Supplementary Information

Modulation engineering of in-situ cathodic activation of FeP_x based on W-incorporation for hydrogen evolution

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Experimental

Materials

Iron foam (thickness: 1.5 mm, bulk density: 0.1 g cm^{-3}) was purchased from Heze Tianyu Technology Development Co., Ltd. Iron sulphate heptahydrate ($FeSO_4\cdot7H_2O$), sodium tungstate dehydrate ($Na_2WO_4\cdot2H_2O$), boric acid (H_3BO_3), sodium gluconate ($C_6H_{11}NaO_7$), sodium chloride (NaCl), sodium hydroxide (NaOH), nitric acid (HNO_3), hydrogen peroxide (H_2O_2, 30 wt. %), potassium hydroxide (KOH), and sodium hypophosphite ($NaH_2PO_2\cdot H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification and all aqueous solutions were prepared with ultrapure water (>18.25 MΩ cm) obtained from Millipore system.

Characterizations

Scanning electron microscopic (SEM) images and corresponding elemental distribution analyses were performed on JEOL JSM-7500F at an acceleration voltage of 5.0 kV equipped with an energy dispersive X-ray spectrometer. High-resolution transmission electron microscopic (HRTEM) images were taken on FEI Tecnai G20. X-ray diffraction patterns (XRD) were obtained from BRUKER D2 PHASER. ICP-AES was performed by inductively coupled plasma spectrometry (Agilent 720) and X-ray photoelectron spectroscopy (XPS) was conducted on Thermo Fisher Scientific Escalab 250Xi using Al Kα radiation

Electrochemical measurements

The electrochemical measurements were conducted with Gamry Reference 600 electrochemical workstation with a three-electrode system in 1.0 M KOH, using carbon rod, SCE as counter electrode and reference electrode, respectively. The working electrode included W-FeP_x/IF, W-FeO_x/IF, FeP_x/IF, WO_x/IF, and Blank IF. The potential conversion from SCE to RHE (reversible hydrogen electrode) was based on the following equation: $E_{RHE} = E_{SCE} + 0.243 + 0.0591\times$ pH. Linear sweep voltammetry (LSV) curves were performed at a scan rate of 5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were conducted at -1.165 V (vs. SCE) with frequency from 10^5 Hz to 0.01 Hz at an AC voltage of 5 mV. CV tests were performed from -1.08 to -1.18 V (vs. SCE) at scan rates of 40, 60, 80, 100, and 120 mV s^{-1}. Stability tests were measured by chronoamperometry of 100 h and CV of 10000 cycles.

The advantages of iron foam as substrate are described as follows: (i) Compared to other expensive metal substrates like Ni foam, NiFe alloy and Cu foil, iron foam with ultralow cost as the substrate shows great promise in large-scale commercial generation of hydrogen. (ii) Except Fe and W, there are no other kinds of metal compounds in the W-FeO_x sample, which could also exert influence in catalytic performance.

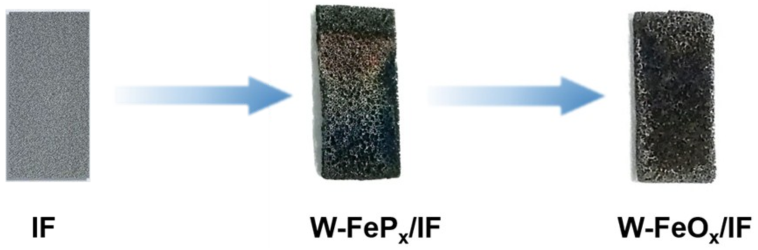

Fig. S1 Photographs of prepared electrocatalysts.

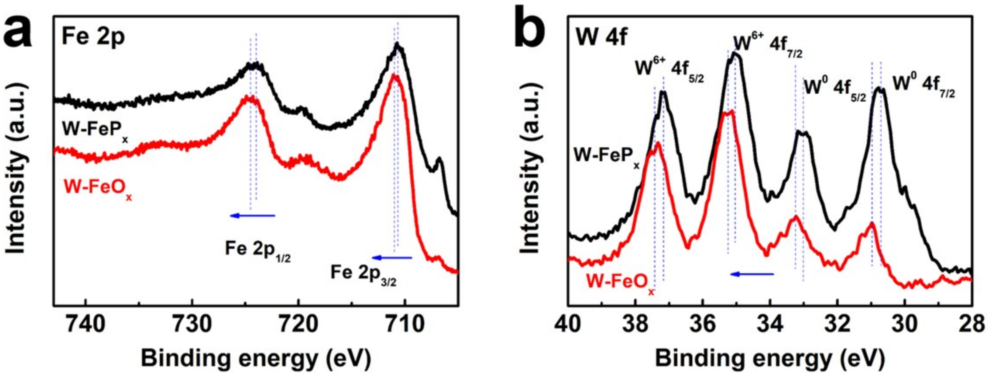

Fig. S2 XPS peaks shift of (a) Fe 2p, (b) W 4f after in-situ cathodic activation.

Table S1 The elemental content (mass ratio) of as-prepared W-FeO_x/IF by ICP-AES.

Sample	Fe	W	P
W-FeO_x/IF	79.19%	6.03%	0.07%

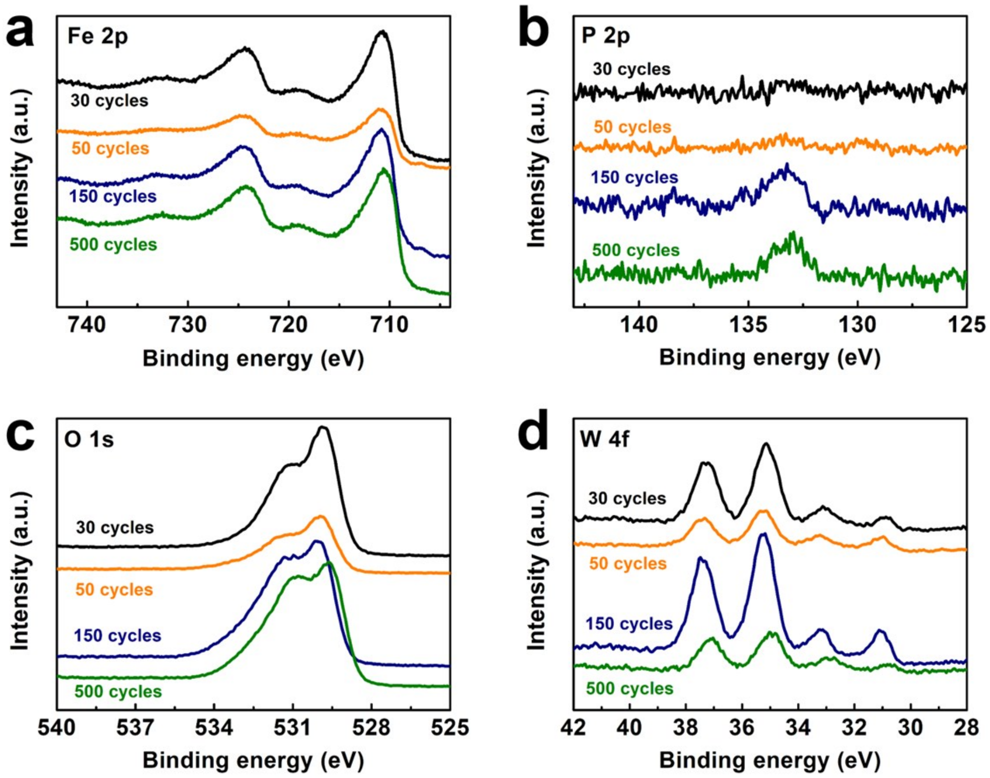

Fig. S3 XPS spectra comparison of W-FeO$_x$/IF obtained in different CV cycles. (a) Fe 2p, (b) P 2p, (c) O 1s, (d) W 4f.

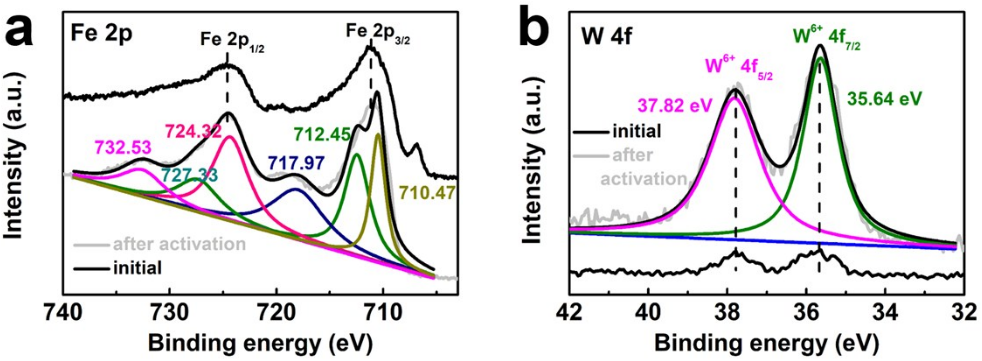

Fig. S4 XPS spectra comparisons for monometallic materials before and after in-situ cathodic activation. (a) Fe 2p for FeO_x/IF, (b) W 4f for WO_x/IF.

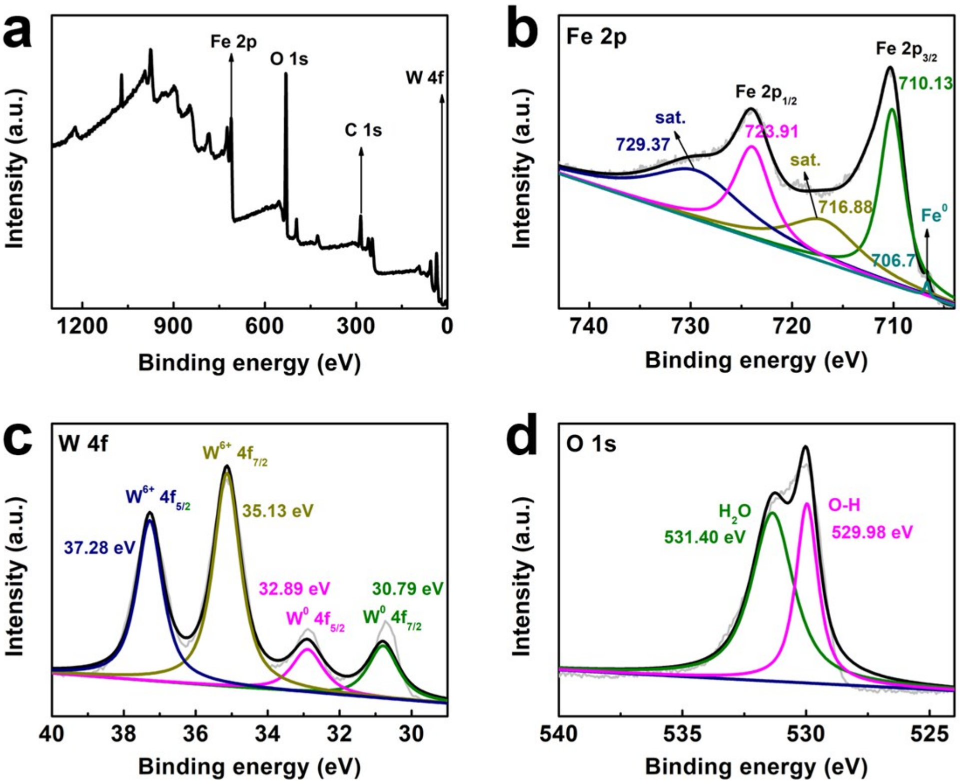

Fig. S5 XPS spectra of FeW(OH)$_x$/IF. (a) survey, (b) Fe 2p, (c) W 4f, (d) O 1s.

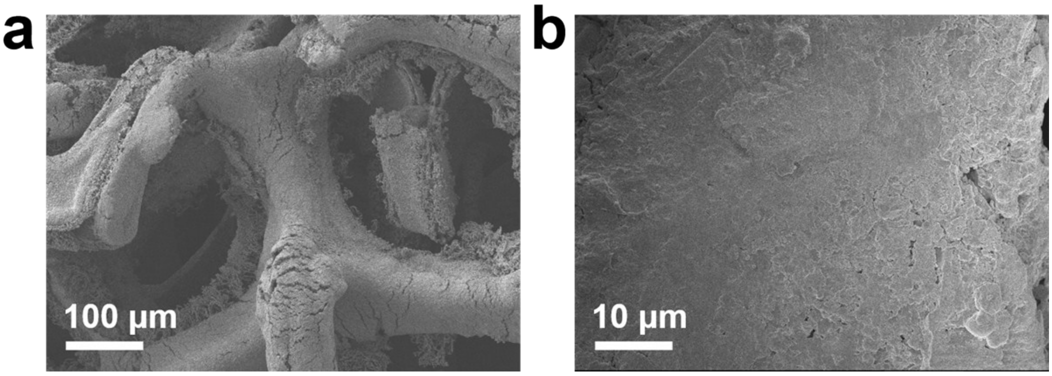

Fig. S6 SEM images of (a,b) IF.

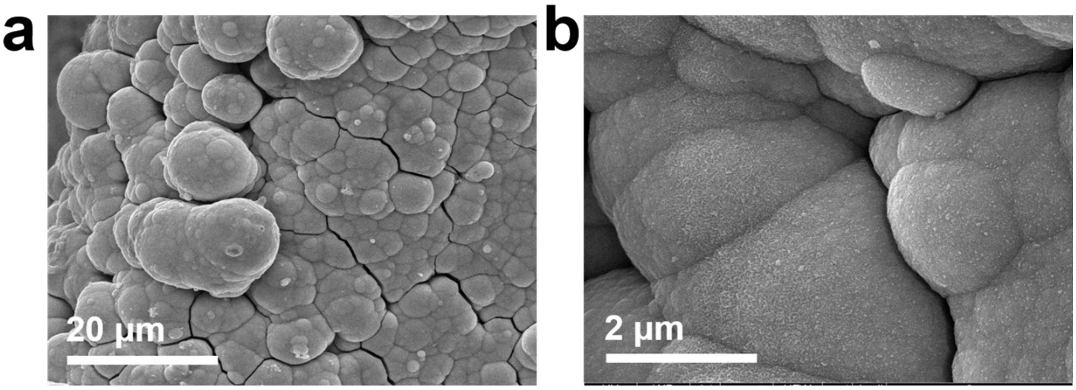

Fig. S7 SEM images of (a,b) FeW(OH)$_x$/IF.

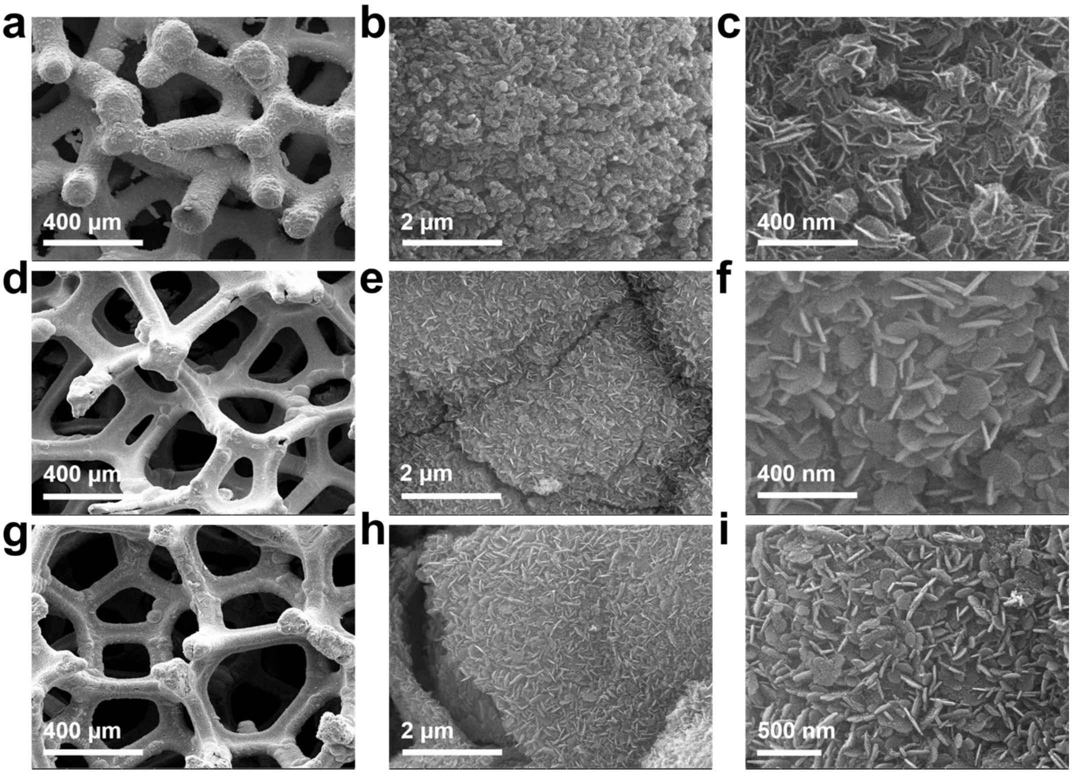

Fig. S8 SEM images of W-FeO_x/IF after (a-c) 30 cycles, (d-f) 150 cycles, and (g-i) 500 cycles of CV.

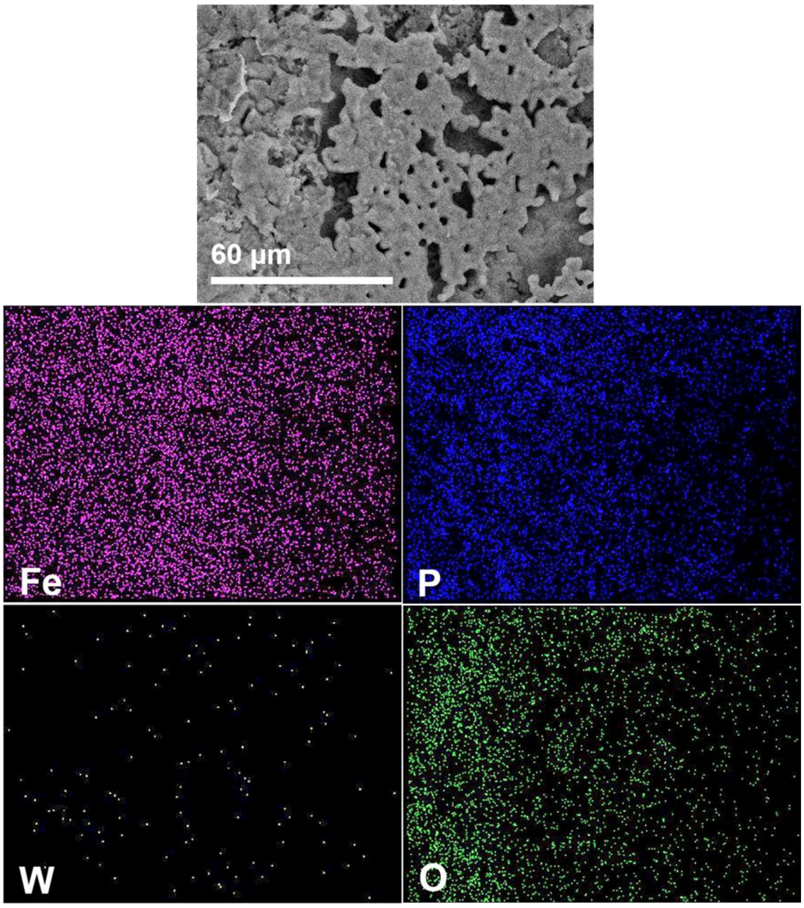

Fig. S9 SEM image and corresponding elemental mapping of W-FeP$_x$/IF.

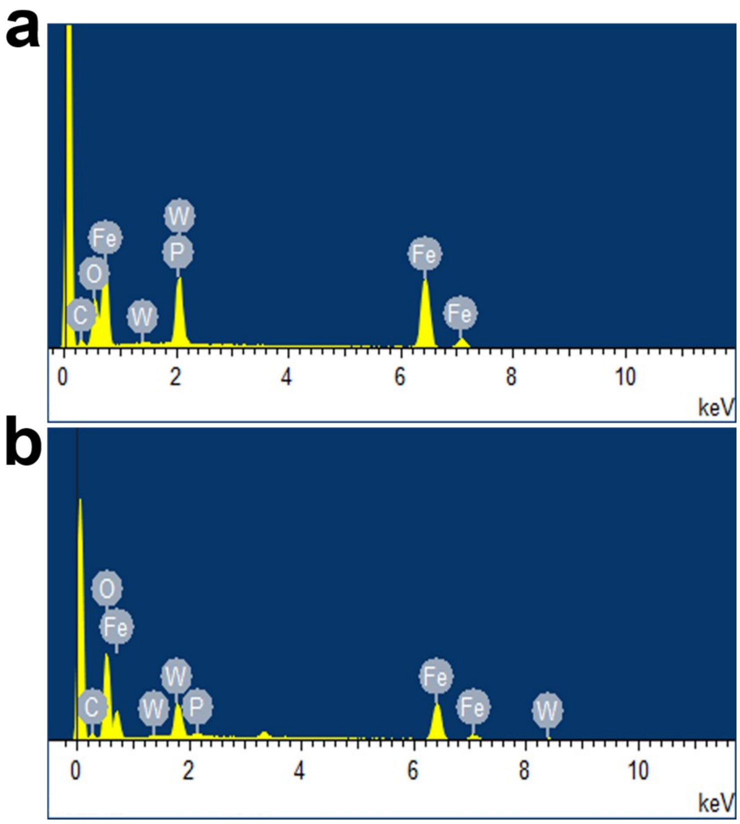

Fig. S10 EDX spectra of (a) W-FeP$_x$/IF and (b) W-FeO$_x$/IF.

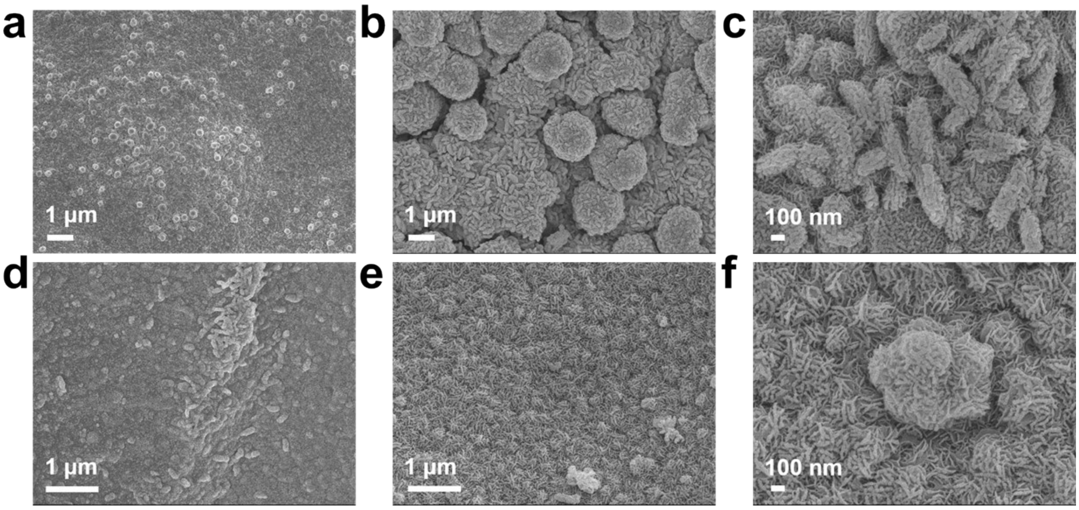

Fig. S11 SEM images of FeO_x/IF (a) before and (b, c) after 50 cycles of CV, and WO_x/IF (d) before and (e, f) after 50 cycles of CV.

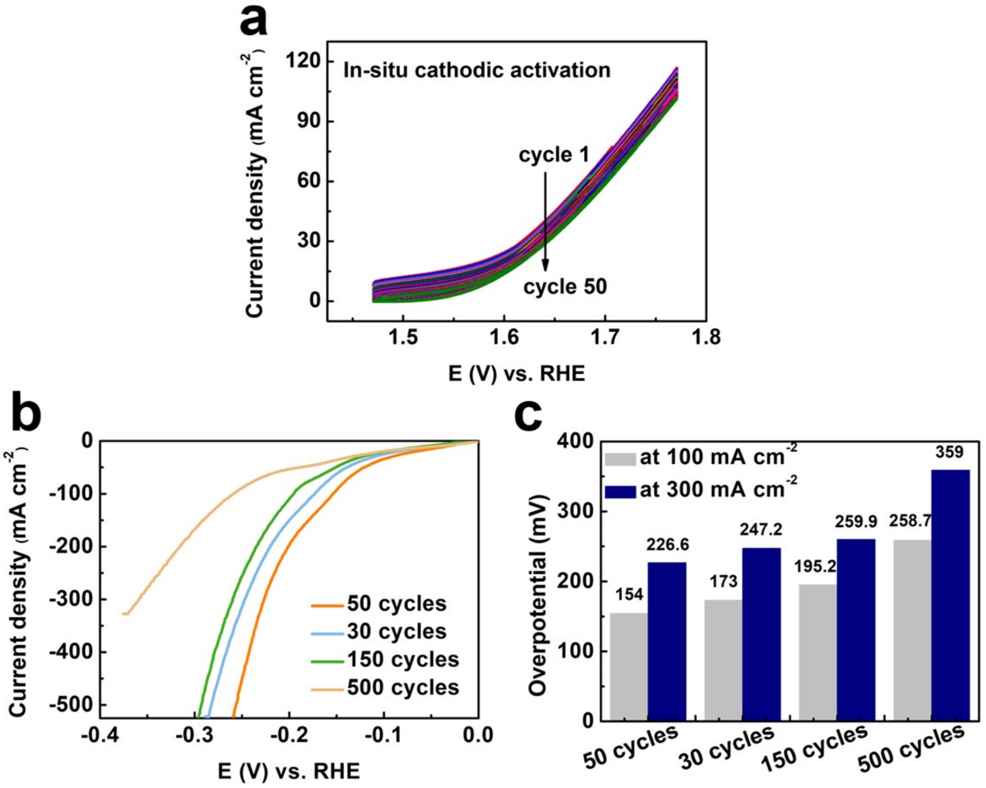

Fig. S12 (a) In-situ cathodic activation applied by CV scanning at 10 mV s^{-1} for 50 cycles between 0.4-0.7 V (vs. SCE), (b) LSV polarization curves of W-FeO$_x$/IF in different CV cycles, and (c) corresponding overpotentials comparison at the same current density.

Table S2 The calculated ECSA values of as-prepared samples.

Sample	C_{dl} mF	C_s mF cm^{-2}	ECSA cm^2
W-FeO$_x$/IF	24.86	0.04	621.5
W-FeP$_x$/IF	24.63	0.04	615.75
FeO$_x$/IF	6.8	0.04	170.0
WO$_x$/IF	4.87	0.04	121.8
Blank IF	2.3	0.04	57.5

The calculation of electrochemically active surface area (ECSA)

The calculation of ECSA and roughness factor (RF) are based on the following equation:

$$ECSA=C_{dl}/C_s \quad (1)$$

In eq (1), C_{dl} is the measured double layer capacitance of samples in 1.0 M KOH (mF) and C_s is the specific capacitance of the catalyst (C_s = 0.04 mF cm^{-2} in 1.0 M KOH).

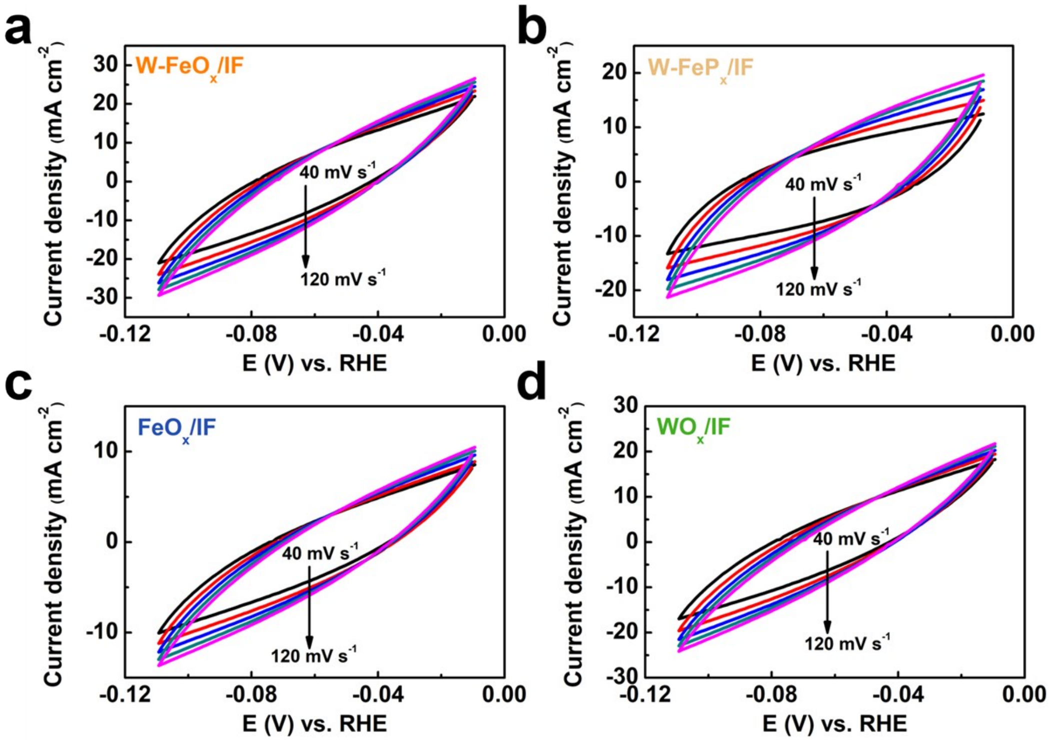

Fig. S13 CV scans of double-layer capacitance measurement of (a) W-FeO$_x$/IF, (b) W-FeP$_x$/IF, (c) FeO$_x$/IF, and (d) WO$_x$/IF at different scanning rates.

Table S3 Elemental values of fitted equivalent circuit.

Samples	R_s (Ω)	R_{ct} (Ω)
W-FeO_x/IF	1.047	5.578
W-FeP_x/IF	1.307	25.08
FeO_x/IF	0.695	10.43
WO_x/IF	0.619	27.71
Blank IF	0.627	34.94

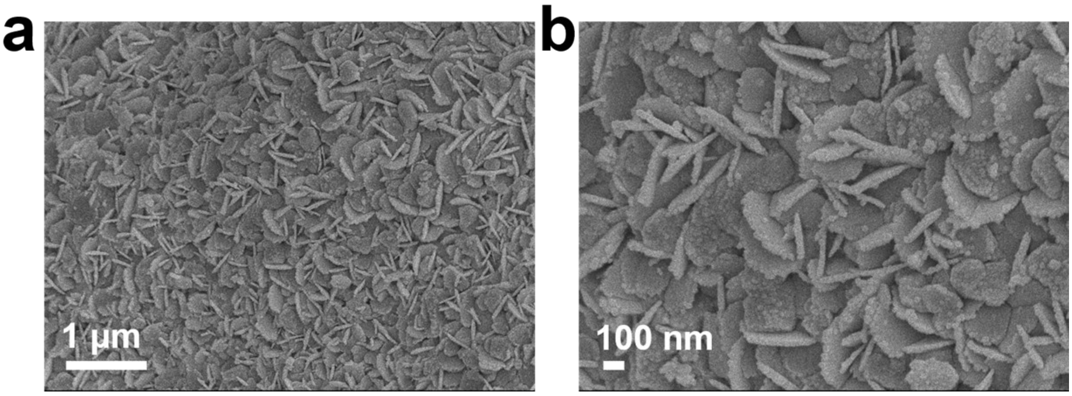

Fig. S14 SEM images of (a, b) W-FeO$_x$/IF after 100 h of chronoamperometry test and 10000 cycles of CV test.

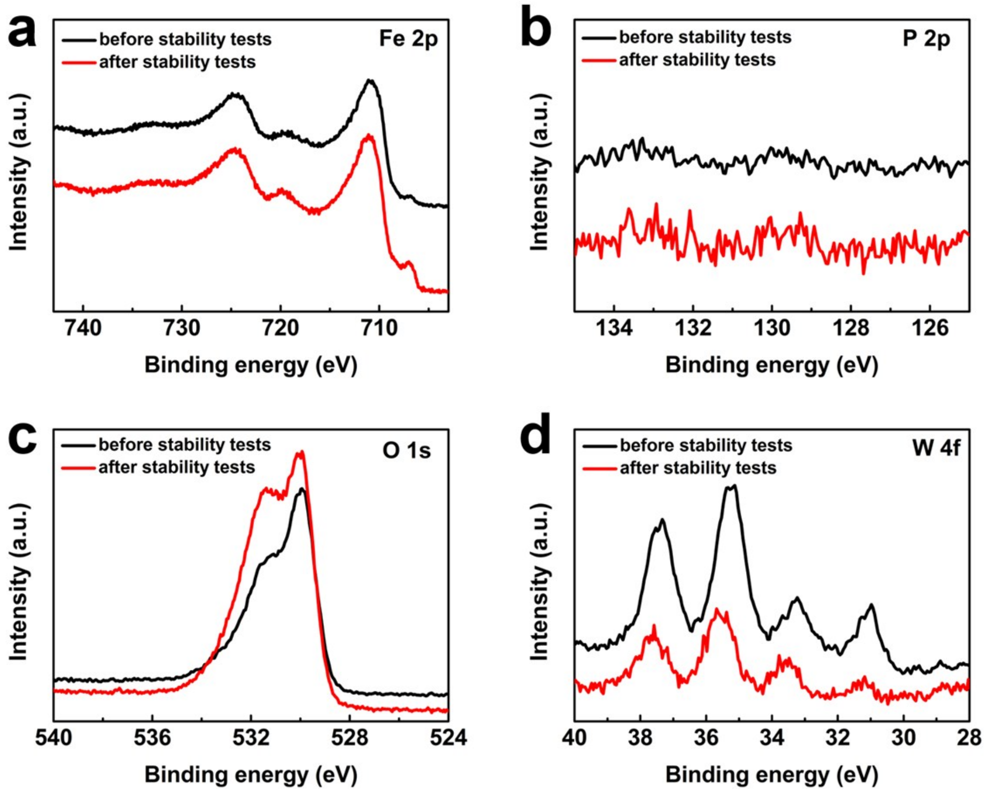

Fig. S15 (a) Fe 2p, (b) P 2p, (c) O 1s and (d) W 4f XPS spectra of W-FeO$_x$/IF before and after stability tests (100 h chronoamperometry at 100 mA cm^{-2} and further10000 cycles of CV) for HER in 1 M KOH.

Table S4 Comparison of HER performance of W-FeO_x/IF with other recently reported nonprecious electrocatalysts in 1 M KOH. (*j*: current density; *η*: overpotential)

Catalysts	***j*** **(mA cm^{-2})**	***η*** **(mV)**	**Stability**	**Reference**
W-FeP_x/IF	100	237.7	--	This work
W-FeO_x/IF	100 500	154.0 256.3	10000 cycles 100 h	
Mo-doped Ni_2Fe_1 oxide	50	>260	--	*J. Mater. Chem. A*, 2018, **6**, 8430-8440
2-cycle $NiFeO_x$/CFP	100	>200	--	*Nat. Commun.*, 2015, **6**, 7261
S-$NiFe_2O_4$/NF	100	>200	--	*Nano energy*, 2017, **40**, 264-273.
$Fe_{1.89}Mo_{4.11}O_7$/MoO_2	10	197	1000 cycles 25 h	*Chem. Sci.* 2018, **9**, 5640-5645.
FeO_x/FeP hybrid	100	>300	45 h	*J. Mater. Chem. A*, 2018, **6**, 9467-9472
g-FeO_x-Cu_3P@Cu	100	176	24 h	*J. Mater. Chem. A*, 2020, **8**, 3351-3356
Ni_2P/Fe_2P Ti foil	100	210	20 h	*Adv. Energy Mater.*, 2018, **8**, 1800484
FeP nanowire arrays	10	194	8 h	*Chem. Commun.*, 2016, **52**, 2819-2822
FeP NAs/CC	10	218	--	*ACS Catal.*, 2014, **4**, 4065
$Ni_{1.5}Fe_{0.5}P$/CF	10	282	12 h	*ACS Sustainable Chem. Eng.*, 2018, **6**, 6146-6156
FeP NPs@NPC	10	214	--	*Nanoscale*, 2017, **9**, 3555-3560
FeP/GA	10	240	5000 cycles 12 h	*Chem Asian J*, 2018, **13**, 679-685
Ni-doped FeP/C-3	100	>165	12 h	*Sci. Adv.*, 2019, **5**, eaav6009
MoO_2-FeP@C	100	190	5000 cycles 24 h	*Adv. Mater.*, 2020, **32**, 2000455