

Electronic Supplementary Information

Electrochemical oxygen evolution reaction catalyzed by a novel nickel-cobalt-fluoride catalyst

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Experimental

Materials Characterization

Transmission Electron Microscopy (TEM) was conducted on Philips TECNAI-12 instrument. Energy-dispersive X-ray spectroscopy (EDX) mapping images were taken under a scanning TEM modal. Samples for TEM were prepared by drop-drying the samples from their diluted ethanol suspensions onto carbon-coated copper grids. High-resolution TEM (HRTEM) and selected area electron diffraction (SAED) were performed on FEI Tecnai G2 F30 STWIN (USA). X-ray diffraction (XRD) was measured on D8 advance super speed powder diffractometer (Bruker) with Cu-K α radiation ($\lambda=0.15148$ nm) operating at 30.0 kV and 20.0 mA. X-ray photoelectron spectroscopy (XPS) were acquired using Thermo Escalab 250 system with Mg-K α X-ray (1253.6eV) excitation source running at 15.0 kV, a hemispherical electron energy analyzer and a multichannel detector.

Preparation of Ni-Co-F-1,1

All chemicals used in the experiments were of analytical grade and used as received.

In the synthesis of Ni-Co-O-F-1,1, 0.1 mmol of Ni(NO₃)₂·6H₂O and 0.1 mmol of Co(NO₃)₂·6H₂O were dissolved in a mixture of deionized water (0.6 mL) and [BMIM][BF₄] (0.4 mL). Then, 0.3 mmol of H₂C₂O₄ and 0.1 mL of NaOH aqueous solution (0.5 M) were added under stirring for 10 min. The mixture was heated for 5 min in a microwave oven (M1-L213B). After cooling down to room temperature, the product was separated by filtration, washed with deionized water and absolute ethanol for a few times and then dried in air. Finally, the sample was placed in a quartz tube and calcined at 300 °C for 2h under protection of N₂ at a ramping rate of 5 °C min⁻¹ to obtain the Ni-Co-F-1,1.

Preparation of Ni-Co-F-1,2

The Preparation of Ni-Co-F-1,2 was synthesized via the same method as that for preparation of Ni-Co-F-1,1 except that the amount of Co(NO₃)₂·6H₂O was changed to 0.2 mmol.

Preparation of Ni-Co-F-2,1

The Preparation of Ni-Co-F-2,1 was synthesized via the same method as that for preparation of Ni-Co-F-1,2 except that the amount of Ni(NO₃)₂·6H₂O was changed to 0.4 mmol.

Electrochemical characterization

Electrochemical experiments were conducted in a standard three-electrode cell using an electrode of glassy carbon (GC, 3 mm diameter, 0.07 cm²) as support working electrode. They are connected to a Gamry electrochemical workstation to collect data at room temperature (25 °C). The GC electrode was polished to mirror finish by 0.3 micron alumina suspension then 0.05 micron suspension on a polishing cloth, and thoroughly cleaned before used as the working electrode. A saturated calomel electrode was used as the reference electrode, and a Pt foil was used as the counter electrode. The potentials reported in our work were converted to the reversible hydrogen electrode (RHE) by $E(\text{RHE}) = E(\text{SCE}) + 0.0591 \cdot \text{pH} + 0.24\text{V}$. The equation of $\eta(\text{V}) = E(\text{RHE}) - E_0$ was used to calculate overpotentials of these electrocatalysts, where E_0 represents the thermodynamic potential for OER (1.23 V vs. RHE). The Ni-Co-F/GC was used as the working electrodes and it was prepared as following: Ni-Co-F ink was prepared by dispersing 5 mg of catalyst in 950 μL of C₂H₅OH with 50 μL of 5 wt% Nafion solution. The mixture was ultrasonicated for about 1 h to form a homogeneous ink. Then 10 μL of the catalyst ink was loaded on glassy carbon and dried at room temperature. The mass loading was about 0.4 mg cm⁻². All data are presented with IR compensation.

Before conducting the electrochemical experiments, the electrolyte (1 M KOH, 99% metal purity) was purged by pure N₂ for approximately 30 min. Then the freshly prepared working electrode was immersed in the electrolyte. The linear scan voltammogram (LSV) curves were obtained by sweeping the potential from 0 to 0.7 V vs. SCE at room temperature, with a sweep rate of 5 mV s⁻¹. Tafel plots were recorded at a scan rate of 5 mV s⁻¹ via LSV curves.

Durability test was carried out for 1000 cycles within the potential range from 0 to 0.7 V vs. SCE in 1 M KOH at a scan rate of 100 mV s⁻¹, afterward a linear sweep was measured under a sweep rate of 5 mV s⁻¹ after 1000 cycles. With the aim of clarifying the electrochemically active surface areas (ECSA) of the products, the double-layer capacitance of the catalytic surface was taken in a potential range of -0.2 to -0.1 V vs. SCE where no faradic processes were observed to measure the capacitive current from double layer charging by cyclic voltammetry (CV). Data of chronoamperometry (CA) were collected at the potential of 1.56 V vs. RHE for 10 hours. The

electrochemical impedance spectroscopy (EIS) measurements were performed for catalysts on GC electrode over a frequency range from 100 kHz to 0.01 Hz in 1 M KOH.

Electrochemically active surface areas calculation: The double-layer charging current (i /mA) is proportional to the scan rate ν (mV/s), and C_{DL} , the specific capacitance of the electrode double layer can be calculated following equations below.¹

$$i = \nu \cdot C_{DL} \quad (1)$$

Thus plots of i against ν were illustrated in Fig. S5, which gave three straight lines and the slopes were equal to the CDL of the three samples, respectively. Then, the ECSA of catalyst was calculated:

$$ECSA = C_{DL} / C_s \quad (2)$$

Here, we use the general specific capacity (C_s) of 0.040 mF cm⁻² to calculate the electrochemically active surface areas (ECSA).

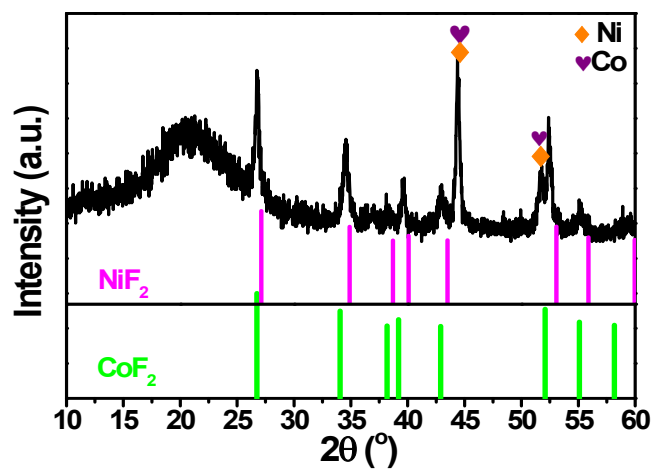


Fig.S1 XRD patterns of Ni-Co-F-1,1 obtained after the microwave treatment and before calculation. The peak at 20° is from the silicon support.

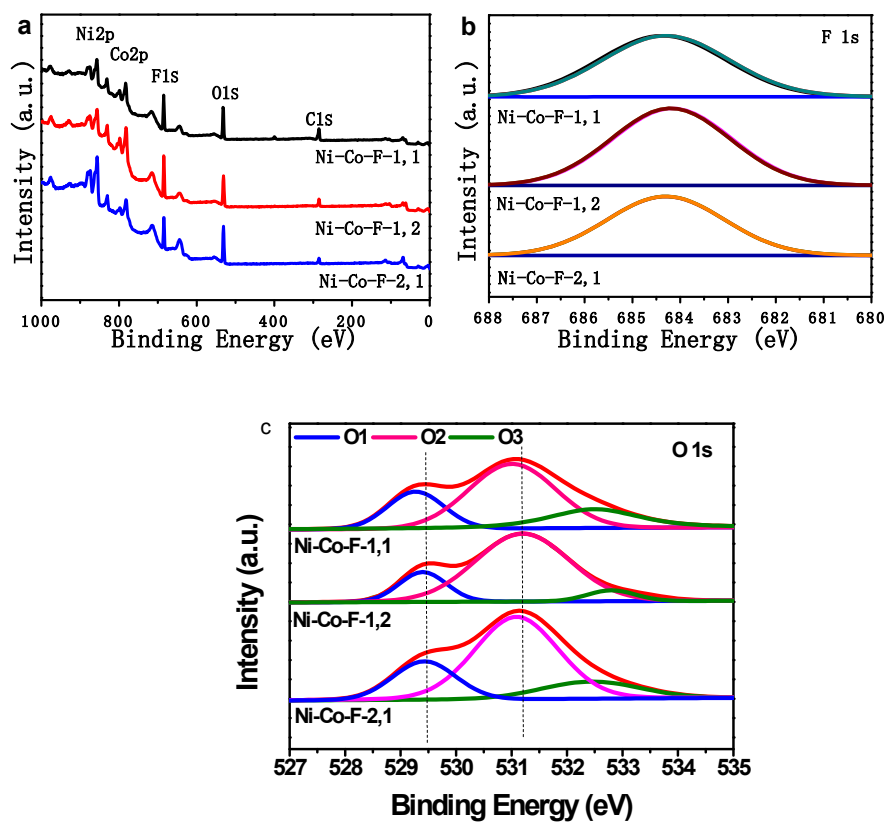


Fig. S2 (a) XPS survey of Ni-Co-F-1,1, Ni-Co-F-1,2 and Ni-Co-F-2,1. High-resolution XPS of (b) F 1s (c) O 1s of Ni-Co-F-1,1, Ni-Co-F-1,2 and Ni-Co-F-2,1.

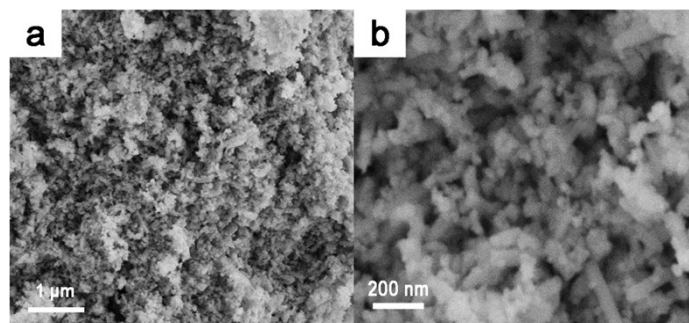


Fig. S3a SEM images of nanostructured Ni-Co-F-1,1 catalyst.

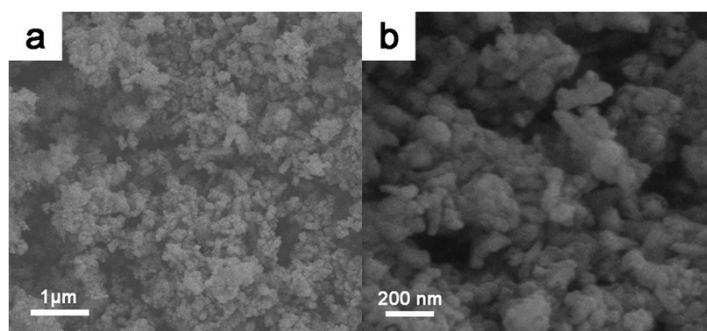


Fig. S3b SEM images of Ni-Co-F-1,1 obtained after the microwave treatment and before calcination.

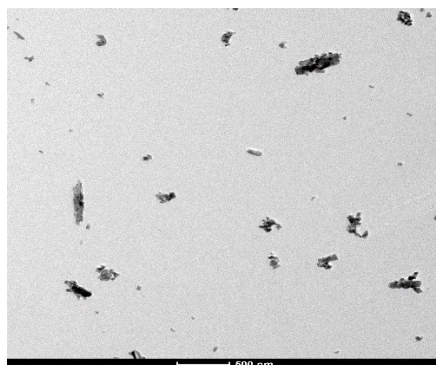


Fig. S3c TEM images of nanostructured Ni-Co-F-1,1 catalyst.

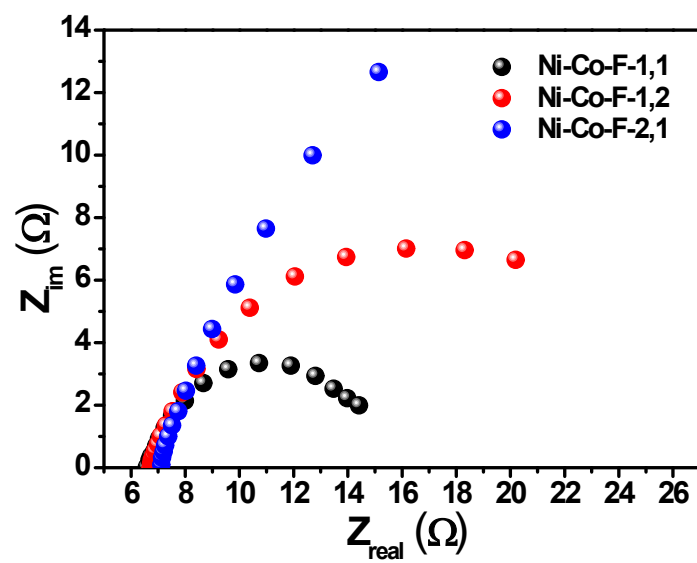


Fig. S4 Electrochemical impedance spectra of Ni-Co-F-1,1, Ni-Co-F-1,2 and Ni-Co-F-2,1 in 1 M KOH at 1.62 V (vs. RHE).

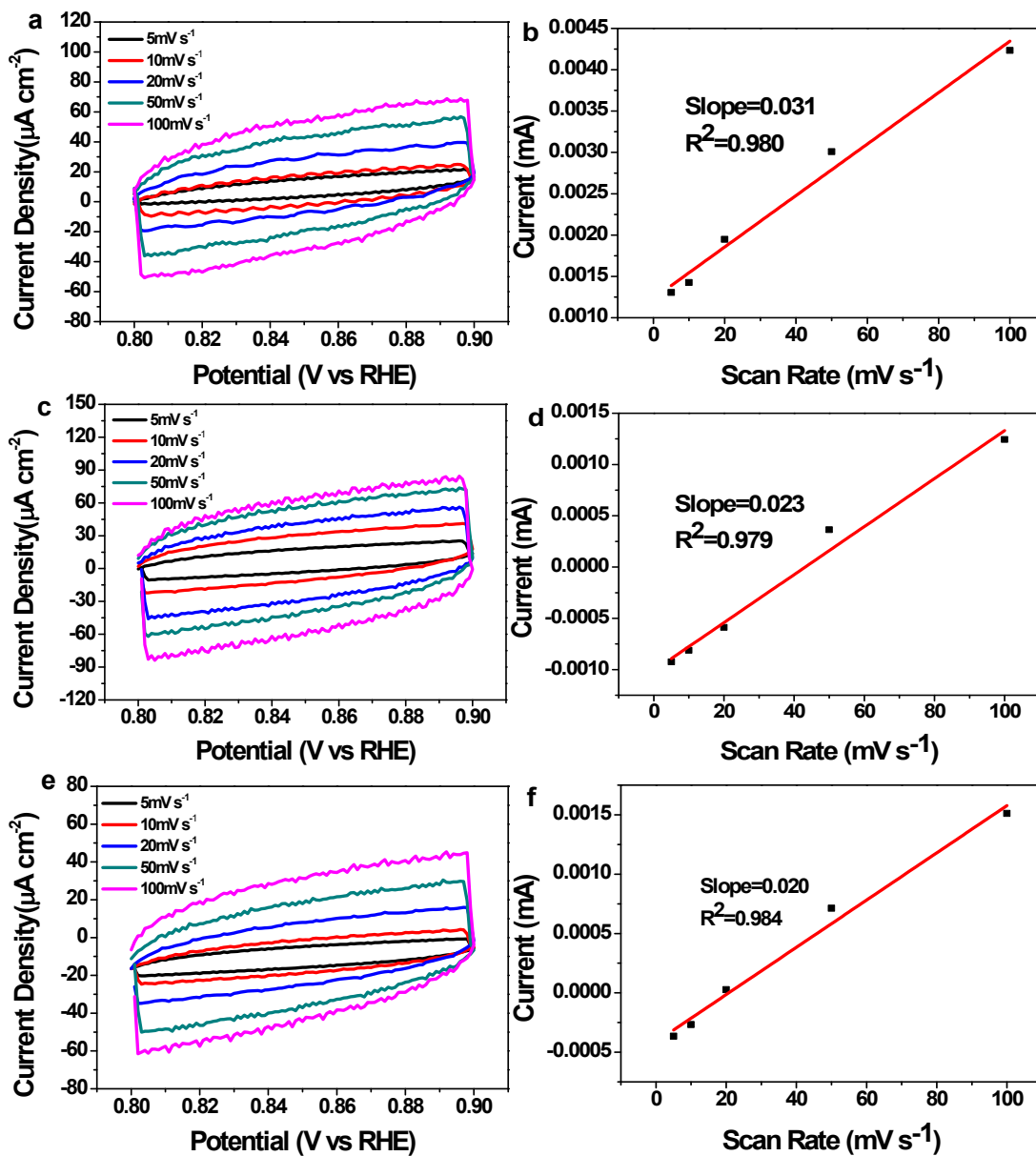


Fig. S5 Scan-rate dependent CVs of (a) Ni-Co-F-1,1; (c) Ni-Co-F-1,2 and (e) Ni-Co-F-2,1 at potential of 0.80 V–0.90 V in 1 M KOH; linear plot of capacitive current density vs. scan rate for (b) Ni-Co-F-1,1; (d) Ni-Co-F-1,2 and (f) Ni-Co-F-2,1.

Table. S1 The content of Ni and Co with different valence states in Ni-Co-F-1,1, Ni-Co-F-1,2 and Ni-Co-F-2,1 catalysts.

	Ni ³⁺	Ni ²⁺	Co ³⁺	Co ²⁺
Ni-Co-F-1,2	38.1%	61.9%	23.4%	76.5%
Ni-Co-F-1,1	45.9%	54.1%	11.8%	88.2%
Ni-Co-F-2,1	23.3%	76.7%	28.3%	71.4%