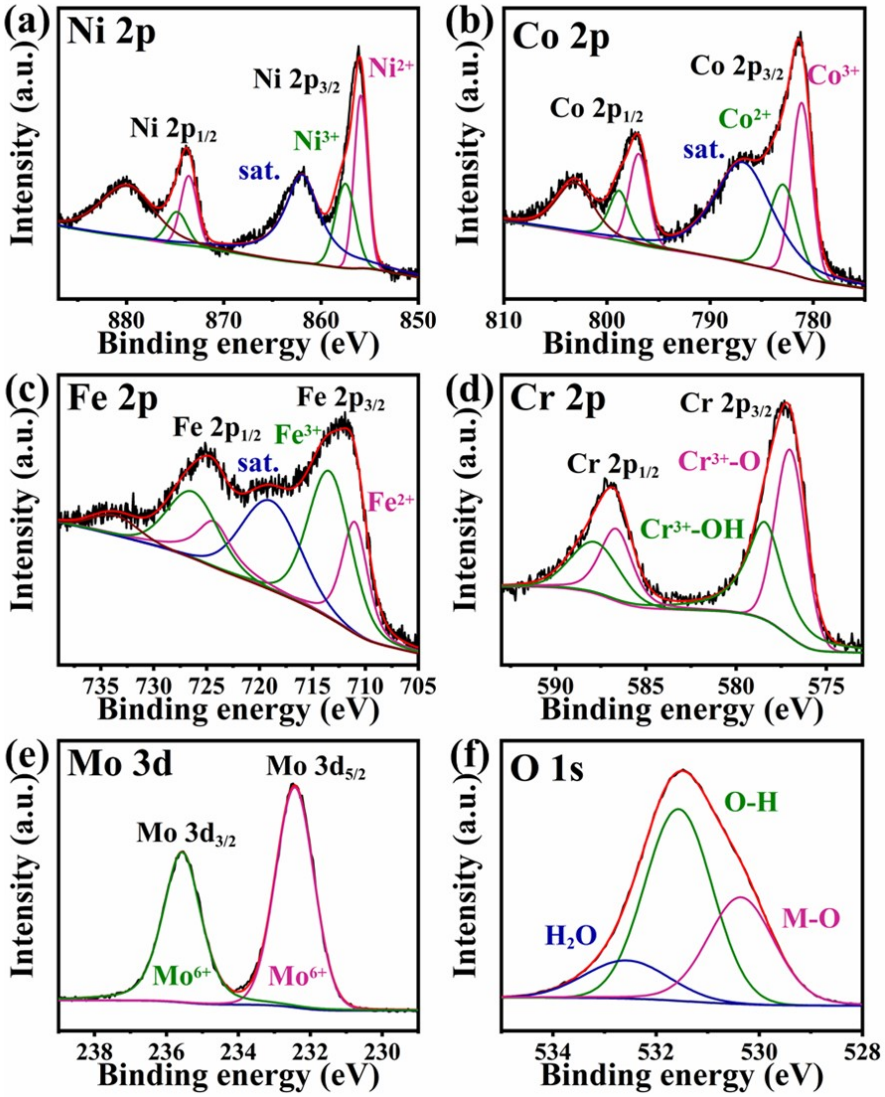

Figure S6. XPS spectra of HEH: (a) Ni 2p, (b) Co 2p, (c) Fe 2p, (d) Cr 2p, (e) Mo 3d and (f) O 1s.

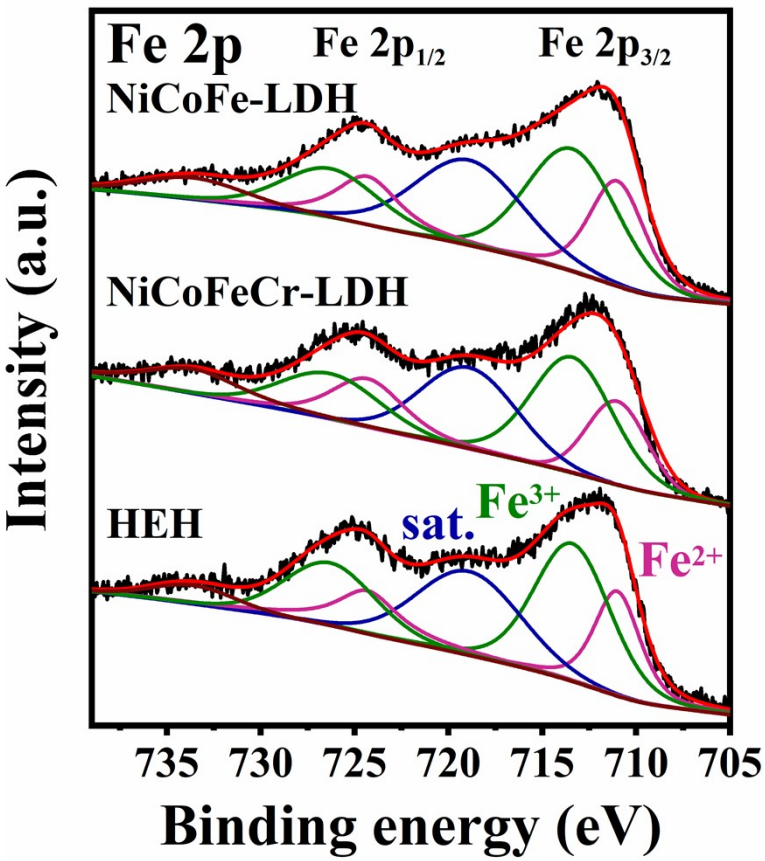

Figure S7. XPS spectra of Fe 2p of different samples for comparison.

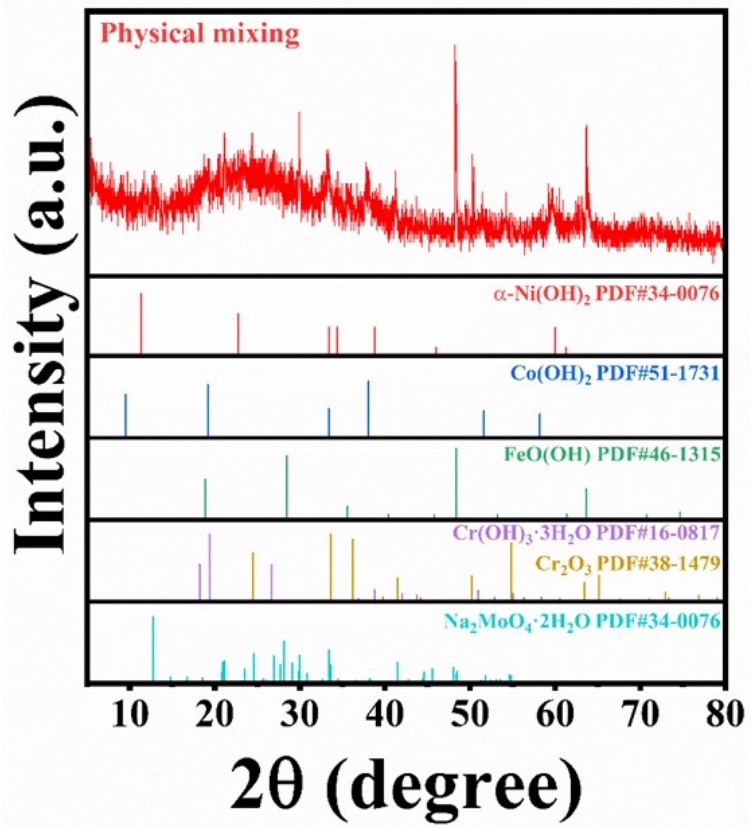

Figure S8. XRD pattern of physical mixing sample.

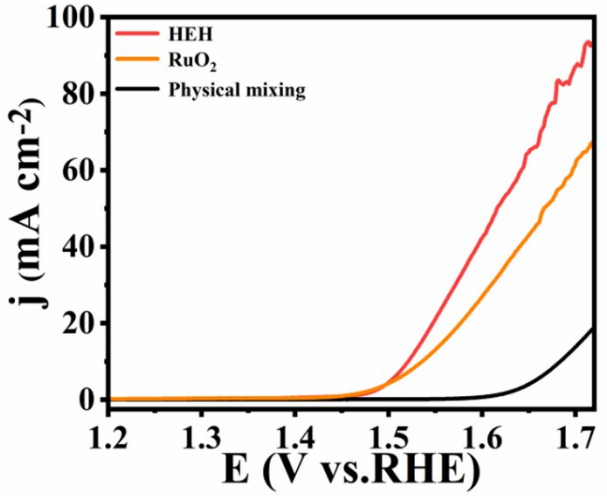

Figure S9. LSV of HEH, RuO_2 and physical mixing sample.

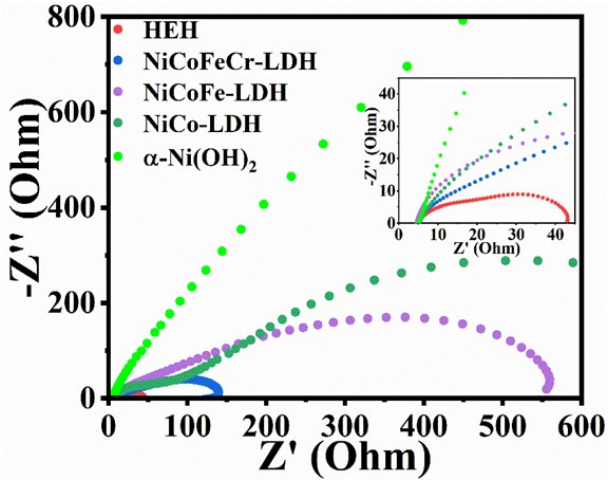

Figure S10. Nyquist plot of each catalyst.

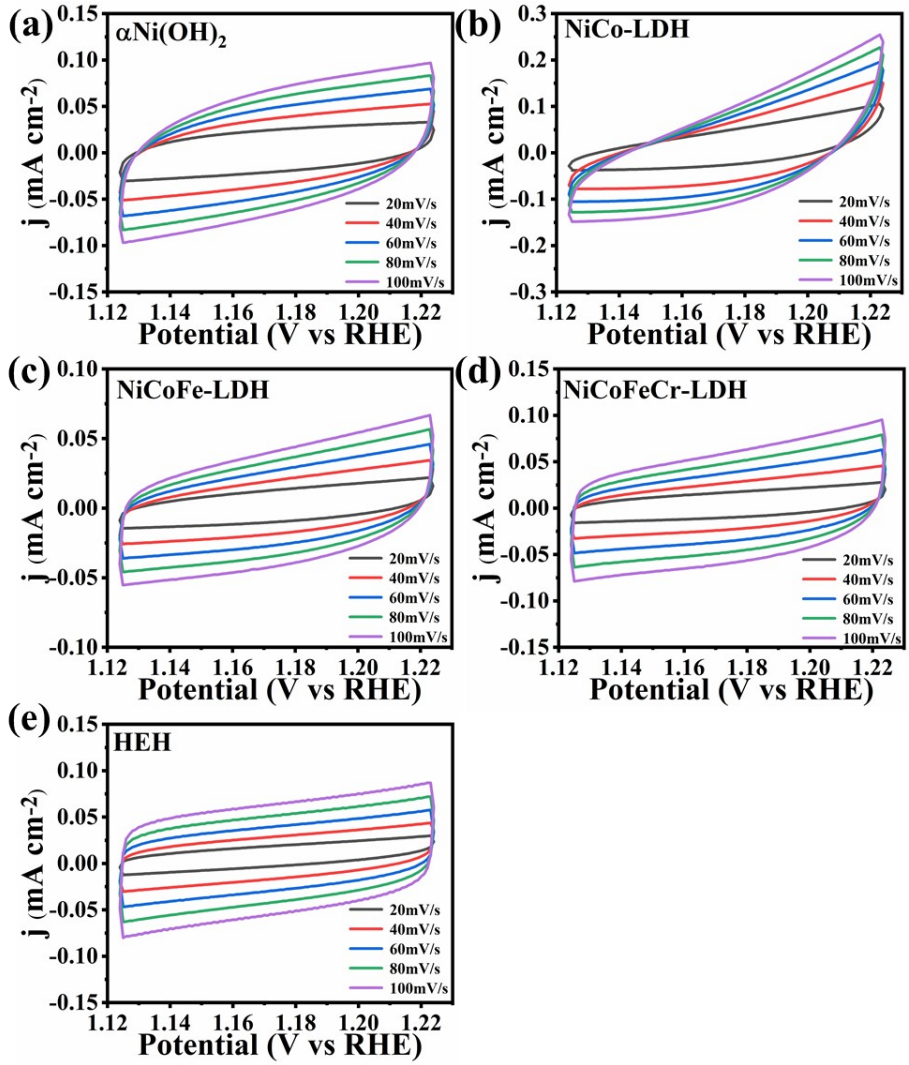

Figure S11. CV curves of different samples. (a) α-Ni(OH)$_2$, (b) NiCo-LDH, (c) NiCoFe-LDH, (d) NiCoFeCr-LDH, (e) HEH.

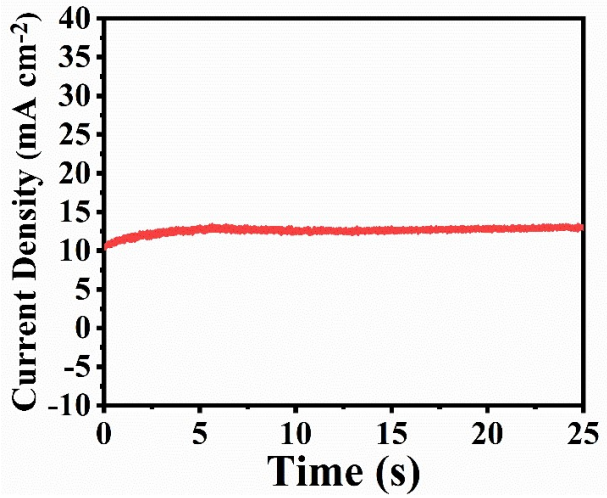

Figure S12. The current-time curve of HEH.

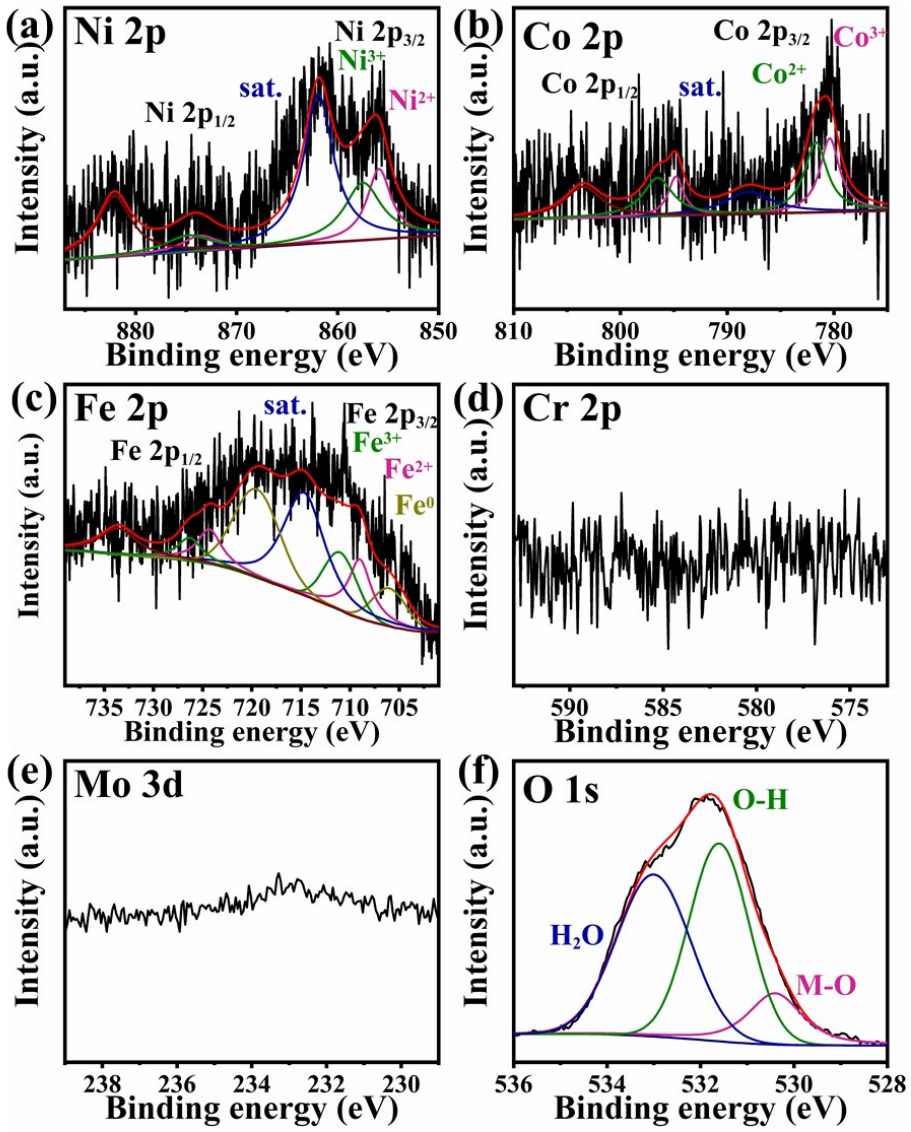

Figure S13. XPS spectra of HEH after long-term stability test.

Table S1. EDS analysis attached in SEM equipment of the obtained samples.

Samples	Ni (atom%)	Fe (atom%)	Co (atom%)	Cr (atom%)	Mo (atom%)
NiCo-LDH	43.80	56.20	-	-	-
NiCoFe-LDH	37.90	32.47	29.63	-	-
NiCoFeCr-LDH	25.32	24.16	25.04	25.46	-
HEH	19.21	22.50	23.84	22.30	12.12

Table S2. Data of M^{3+}/M^{2+} ratio of different samples.

Sample	NiCo-LDH	NiCoFe-LDH	NiCoFeCr-LDH	HEH	After OER
Ni^{3+}/Ni^{2+}	0.472	0.511	0.554	0.671	1.301
Co^{3+}/Co^{2+}	1.680	1.155	0.990	1.359	0.753
Fe^{3+}/Fe^{2+}	-	1.526	1.600	1.754	0.844

Table S3. Comparision for OER activity of HEH with other electrocatalysts.

Catalyst	Overpotential η [mV] at 10 mA cm^{-2}	Tafel slope [mV $decade^{-1}$]	Ref
HEH	**292**	**54.31**	**This work**
Au-$Ni(OH)_2$/CC	288	55	Inorg. Chem., 2021, 60, 15818.
NiCo-LDH/$ZnCo_2O_4$/GC	260	62	J. Colloid Interf. Sci., 2021, 604, 832
$NiSn(OH)_6$@OOH/GC	370	58.4	J. Mater. Chem. A, 2022, 10, 1369
$Fe_{0.5}CoNiCuZn_{0.8}$	340	48	J. Mater. Sci. Technol., 2021, 93, 110
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})_3O_4$/GC	322	54.5	Chem. Eng. J., 2022, 431, 133448
$(FeCoNiCrMn)_3O_4$-400/CP	288	60	Sustain. Energy Fuels, 2022, 6, 1479
CoNiCuMnAl@C/NF	215	35.6	Chem. Eng. J., 2022, 429, 132410
CoFeCuMoOOH@Cu/Cu foil	199	48.8	Adv. Mater., 2021, 22, e2100745
FeCoNiMnCu/Alloy	280	59	Chem. Eng. J., 2021, 425, 131533
NiFeCe-LDH/Mxene/GC	260	42.8	J. Energy Chem., 2021, 52, 412
NiFe25/PGS	332	33	Int. J. Hydrogen. Energy, 2022, 47, 8786.
NiFe-25/NF	299	48.9	Chem. Eng. J., 2021, 423, 130204.
NiFe LDH-A50/GC	308	50	ChemSusChem. 2020, 12, 811.
NiO/C@NiFe-LDHs/RDE	299	45	J. Electrochem. Soc. 2020, 167, 024501.
CoFe-Ni_3S_4/NF	230	63	Chem. Eng. J., 2022, 427, 130742.
$K_{0.8}Na_{0.2}(MgMnFeCoNi)F_3$	314	55	J. Am. Chem. Soc. 2020, 142,

Table S4. Data for TOF calculation.

Sample	HEH	NiCoFeCr-LDH	NiCoFe-LDH	NiCo-LDH
Weight%(Ni) from EDS	11.3	18.56	15.06	17.3
n(Ni)/mol	$6.28*10^{-7}$	$1.03*10^{-6}$	$8.37*10^{-7}$	$9.61*10^{-7}$