

Amorphous FeCoNiBO_x Nanosheets as Highly Active and Durable Electrocatalysts for Oxygen Evolution Reaction in Alkaline Electrolyte

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1. Experimental Section

1.1 Chemicals

FeCl₂·4H₂O (99%), CoCl₂·6H₂O (98%), NiCl₂·6H₂O (98%), potassium hydroxide (KOH), polyvinylpyrrolidone (PVP), and diethylene glycol (DEG) were purchased from Shanghai Aladdin, China. Anhydrous ethanol and NaBH₄ was purchased from Xinbote Chemical Co., Ltd. and Tianjin Obokai Chemical Co., Ltd, respectively.

1.2 Catalysts synthesis

The FeCoNiBO_x was synthesized through a low-temperature chemical reduction method. Firstly, FeCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O in equimolar ratio according to the designed composition (a total of 1 mmol) were dissolved in DEG (5 mL). The

mixed solution was continuously stirred for 2 h until a clear and transparent metal salt precursor solution was obtained. Meanwhile, a solution was prepared by mixing NaBH_4 (5 mmol) with a mixture of DEG (30 mL)/PVP (5 mmol) that was kept in the ice-bath for 10 minutes. Then the above two solutions were mixed together and vigorously stirred for 30 minutes. The obtained reaction product FeCoNiBO_x was washed several times with absolute ethanol and deionized water followed by centrifugation and finally dried in air at 40 °C for 8 hours.

1.3 Materials characterizations

The crystallinity of FeCoNiBO_x was detected using an X-ray diffractometer (XRD SMARTLAB 9) from 10°–80° with a scanning rate of 5° min⁻¹. Scanning electron microscopy (SEM, ZEISS SUPRA55, scanning voltage @ 15 k V) and energy dispersive spectroscopy (EDS) were used to obtain the morphology and elemental composition of the samples. Transmission electron microscopy (TEM, Thermo Fischer, 200 kV) was used to further investigate the microstructure of the sample. The surface chemical state of FeCoNiBO_x before and after the reaction was obtained by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K- Alpha).

1.4 Electrode Preparation

5 mg FeCoNiBO_x powder and 1.5 mg carbon black treated with HNO_3 were first dissolved in 0.5 ml N, N-Dimethylformamide (DMF), and mixed with 10 μl nafion. The obtained solution was sonicated for 60 min to form a uniform ink. The FeCoNiBO_x electrode was prepared by spreading 20 μl ink on a piece of carbon paper of 3*3 mm².

1.5 Electrochemical measurements

Electrochemical measurements were carried out using a typical three-electrode system soaked in 1 M KOH solution and connected to an electrochemical workstation (CHI 760E). The as-prepared carbon paper, Pt sheet, and Hg/HgO were used as the working, counter, and reference electrode, respectively. The reference electrode was calibrated according to the reversible hydrogen electrode (RHE) in an O₂ saturated solution. Linear sweep voltammetry (LSV) test was performed at a scan rate of 1 mV s⁻¹ without IR compensation. Before the LSV measurement, the samples were activated by cyclic voltammetry test (CVs) for 20 cycles. The electrochemical impedance spectroscopy (EIS) measurement was performed in a frequency range from 100 k to 0.1 Hz with an amplitude of 5 mV. All voltages were calibrated to RHE by the equation:

$$E(\text{RHE}) = E(\text{Hg/HgO}) + 0.059 \text{ pH} + 0.098 \text{ V}.$$

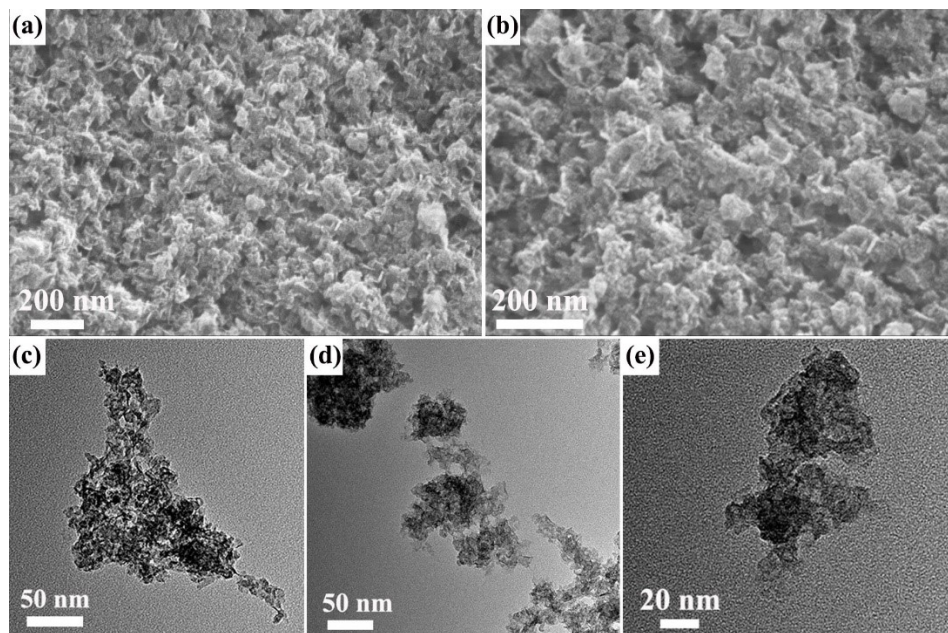


Fig. S1 SEM (a, b) and TEM (c, d, e) of FeCoNiBO_x .

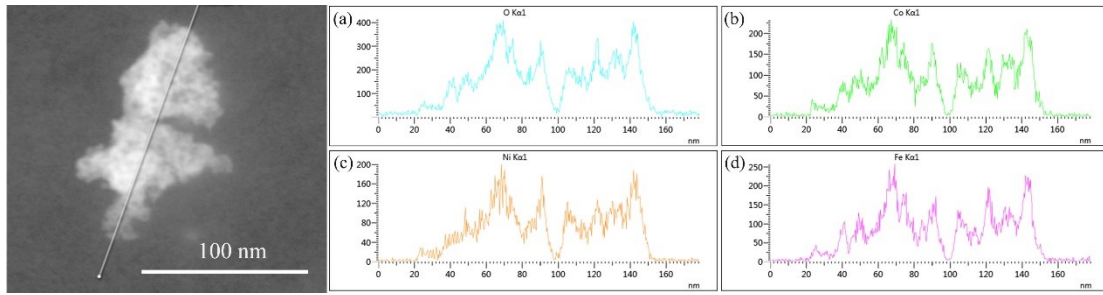


Fig. S2. Line scan and element distribution images of FeCoNiBO_x

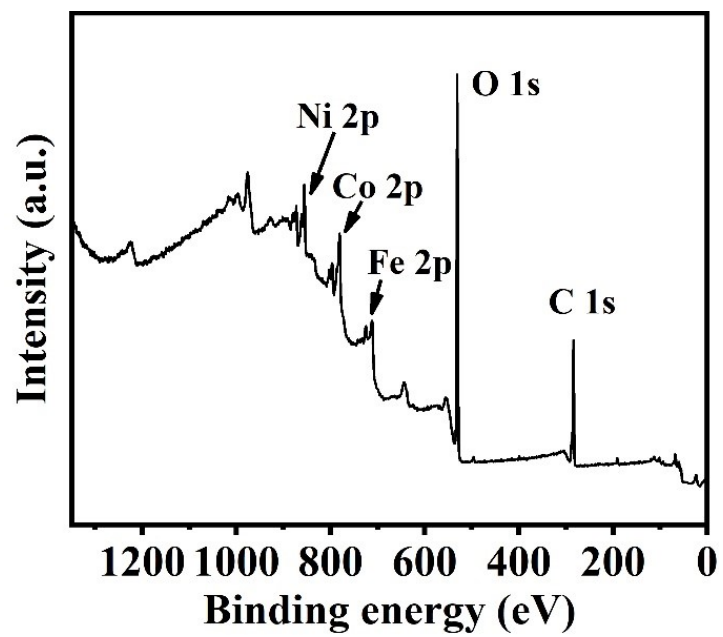


Fig. S3 XPS full spectra of FeCoNiBO_x.

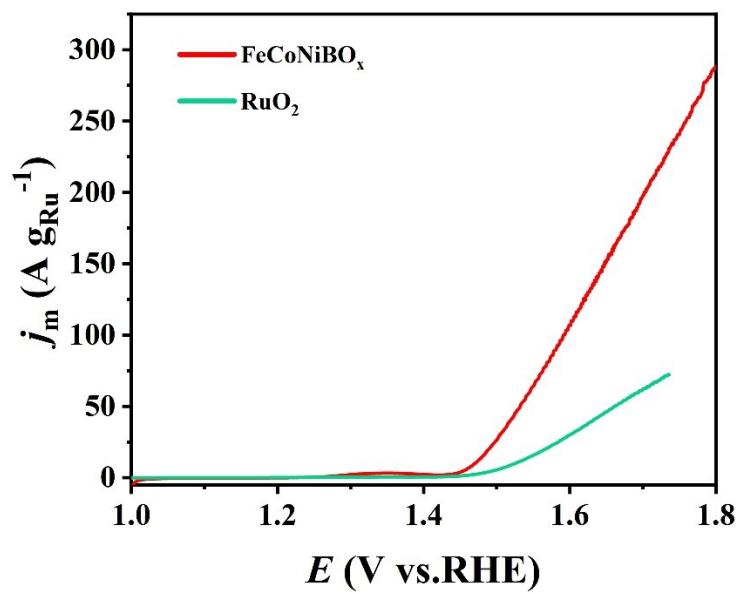


Fig. S4 LSV curves of FeCoNiBO_x and RuO_2 .

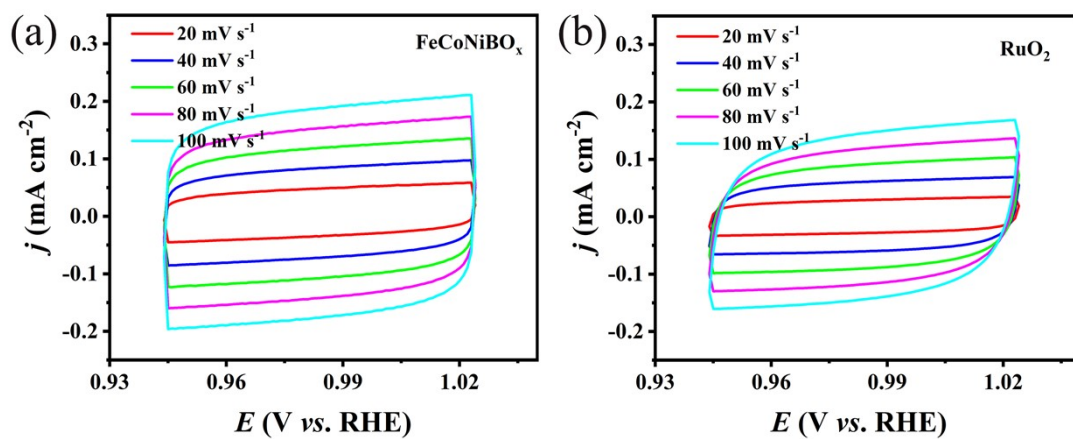


Fig. S5 Cyclic voltammetry curves with different scanning speeds (20, 40, 60, 80, 100 mV s⁻¹) of (a) FeCoNiBO_x and (b) RuO₂.

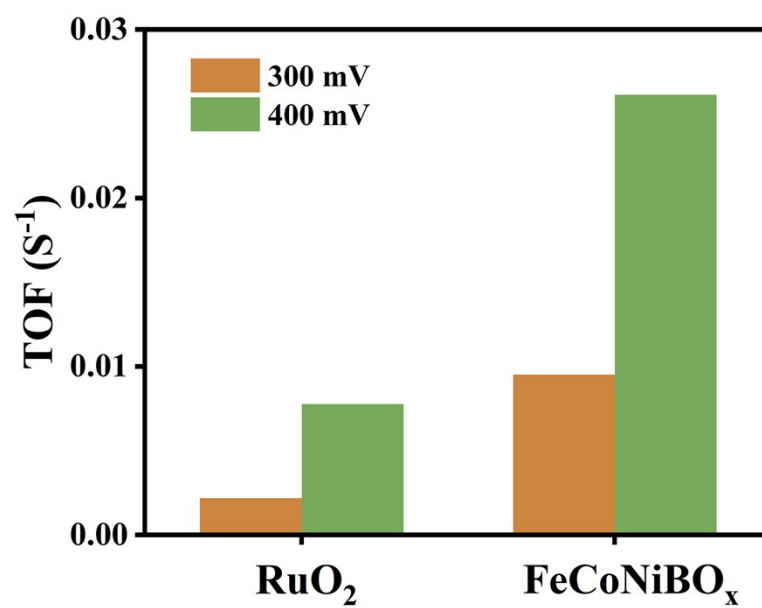


Fig. S6 TOF of $FeCoNiBO_x$ and RuO_2 .

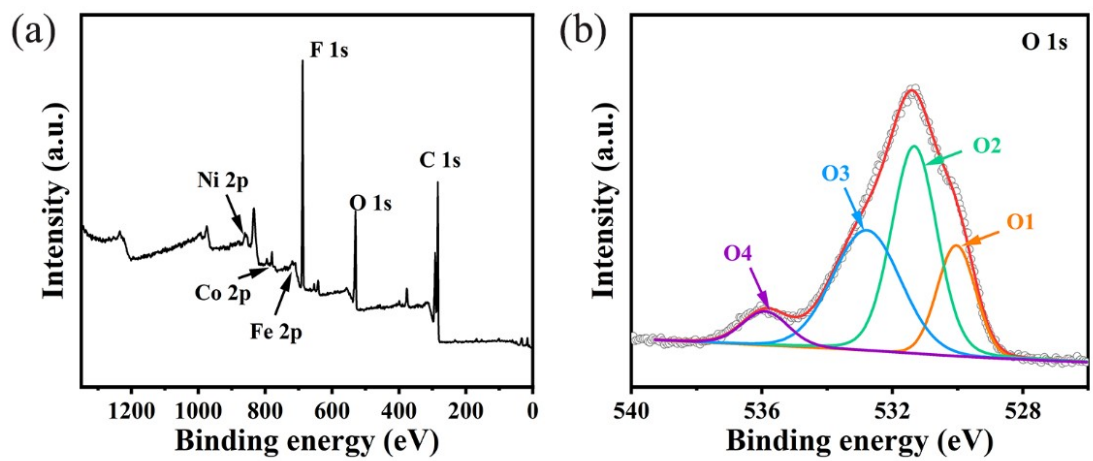


Fig. S7 (a) XPS full spectra and (b) O 1s spectrum of FeCoNiBO_x after OER.

Table S1. Comparison of the OER performances of FeCoNiBO_x and the recently reported electrocatalysts

Catalysts	Overpotential /mV	Tafel slope/mV dec ⁻¹	Electrolyte	Ref.
NixB	280	89	1 M KOH	1
FeB ₂	296	52.4	1 M KOH	2
FeCo _{2,3} NiB	274	38	1 M KOH	3
Cox-Fe-B	298	62.6	1 M KOH	4
Ni-B	360	76	1 M KOH	5
NiB on Ni ₃ B	302	52	1 M KOH	6
Co ₂ B	287	50.7	1 M KOH	7
Ni ₃ B/rGO	290	88.4	1 M KOH	8
NiB _{0.45} /NiOx	296	58	1 M KOH	9
NixB/f-MWCNT	286	46.3	1 M KOH	10
FeNi ₃ -B/G	230	50	1 M KOH	11
Co-P-B	290	42	1 M KOH	12
Co-B/NF	265	55.6	1 M KOH	13
NiCoFeB	284	46	1 M KOH	14
Co-Bi/G	290	53	1 M KOH	15
Ni-Bi/rGO	329	79	1 M KOH	16
Ni-Bi@NiB	302	52	1 M KOH	17
Ni-Fe-Bi	230	32	1 M KOH	18
NiFe@NiFeBi/CC	294	96	1 M KOH	19
NiCo-Bi/CC	388	142	1 M KOH	20
Ni-Bi/CC	407	117	1 M KOH	21
Co _{0.75} Fe _{0.25} Bi/CP	227	43.2	1 M KOH	22
FeBi@FeNi LDH	246	56.48	1 M KOH	23
FeCoNiBO _x	245	59.4	1 M KOH	This work

Table S2. Atomic ratio from EDS and XPS.

Element	EDS	XPS
Fe2p	10.60	9.16
Co2p	11.31	8.81
Ni2p	10.98	8.58
B1s	-	8.25
O1s	67.11	65.20

Table S3. Chemical composition of FeCoNiBO_x at initial and after 40 h.

ID	Fe ³⁺ /Fe ²⁺	Co ³⁺ /Co ²⁺	Ni ³⁺ /Ni ²⁺
Initial	0.57	1.94	-
After 40 h	1.4	2.80	0.6

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