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Supporting information

Morphology Regulation of Metal-Organic Framework-Derived Nanostructures for Efficient Oxygen Evolution Electrocatalysis

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Experiment Section

Materials and general methods: $Fe(ClO_4)_2 \cdot xH_2O$ and Nafion was purchased from Alfa Aesar. $K_2[Ni(CN)_4] \cdot xH_2O$ was purchased from Aldrich. Pyrazine was purchased from Energy Chemical. Polyvinyl Pyrrolidone was purchased from Macklin. Methanol was purchased from Gaojing Chemical. All the chemicals were used without purification.

Synthesis of FeNi-1C-MOF: $Fe(ClO_4)_2 \cdot xH_2O$ (0.3 mmol) was dissolved in a mixture of 20 mL deionized water and 20 mL methanol to form solution A. Pyrazine (0.3 mmol) were dissolved in another mixture of 20 mL deionized water and 20 mL methanol to form solution B. Separately, $K_2[Ni(CN)_4] \cdot xH_2O$ (0.3 mmol) was dissolved in 10 mL of deionized water and the solution was added into the mixture of A and B. After vigorously stirring for 3 hours, and washed with water and methanol for several times, the as-obtained orange MOFs dried at 60 ℃ for 12 hours.

Synthesis of FeNi-1C-PVP-MOF: $Fe(ClO_4)_2 \cdot xH_2O$ (0.3 mmol) was dissolved in a mixture of 20 mL deionized water and 20 mL methanol to form solution A. Pyrazine (0.3 mmol) and Polyvinyl Pyrrolidone (PVP, 0.6 g, M_w=58000) were dissolved in another mixture of 20 mL deionized water and 20 mL methanol to form solution B. Separately, $K_2[Ni(CN)_4] \cdot xH_2O$ (0.3 mmol) was dissolved in 10 mL of deionized water and the solution was added to the mixture of A and B. After vigorously stirring for 3 hours and washed with water and methanol for several times, the as-obtained orange MOFs dried at 60 ℃ for 12 hours.

Synthesis of FeNi-10C-MOF: $Fe(ClO_4)_2 \cdot xH_2O$ (3 mmol) was dissolved in a mixture of 20 mL deionized water and 20 mL methanol to form solution A. Pyrazine (3 mmol) were dissolved in another mixture of 20 mL deionized water and 20 mL methanol to form solution B. Separately, 3 mmol of $K_2[Ni(CN)_4] \cdot xH_2O$ (3 mmol) was dissolved in 10 mL of deionized water and the solution was added to the mixture of A and B. After vigorously stirring for 3 hours and washed with water and methanol for several times, the as-obtained deep orange MOFs dried at 60 ℃ for 12 hours.

Synthesis of FeNi-10C-PVP-MOF: $Fe(ClO_4)_2 \cdot xH_2O$ (3 mmol) was dissolved in a mixture of 20 mL deionized water and 20 mL methanol to form solution A. Pyrazine (3 mmol) and Polyvinyl Pyrrolidone (PVP, 6 g, M_w=58000) were dissolved in another mixture of 20 mL deionized water and 20 mL methanol to form solution B. Separately, 3 mmol of $K_2[Ni(CN)_4] \cdot xH_2O$ (3 mmol) was dissolved in 10 mL of deionized water and the solution was added to the mixture of A and B. After vigorously stirring for 3 hours andwashed with water and methanol for several times, the as-obtained deep orange MOFs dried at 60 ℃ for 12 hours.

Synthesis of MOF-derived electrocatalysts: The above-obtained four MOFs were placed in a tube furnace under Ar atmosphere and heated to 800 ℃ for 2h at a rate of 5 ℃ min^{-1}. Then the black powders were immersed into 0.5 M H_2SO_4 for 24 hours to remove accessible Fe or Ni species on the surface. The black carbon materials were

placed in a tube furnace under an air flow at 350 ℃ for 3 hours with a heating rate of 2 ℃ min^{-1}. According to the different morphologies, the as-obtained MOFs-derived electrocatalysts were denoted as FeNi NSs (nanosheets), FeNi NFs (nanoflowers), FeNi NTs (nanotubes) and FeNi AGs (carbon aggregations), which were derived from FeNi-1C-MOF, FeNi-1C-PVP-MOF, FeNi-10C-MOF, FeNi-10C-PVP-MOF respectively.

Electrochemical Measurement: The electrochemical measurement was conducted on the Zahner Zennium electrochemical workstation in 1 M KOH through a typical three-electrode system. A graphite rod was used as the counter electrode and Ag/AgCl electrode was used as reference electrode. As for the fabrication process of the working electrode, 8 mg catalyst was dispersed in 1 mL of ethanol and treated with sonication for 1 hour, 50 μL of Nafion (5 wt%) was added and treated with the ink for another 30 minutes. 100 μL of ink was loaded on 1 cm × 1 cm of nickle foam (loading ~0.8 mg cm^{-2}) and the electrode was allowed to fully dry at room temperature before the electrocatalytical measurements. The LSV curves were conducted without iR compensation. The Tafel slope and EIS curves were obtained while loading on glass carbon (GC). The fabrication process of GC as working electrode is as follow: 5 mg sample was dispersed in 1 mL mixture of isopropanol and deionized water (v/v: 1/1). After treated with sonication for 1 hour, 30 μL of Nafion (5 wt%) was added and the sample was treated with sonication for another 30 minutes. Finally, 5 μL of the ink was dropped cast on polished GC and the electrode was fully dried at room temperature before use.

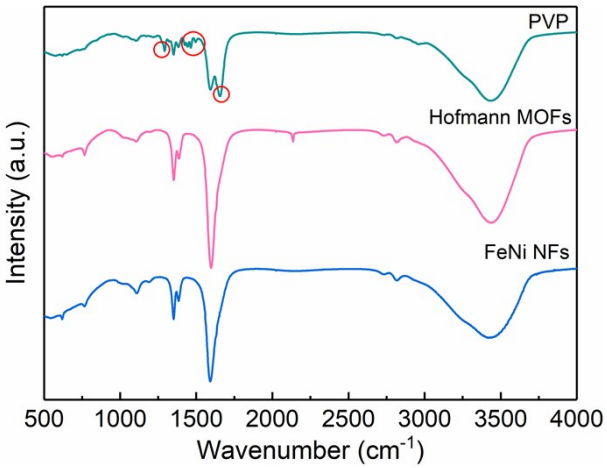

Fig. S1 The FT-IR patterns of PVP, Hofmann MOFs and FeNi NFs.

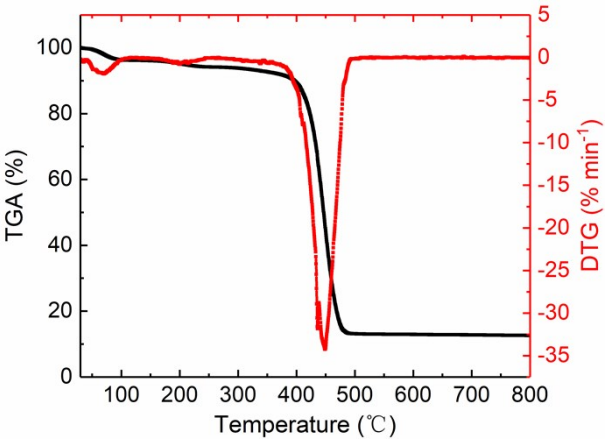

Fig. S2 The TGA (black) curve and the DTG (red) curve via TG.

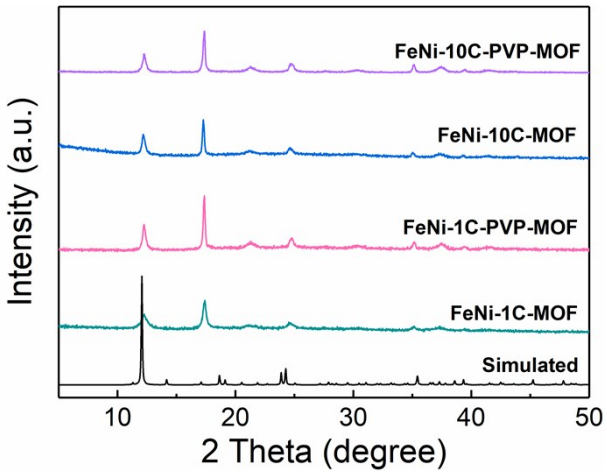

Fig. S3 The PXRD patterns of four MOFs with different morphologies.

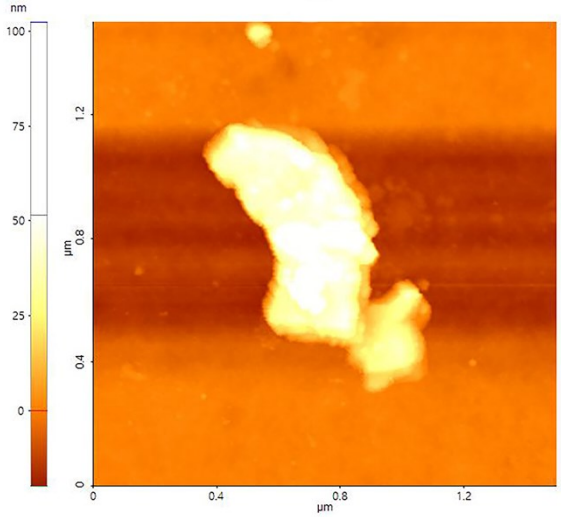

Fig. S4 The AFM image of nanosheet MOFs.

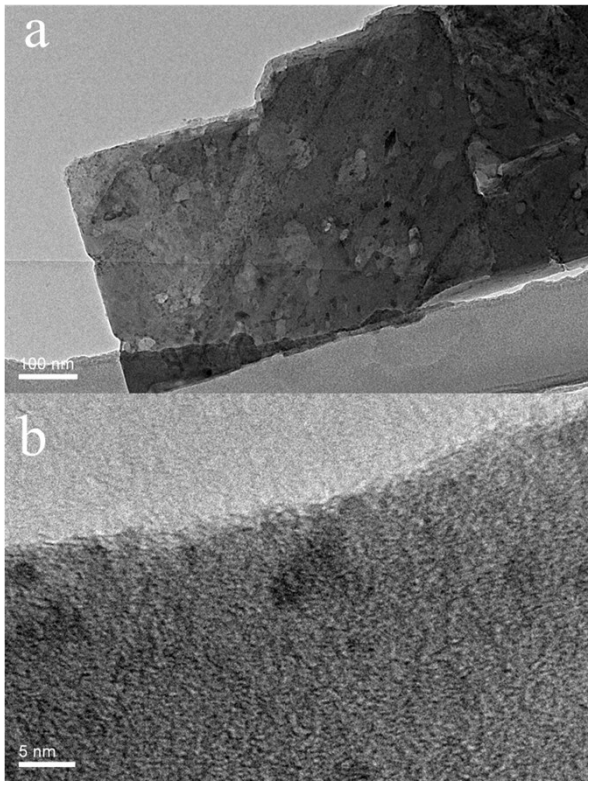

Fig. S5 The TEM image of nanosheet MOFs.

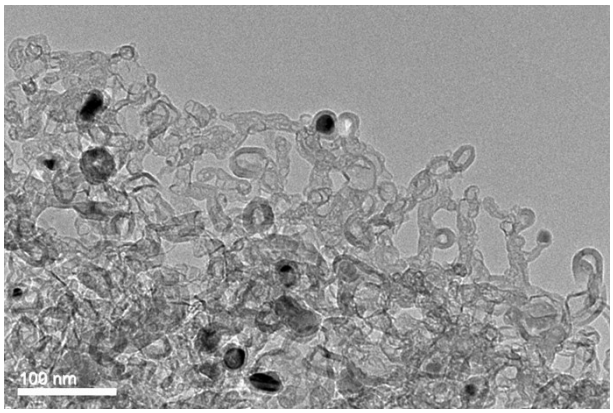

Fig. S6 The low resolution TEM image of FeNi NSs.

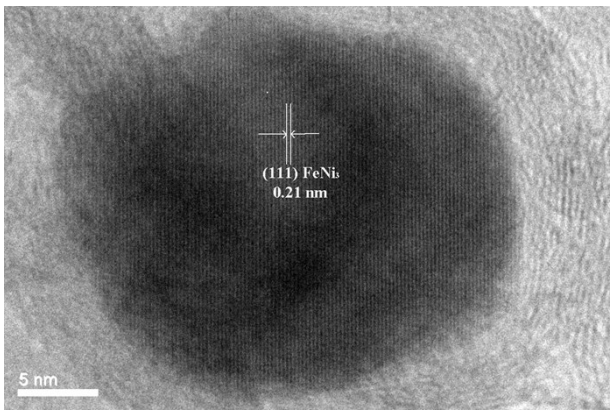

Fig. S7 The lattice fringes of FeNi NSs in HRTEM images.

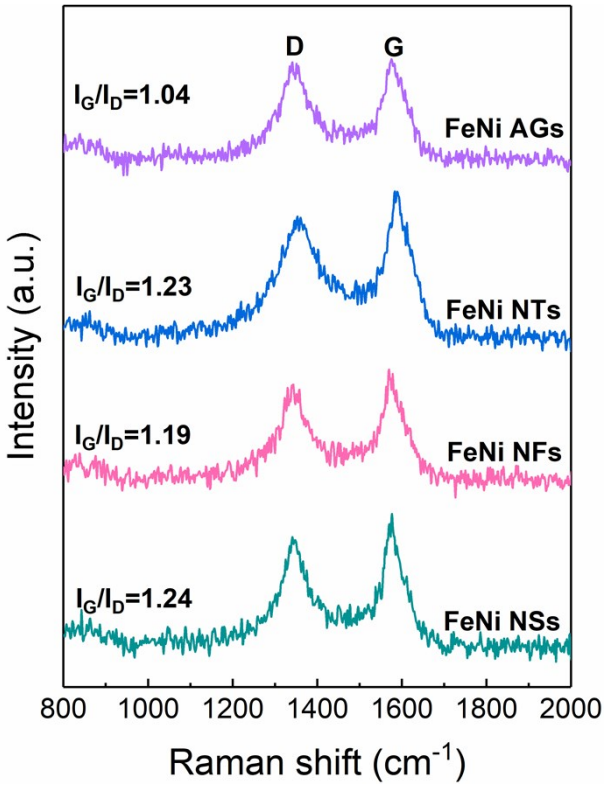

Fig. S8 The Raman spectra of FeNi NSs, FeNi NFs, FeNi NTs, and FeNi AGs.

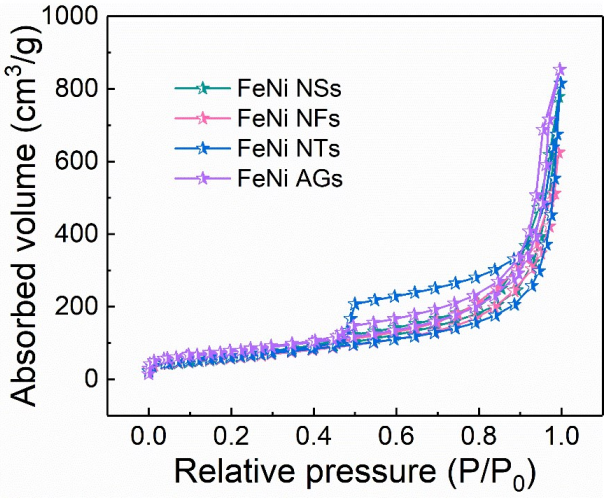

Fig. S9 The nitrogen adsorption-desorption isotherms for FeNi NSs, FeNi NFs, FeNi NTs, and FeNi AGs.

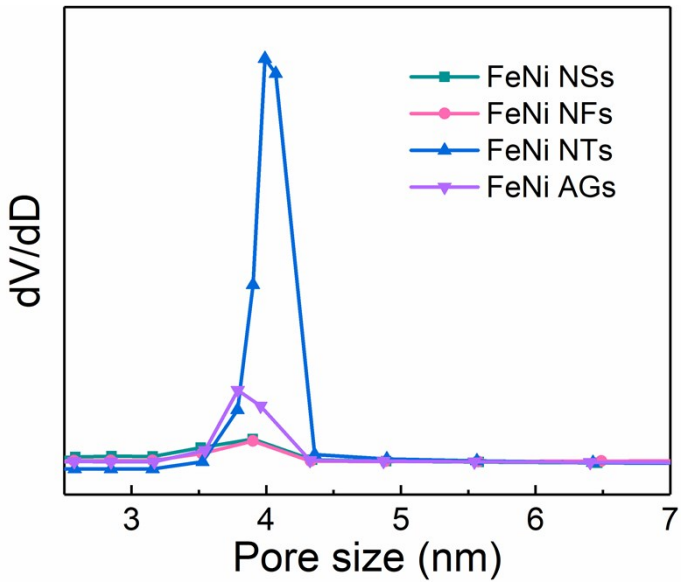

Fig. S10 Barrett-Joyner-Halenda (BJH) analysis for FeNi NSs, FeNi NFs, FeNi NTs, FeNi AGs.

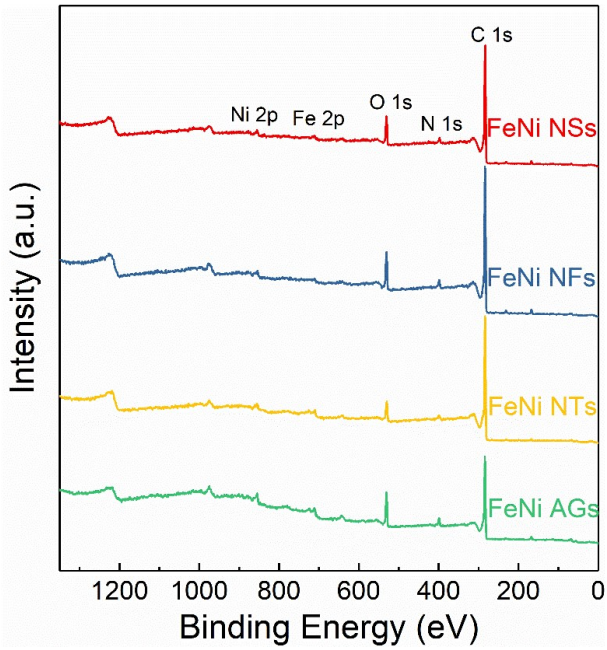

Fig. S11 The XPS survey scans of FeNi NSs, FeNi NFs, FeNi NTs, and FeNi AGs.

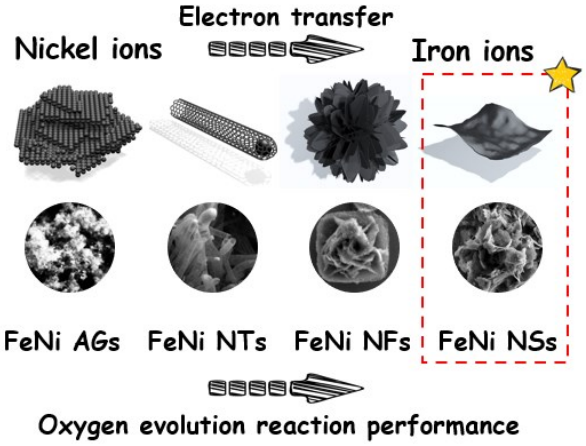

Fig. S12 The schematic illustration of enhancing OER performance via morphology.

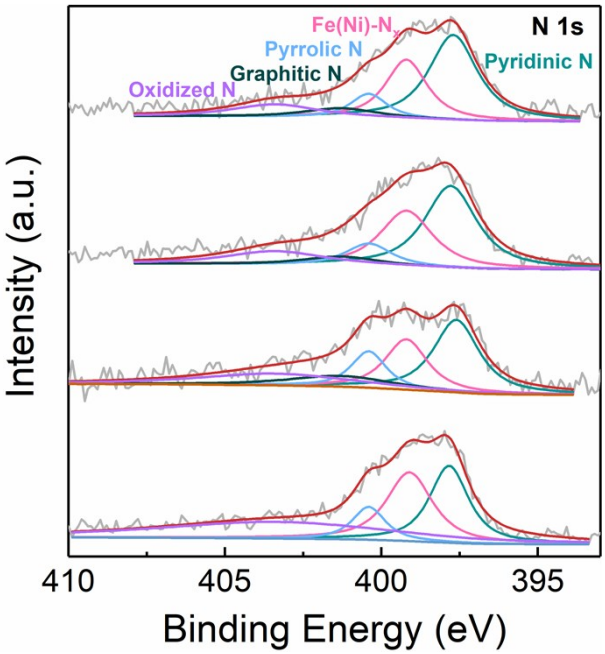

Fig. S13 N 1s XPS spectra for FeNi NSs, FeNi NFs, FeNi NTs and FeNi AGs.

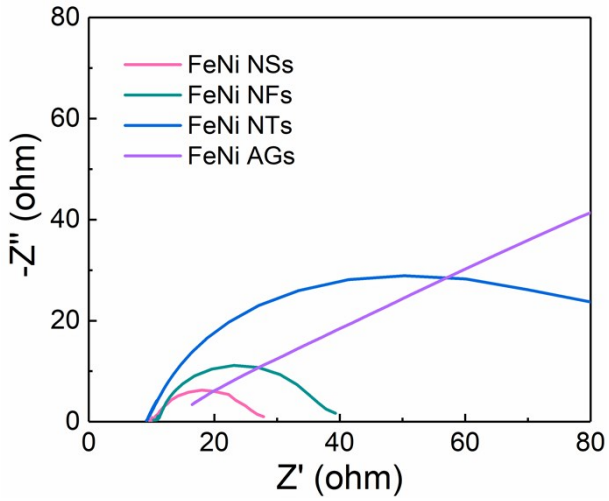

Fig. S14 The EIS results of FeNi NSs, FeNi NFs, FeNi NTs and FeNi AGs.

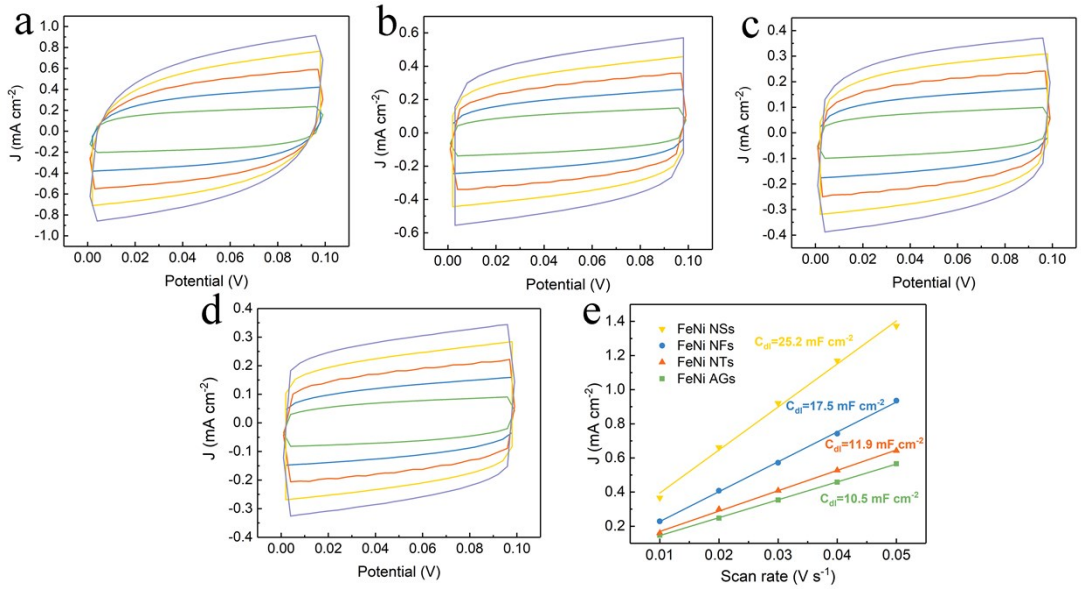

Fig. S15 CVs of (a) FeNi NSs, (b) FeNi NFs, (c) FeNi NTs and (d) FeNi AGs at different scan rates from 10 to 50 mV s^{-1} in the potential from 0 to 100 mV. (e) C_{dl} calculated for four catalysts.

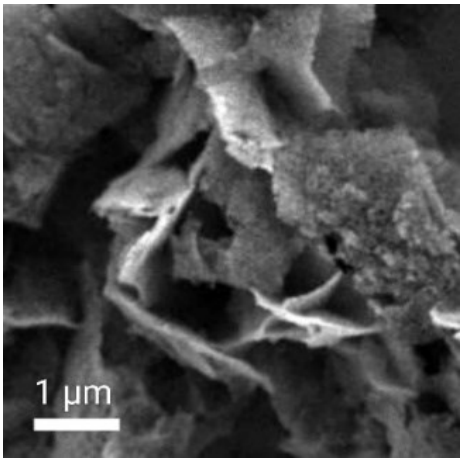

Fig. S16 The SEM image of FeNi NSs after electrocatalysis.

Table S1 The quantitative analyses of element content calculated by XPS.

	C	N	O	Fe	Ni
FeNi NSs	61.0%	5.3%	18.3%	8.2%	7.2%
FeNi NFs	59.3%	5.2%	19.3%	6.3%	9.9%
FeNi NTs	60.7%	4.3%	11.7%	14.6%	8.7%
FeNi AGs	44.9%	5.9%	20.7%	15.3%	13.2%

Table S2 Comparison of the OER electrocatalytic properties of FeNi NSs to recently reported catalysts for OER.

Catalysts	Overpotential (@10 mA cm^{-2})	Tafel slope ($mV\ dec^{-1}$)	Electrode	Reference
FeNi NSs	248 mV	31.2	Ni foam	This work
Co_6W_6C@NC	286 mV	53.9	Carbon cloth	[S1]
$Co_{1.6}Ni_{0.4}P_4O_{12}$-C	230 mV	51.1	Glassy carbon	[S2]
HXP@NC800	307 mV	48	Glassy carbon	[S3]
$SyACo_2Fe$-ST	254 mV	50	Glassy carbon	[S4]
CuCoNC	245 mV	61.9	Copper foam	[S5]
Co/P/N-CNP-5	311 mV	67.7	Glassy carbon	[S6]
MIL-88A/$Ni(OH)_2$	250 mV	36.4	Carbon cloth	[S7]
CoFe-PBA NS@NF	256 mV	48	Ni foam	[S8]
SNNU-5-FeCoNi	317 mV	37	Glassy carbon	[S9]
aMOF-NC	249 mV	39.5	Glassy carbon	[S10]
FeNiCo@NC-P	310 mV	64	Gold electrode	[S11]
PCN-Fe2Co-Fe-2Ni	271 mV	67.7	Glassy carbon	[S12]
$FeNi_3$-Fe_3O_4	234 mV	37	Glassy carbon	[S13]
Ni-ZIF/Ni-B@NF	234 mV	57	Ni foam	[S14]
Ni-S/MIL-53(Fe)	256 mV	39	Ni foam	[S15]

Ni-Fe-MOF NSs	221 mV	56	Glassy carbon	[S16]

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