

Electronic Supplementary Information

Electrolyte Modification Method Induced Atomic Arrangement in FeO_x/NF Nanosheets for Efficient Overall Water Splitting

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Experimental

FeO_x/NF were grown by hydrothermal deposition as described previously.¹ In a typical experiment, Ni foam (NF) was cleaned with diluted hydrochloric acid, ethanol and deionized water for several times. 1 mmol of Fe(NO₃)₃·9H₂O was dissolved into 70 mL of deionized water to form a uniform solution, followed by addition of 1 mmol of NH₄F and 2 mmol of urea with vigorous magnetic stirring. After stirring for 1 h, the solution was transferred into the Teflon-lined autoclave, and then the pretreated NF was immersed into the reaction solution. The autoclave was sealed and maintained at 120 °C for 12 h in an electric oven. After cooling to room temperature, the sample was collected and washed with deionized water and absolute ethanol for several times and then dried at 60 °C for 10 h. Afterward, the sample was annealed at 400 °C for 2 h to obtain the FeO_x/NF material. Li half-cells were then assembled with the FeO_x/NF electrodes in 2032-type coin cells. A pure commercialized LP40 [1 M LiPF₆, ethylene carbonate (EC)/diethyl carbonate (DEC) = 1:1] was used as a reference electrolyte solvent. Fluoroethylene carbonate (FEC) as an electrolyte additive was used as

received. Detailed contents of FEC are as follow: (i) 0.5%FEC/LP40 which consists of 99.5 vol% LP40 and 0.5 vol% FEC; (ii) 1%FEC/LP40 which consists of 99 vol% LP40 and 1 vol% FEC; (iii) 2%FEC/LP40 which consists of 98 vol% LP40 and 2 vol% FEC. Coin cell assembly was carried out in an Ar-filled glovebox ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm). The coin cells were discharged to 0.01 V versus Li/Li^+ at room temperature at a constant current (0.01 mA) for the first cycle. After cycling, the cells were disassembled and the extracted electrodes were afterwards repeatedly rinsed by ethanol and deionized water. The loading mass densities of FeO_x/NF , $\text{FeO}_x/\text{NF-Li}$ and $\text{FeO}_x/\text{NF-Li-FEC}_1$ were about 1.09, 1.12 and 1.11 mg cm^{-2} , respectively.

Materials characterization

The morphologies of electrodes were characterized by scanning electron microscopy (SEM, JEOL JSM-7800F) operated at 3 kV. Transmission electron microscopic (TEM) images and corresponding elemental distribution analyses were recorded on a FEI Tecnai G2 F30 equipped with an energy dispersive X-ray spectrometer, working on an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried on an AXIS Ultra DLD system.

Electrochemical measurements

All electrochemical measurements were performed on an electrochemical workstation (Autolab PGSTAT302N, Metrohm) using a conventional three-electrode cell in 1.0 M NaOH electrolyte (pH = 13.6). The as-prepared electrodes, a platinum plate, a saturated calomel electrode (SCE) was employed as the working electrode, counter electrode and reference electrode, respectively. The possibility of Pt-deposition of the working electrode for HER electrocatalysis was excluded by the virtually identical LSV curves of $\text{FeO}_x/\text{NF-Li-FEC}_1$ by using Pt and graphite as counter electrodes (Fig. S1). All measured potentials were calibrated versus reversible hydrogen electrode (RHE) according to the equation $E_{\text{RHE}} = E_{\text{SCE}} + 0.244 + 0.059 \times \text{pH}$. The linear sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV s^{-1} . All the LSV curves were 85% iR -corrected, with iR -corrected potential determined directly from the experimentally measured solution resistances. Electrochemical impedance spectroscopy (EIS) was performed over a frequency in

the range from 100 kHz to 0.1 Hz. The long-term durability test was taken out using the chronopotentiometry method. The C_{dl} values for as-prepared working electrodes were determined from the cyclic voltammogram (CV) within a narrow potential range (0.0-0.1 V vs. RHE for HER) at different scan rates.

Overall water splitting measurements were taken out in a two electrodes system consisting of $\text{FeO}_x/\text{NF-Li-FEC}_1$ as anode and $\text{FeO}_x/\text{NF-Li-FEC}_1$ as cathode. The LSV curve for overall water splitting was recorded in 1.0 M NaOH at a rate of 5 mV s^{-1} with iR compensation.

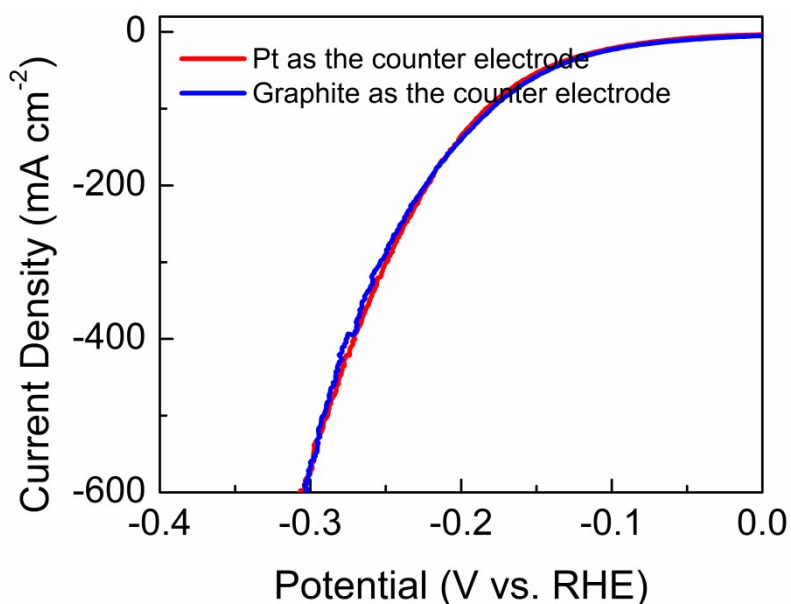


Fig. S1 LSV curves of $\text{FeO}_x/\text{NF-Li-FEC}_1$ by using Pt and graphite as counter electrode.

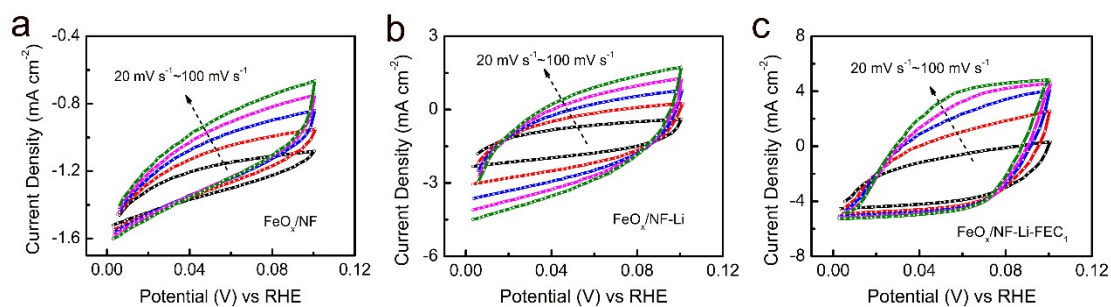


Fig. S2 (a-c) The CV measurements for ECSAs in the region of 0-0.1 V vs RHE upon HER.

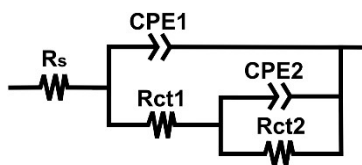


Fig. S3 Equivalent circuit for fitting the impedance value of all catalytic.

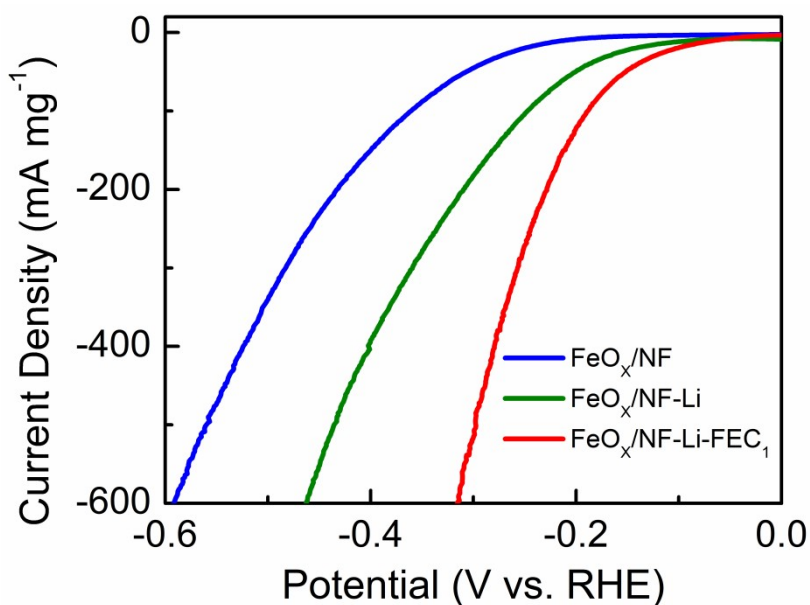


Fig. S4 HER polarization curves of FeO_x/NF, FeO_x/NF-Li and FeO_x/NF-Li-FEC₁ in terms of mass activity.

Table 1. C 1s, Fe 2p, O 1s, F 1s, and Li 1s relative concentrations on the surface of FeO_x/NF-Li and FeO_x/NF-Li-FEC₁ from the XPS results

	C 1s	Fe 2p	O 1s	F 1s	Li 1s
FeO _x /NF-Li (At%)	56.14	1.35	29.44	1.69	11.39

FeO_x/NF-Li-FEC₁ (At%) 41.83 0.96 41.83 3.16 17.58

Table S2. HER Performance in alkaline solution of our sample compared with recently reported electrocatalysts.

Catalyst	CD (mA cm ⁻²)	OP (mV)	TS (mv dec ⁻¹)	Reference
Pt/C	10	41	87	[2]
Pt-PAF-99	10	56	145	[3]
NiFe ₂ O ₄	10	300	125	[4]
Ni/C-SnO ₂	10	304	136	[5]
Ni@NC	10	236	140	[6]
NF/NiMoO ₄ /NiMo@NiS	10	36	40	[7]
NiFeMo/NF	10	180	124	[8]
Ni ₃ S ₂ @LiMoNiO _x (OH) _y	500	255	78.9	[9]
FeO _x /NF-Li-FEC ₁	200	222	123	This work

Current Density (CD); Overpotential (OP); Tafel Slope (TS).

Table S3. EIS data of all electrodes for HER

	FeO _x /NF	FeO _x /NF-Li	FeO _x /NF-Li-FEC ₁
R _{ct(1)} (Ω)	0.868	0.025	0.256

R_{ct2} (Ω)	9.305	0.755	0.201
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Table S4. Recent progresses in Fe-based materials as bifunctional electrocatalysts for overall water splitting.

Catalyst	Support	A cell voltage (CD_{10})	Reference
CoFe10%-P/NF	NF	1.61 V	[10]
Ni ₃ S ₂ -FeS/NF-2	NF	1.55 V	[11]
NiFeMo/NF	NF	1.62 V	[8]
NiFeSbP/GB	GB	1.72 V	[12]
CoFeZr oxides	NF	1.63 V	[13]
FeP _x @Fe	IF	1.67 V	[14]
Ni-Fe nanoparticles	NF	1.55 V	[15]
CoFeO@BP	CP	1.58 V	[16]
FeO _x /NF-Li-1%FEC	NF	1.56 V	This work

Graphite Bar (GB); Carbon Paper (CP); Current Density at 10 mA cm⁻² (CD_{10}); Ni Foam (NF); Iron Foam (IF).

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