

Electronic Supplementary Information

Experimental Section

Materials: Hydrated nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), sodium molybdenum ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), ammonia solution (25%), zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethylenetetramine (HMT), and potassium permanganate (KMnO_4) were purchased from Beijing Chemical Corp. Potassium hydroxide (KOH) and ethanol were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma-Aldrich. Ti mesh (TiM) was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. The water used throughout all experiments was purified through a Millipore system.

Preparation of ZnO nanorods array on Ti mesh (ZnO NRs/TiM): TiM was firstly washed with acetone, ethanol and water several times to remove the surface impurities. In a typical synthesis, ZnO array was grown on TiM by a wet chemical process. Briefly, TiM was first soaked in 0.5 M KMnO_4 for 30 min to form a seed layer. A precursor solution (100 mL) was prepared containing $\text{Zn}(\text{NO}_3)_2$ (15 mM), HMT (15 mM), and ammonia (4 mL). Then the seeded TiM was dipped into the precursor solution and held at 90 °C for 24 h. Then the ZnO NRs/TiM was taken out and washed with water thoroughly before vacuum dried.

Preparation of ZnO@NiMo NRs/TiM, NiMo HNRs/TiM, and NiMo NPs/TiM: In a typical synthesis, as-fabricated ZnO NRs/TiM was used as the working electrode for cathodic electrodeposition of ZnO@NiMo NRs/TiM under a galvanostatic mode at a cathodic current density of 10 mA cm^{-2} for 2510 s (electrolyte: 0.2 M NiSO_4 , 0.3 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, and 0.02 M Na_2MoO_4 aqueous solution). A saturated calomel electrode (SCE) and graphite rod were used as the reference and counter electrode, respectively. After the electrodeposition, the working electrode was rinsed several times with water and dried. The NiMo HNRs/TiM was obtained after dissolving ZnO template in ammonia solution (25%). NiMo NPs/TiM was directly electrodeposited on bare TiM using the similar method.

Characterizations: Scanning electron microscopy (SEM) measurements were made on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) data was recorded on a RigakuD/MAX 2550 diffractometer. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed on ThermoScientific iCAP6300.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional one-component three-electrode cell was used, including a piece of NiMo HNRs/TiM as the working electrode, a SCE as the reference electrode, and graphite rod as the counter electrode. All the experiments were carried out without activation process at ambient temperature. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of $(0.242 + 0.059\text{pH})$ V. RuO₂ and Pt/C ink was prepared by dispersing 2.5 mg of RuO₂ or Pt/C in 500 μL of ethanol with 5 μL of 5 wt % Nafion solution. Then 34 μL of the catalyst ink was loaded onto TiM surface and air-dried at room temperature. Onset overpotentials were determined based on the beginning of linear region in the Tafel plot.

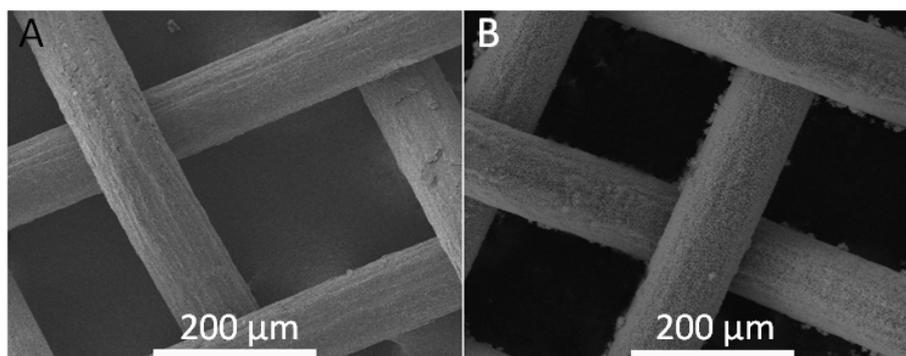


Fig. S1 Low-magnification SEM images of (A) TiM and (B) NiMo HNRs/TiM.

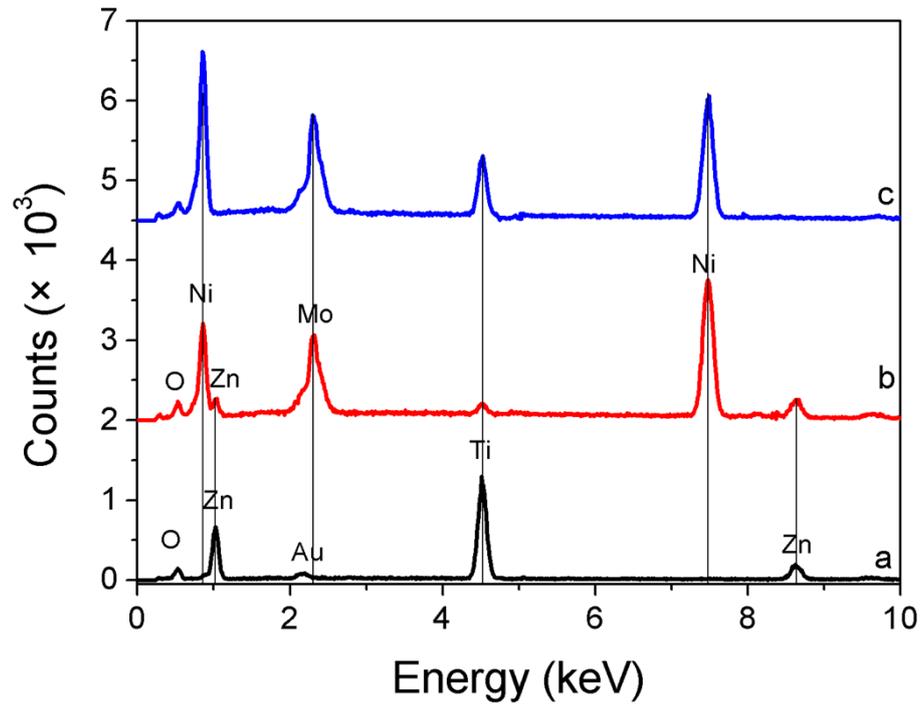


Fig. S2 EDX spectra of (a) ZnO NRs/TiM, (b) ZnO@NiMo NRs/TiM, and (c) NiMo HNRs/TiM.

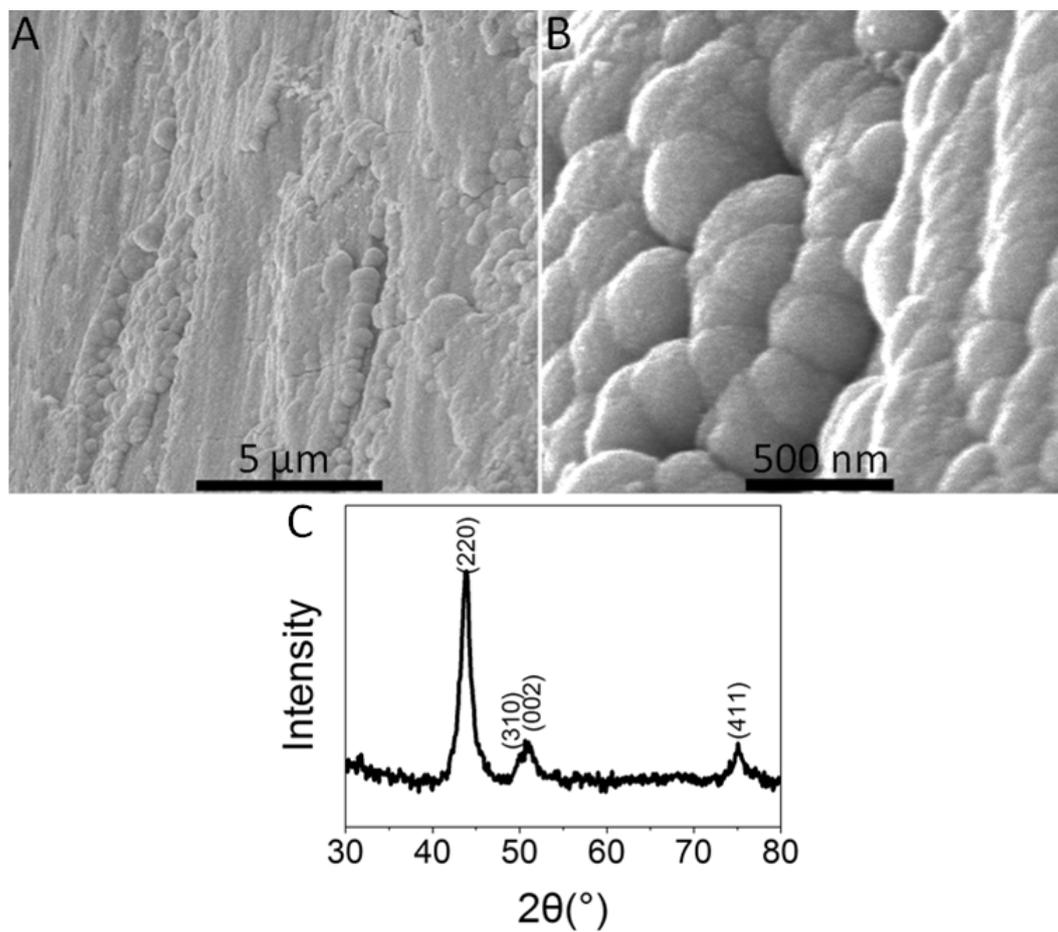


Fig. S3 (A) Low- and (B) high-magnification SEM images of the NiMo NPs/TiM. (C) XRD pattern of the NiMo nanoparticles.

Table S1 Comparison of OER performance in alkaline media for NiMo HNRs/TiM with other non-noble metal OER electrocatalysts (^a catalysts directly grown on current collectors).

Catalyst	Electrolyte	$\eta @ j_{10\text{mA cm}^{-2}}$ (mV)	Ref.
Ni–Co binary oxides NPL	1.0 M KOH	325	1
Co _{0.5} Fe _{0.5} S@N-MC	1.0 M KOH	410	2
CoNi SUNOE	1.0 M KOH	450	3
NiFe SUNOE	1.0 M KOH	550	3
NiCo LDH	1.0 M KOH	367	4
Ni _x Co _{3-x} O ₄ NWs/Ti ^a	1.0 M KOH	~370	5
NiFeO _x	1.0 M KOH	>350	6
Co ₃ O ₄ /NiCo ₂ O ₄ DSNCs	1.0 M KOH	340	7
Ni(OH) ₂ /Ni foam ^a	1.0 M KOH	355	8
Ni+Mo composite	5.0 M KOH	273	9
Fe-Ni oxide	1.0 M KOH	>375	10
NiCo ₂ O ₄ NNs/FTO ^a	1.0 M KOH	565	11
NiMo HNRs/TiM^a	1.0 M KOH	310	This work

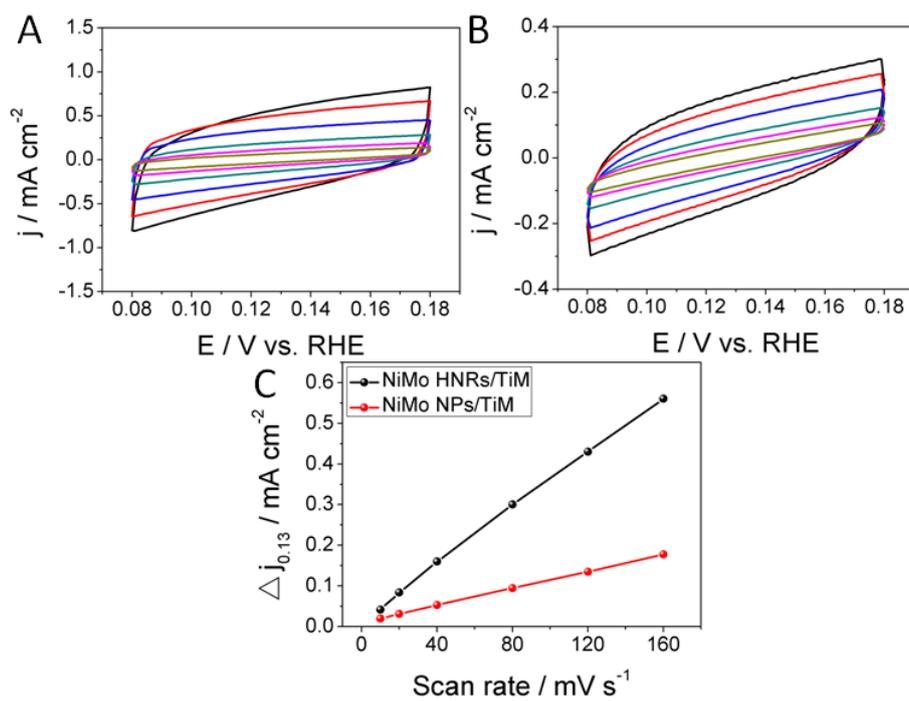


Fig. S4 CVs for (A) NiMo HNRs/TiM and (B) NiMo NPs/TiM. (C) The capacitive currents at 0.13 V as a function of scan rate for NiMo HNRs/TiM and NiMo NPs/TiM ($\Delta j = j_a - j_c$).

Table S2 Comparison of HER performance in alkaline media for NiMo HNRs/TiM with other non-noble metal HER electrocatalysts (^a catalysts directly grown on current collectors).

Catalyst	Current density (j , mA cm ⁻²)	η @ the corresponding j (mV)	Ref.
Co-NCNT/CC ^a	10	180	12
CoP/CC ^a	10	209	13
CoO _x /CN	10	270	14
porous Co phosphide/ phosphate thin film ^a	10	~380	15
Ni ₂ P nanoparticle	10	230	16
NiP ₂ NS/CC ^a	10	102	17
NiO/Ni-CNT	10	~80	18
Ni-Mo nanopowder	10	80	19
Ni wire	10	350	19
NiS ₂ /CC ^a	10	149	20
modified Ni/Ni ₃ N ^a	10	102	21
Ni ₃ S ₂ /NF ^a	10	123	22
bulk MoB	10	218	23
bulk Mo ₂ C	10	192	23
MoC _x nano-octahedrons	10	150	24
Ni ₂ P/NiO _x nanoparticles	10	120	25
NiMo HNRs/TiM^a	10	92	This work

Movie S1 This movie shows hydrogen and oxygen evolution on NiMo HNRs/TiM electrodes in a two-electrode setup driven by a 1.5 V AAA battery in 1.0 M KOH.

References

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