Electronic Supplementary Information

Experimental section

Materials: NH_4F, $(NH_4)_2MoS_4$ and urea were purchased from Beijing Chemical Corp. $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from Aladdin Ltd (China). Ti mesh was purchased from Hangxu filter flagship store. Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma-Aldrich. All chemical regents were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of $Ni(OH)_2$/Ti: $Ni(OH)_2$/Ti was prepared as follows. Typically, a piece of Ti mesh (2×3 cm^2) was washed with HCl, ethanol and deionized water several times to ensure the surface of the Ti mesh was well cleaned before use. The cleaned Ti mesh was immersed into a 40 mL aqueous solution containing 4 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 20 mmol urea, and 8 mmol NH_4F at room temperature. The aqueous solution and Ti mesh were transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 6 h, and then allowed to cool down naturally to room temperature. Then the Ti mesh with precursor was washed with deionized water several times and dried in oven.

Preparation of $NiMoS_4$/Ti: $NiMoS_4$/Ti was prepared by hydrothermal reaction. In a typical synthesis, $(NH_4)_2MoS_4$ (0.06 g) was dissolved in 35 mL water under vigorous stirring for 30 min. Then the solution was transferred into a Teflon-lined stainless autoclave (50 mL) and the as-prepared $Ni(OH)_2$/Ti was immersed into the solution. The autoclave was sealed and maintained at 160 °C for 9 h in an electric oven. After cooled down slowly at room temperature, the $NiMoS_4$/Ti was taken out and washed with deionized water thoroughly before vacuum dried. Loading amount for $NiMoS_4$ is about 1.7 mg cm^{-2}. Other control $NiMoS_4$/Ti samples with different loadings of 0.7, 3.6 and 4.3 mg cm^{-2} were prepared by using 0.1, 1.5 and 2 times reactants concentration.

Preparation of Pt/C modified electrode Ti mesh: 20 mg Pt/C and 10 μL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30-min sonication to form an ink finally. Then 85 μL catalyst ink was loaded on bare Ti mesh

with a catalyst loading of 1.7 mg cm^{-2}.

Characterizations: XRD data were collected on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). SEM measurements were performed on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM images were collected on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. XPS data were acquired on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. $NiMoS_4$/Ti was used as the working electrode. A graphite rod and an SCE electrode were used as the counter electrode and the reference electrode, respectively. The temperature of solution was kept at 25 °C for all the measurements via the adjustment of air condition and heating support, which ensured the variation of diffusion coefficient below 1%. The potentials reported in this work were calibrated to RHE other than especially explained, using the following equation: E_0 (RHE) = E (SCE) + (0.242 + 0.059 pH) V. The iR-correction of LSV curves was done using the following equation: E (RHE) = E_0 (RHE) - I * Rs, I is current (A) and Rs is solution resistance.

Active sites calculation: The $NiMoS_4$/Ti electrode was prepared as mentioned above. CV measurements were carried out in PBS electrolyte (pH: 7). Then, the absolute components of the voltammetric charges (cathodic and anodic) reported during the measurement were added. Assuming one electron redox process, this absolute charge was divided by two. The value was then divided by the Faraday constant to get the number of active sites (n) of the $NiMoS_4$/Ti electrode.

TOF calculation: The turnover frequency (s^{-1}) was calculated following equation:

$$TOF = I/2nF$$

I: Current (A) during the LSV measurement in 0.1 M KOH.

F: Faraday constant (C/mol).

n: Number of active sites (mol).

The factor 1/2 arrives by taking into account that two electrons are required to form one

hydrogen molecule from two protons.

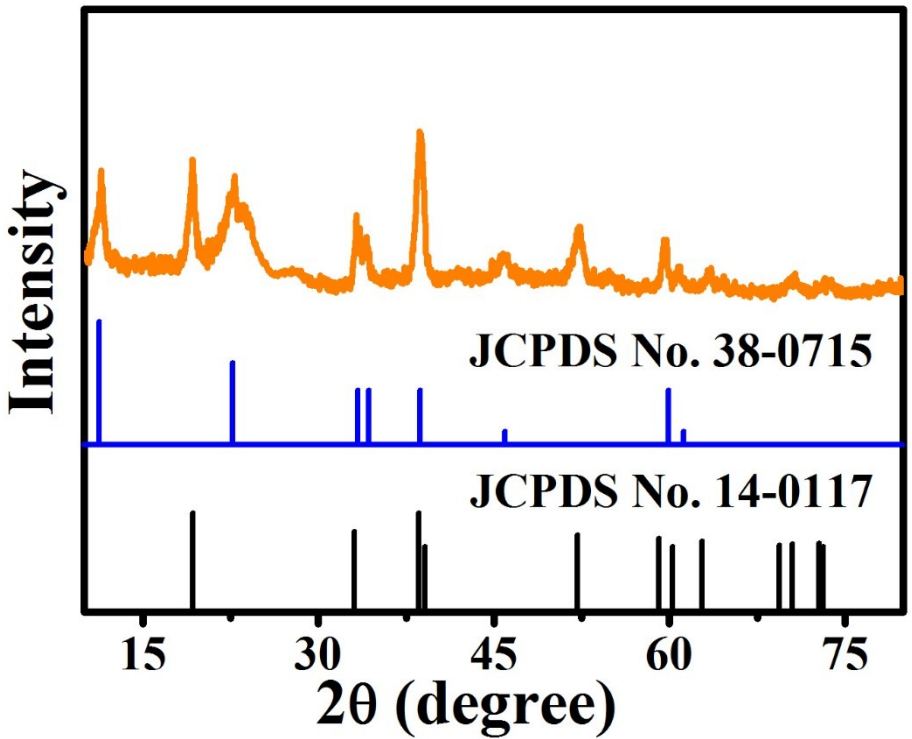

Fig. S1. XRD patterns for $Ni(OH)_2$ nanosheet scraped from Ti mesh.

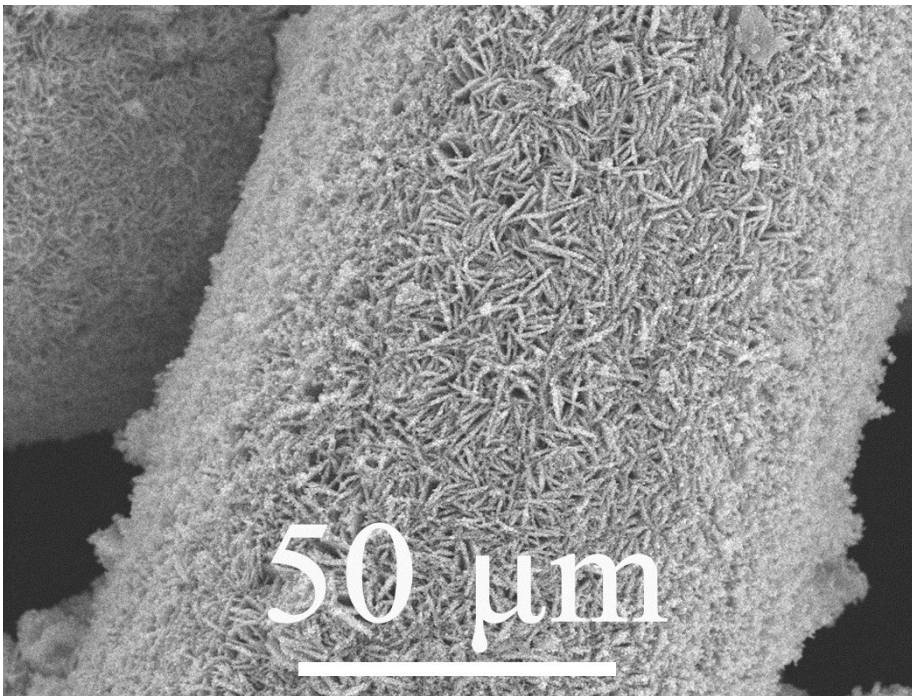

Fig. S2. SEM image of $NiMoS_4$/Ti.

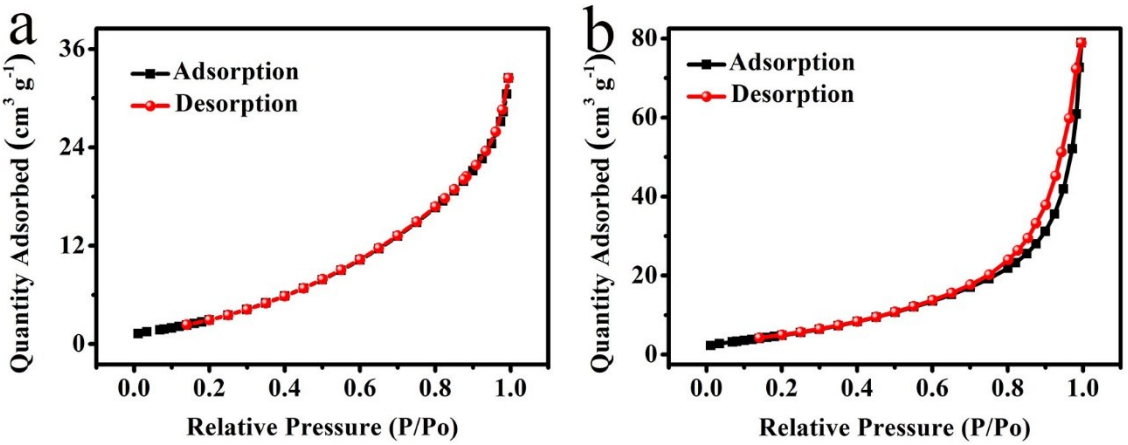

Fig. S3. Nitrogen adsorption/desorption curves of (a) $Ni(OH)_2$ and (b) $NiMoS_4$.

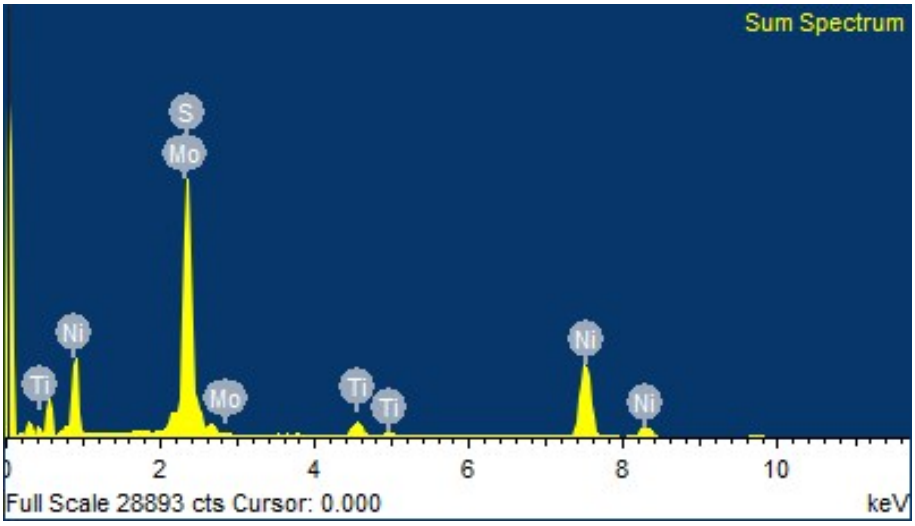

Fig. S4. EDX spectrum for $NiMoS_4$/Ti.

Table S1. EDX data of $NiMoS_4$/Ti

Element	Weight%	Atomic%
S K	43.57	64.15
Ti K	3.85	3.83
Ni K	19.91	15.98
Mo L	32.67	16.04

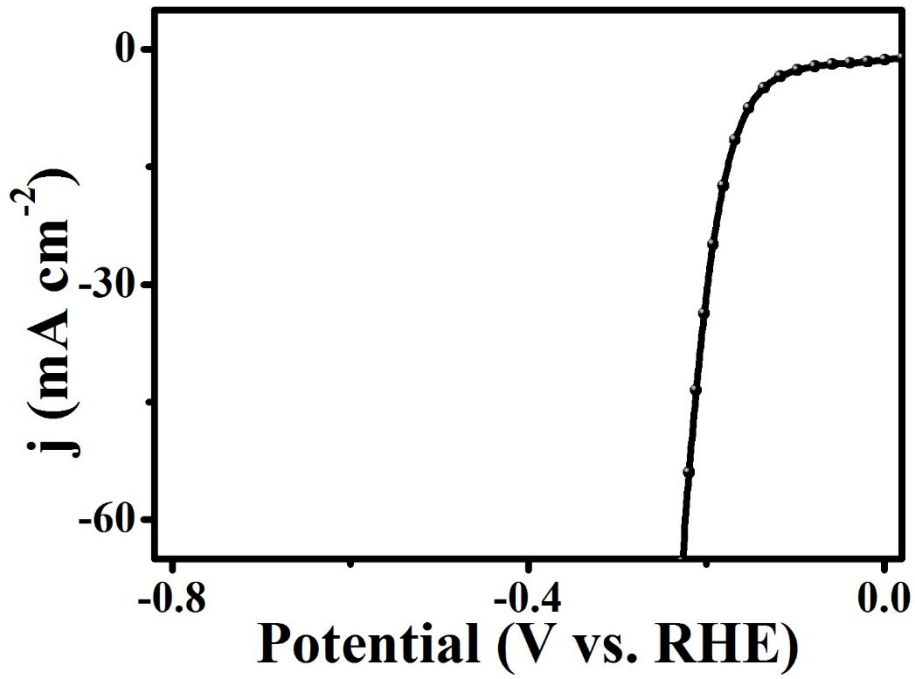

Fig. S5. LSV curve for $NiMoS_4$/Ti with a scan rate of 2 mV s^{-1} for HER in 1.0 M KOH.

Table S2. Comparison of HER performance for $NiMoS_4$/Ti with other non-noble-metal electrocatalysts in alkaline media.

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	Ref.
$NiMoS_4$/Ti	10	194	0.1 M KOH	This work
	50	263		
	10	138	1.0 M KOH	
	50	185		
$NiMo_3S_4$/GC	10	257	0.1 M KOH	1
$Ni(OH)_2$/NF	10	250	1.0 M NaOH	2
NiFe LDH/NF	10	210	1.0 M NaOH	2
$Ni(OH)_2$/Ti	30	~290	0.1 M KOH	3
NiP_2/CC	50	190	1.0 M KOH	4
Ni_2P/GCE	20	250	1.0 M KOH	5
NiS_2/GS	10	190	1.0 M NaOH	6
NiSe/NF	50	190	1.0 M KOH	7
$NiMoS_4$/GCE	10	191	1.0 M KOH	8
Mo_2C	10	270	1.0 M KOH	9
MoB	10	~220	1.0 M KOH	10
CoO_X@CN	10	232	1.0 M KOH	11
Co-NRCNTs	10	370	1.0 M KOH	12
Co-P/Co-PO_4	10	~380	1.0 M KOH	13
CeO_2/$CoSe_2$	10	288	0.1 M KOH	14
Au@Co_3O_4/C	25	420	0.1 M KOH	15
Co_3O_4C-NA	50	390	0.1 M KOH	16
CCHH/MWCNT	50	353	0.1 M KOH	17

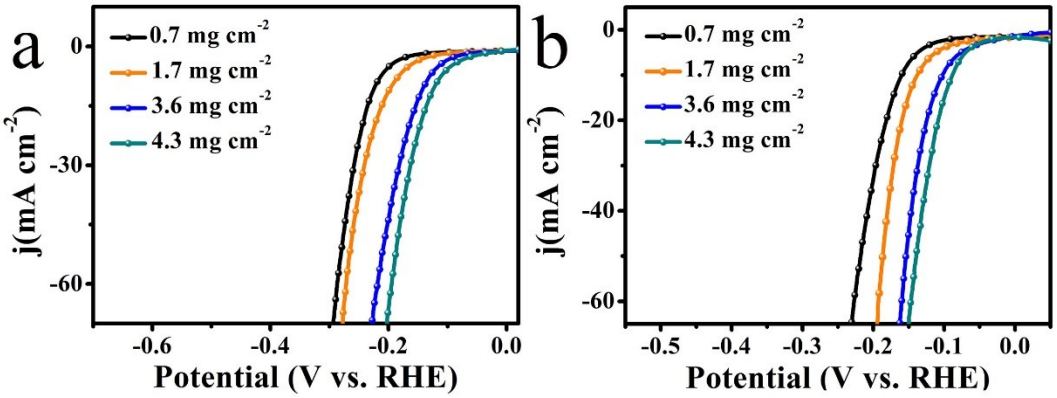

Fig. S6. LSV curves for $NiMoS_4$/Ti with different loadings at a scan rate of 2 mV s^{-1} for HER in (a) 0.1 M KOH and (b) 1.0 M KOH.

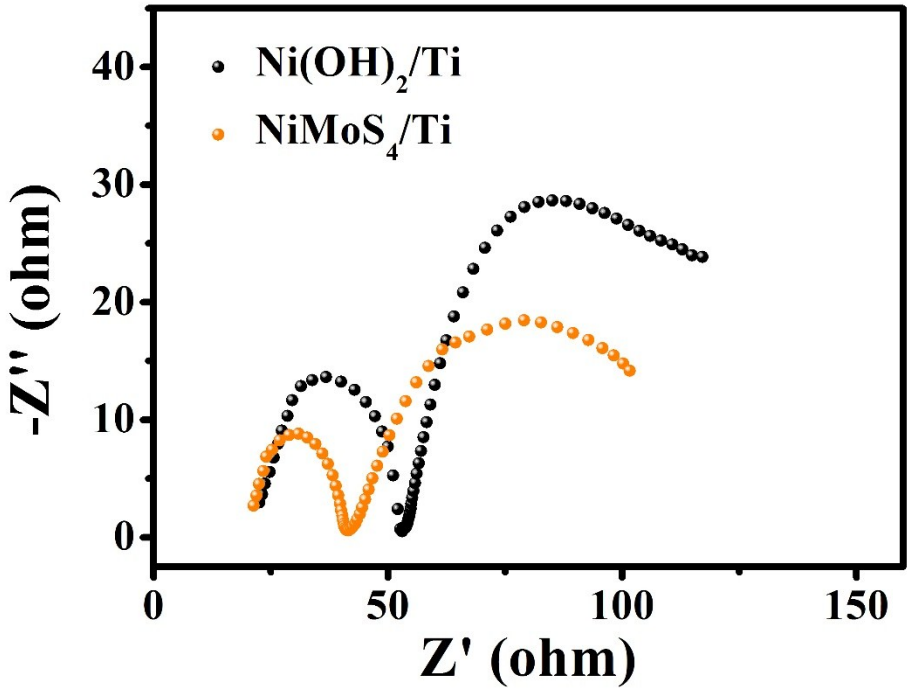

Fig. S7. (a) Nyquist plots of $Ni(OH)_2$/Ti and $NiMoS_4$/Ti recorded in 0.1 M KOH.

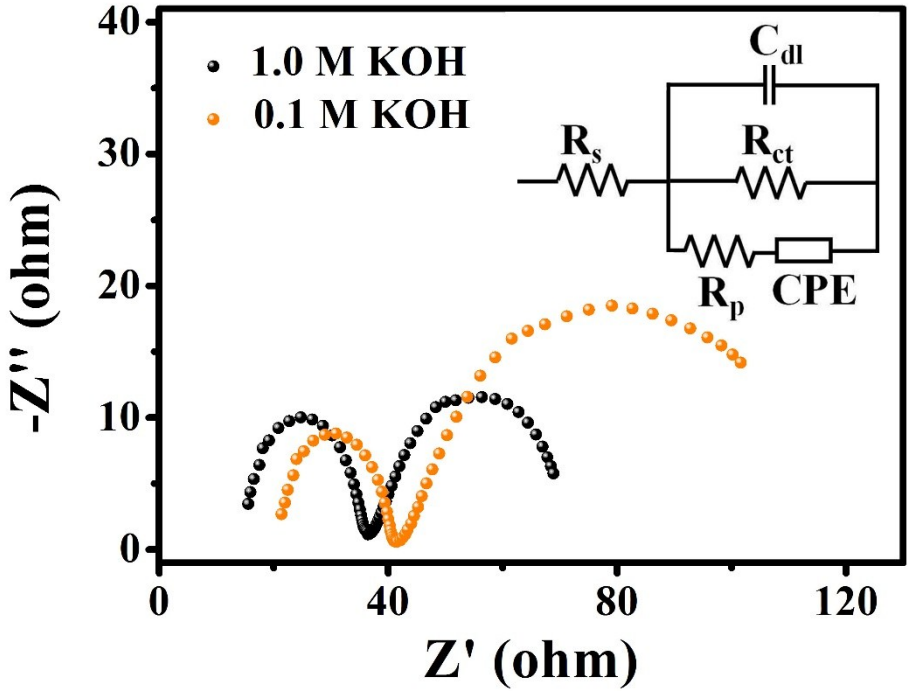

Fig. S8. Nyquist plots of $NiMoS_4$/Ti recorded in 1.0 and 0.1 M KOH. (inset: circuit diagram, where Rs is the solution resistance, Rct is the charge transfer resistance, Rp is related to the porosity of the electrode surface).

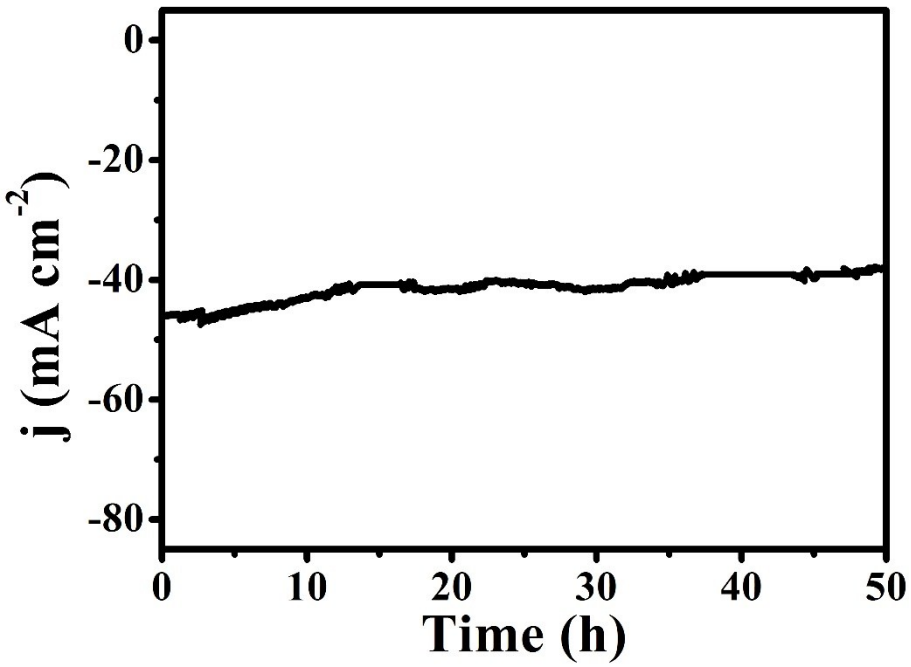

Fig. S9. Time-dependent current density curve at a fixed overpotential of 220 mV for $NiMoS_4$/Ti in 1.0 M KOH.

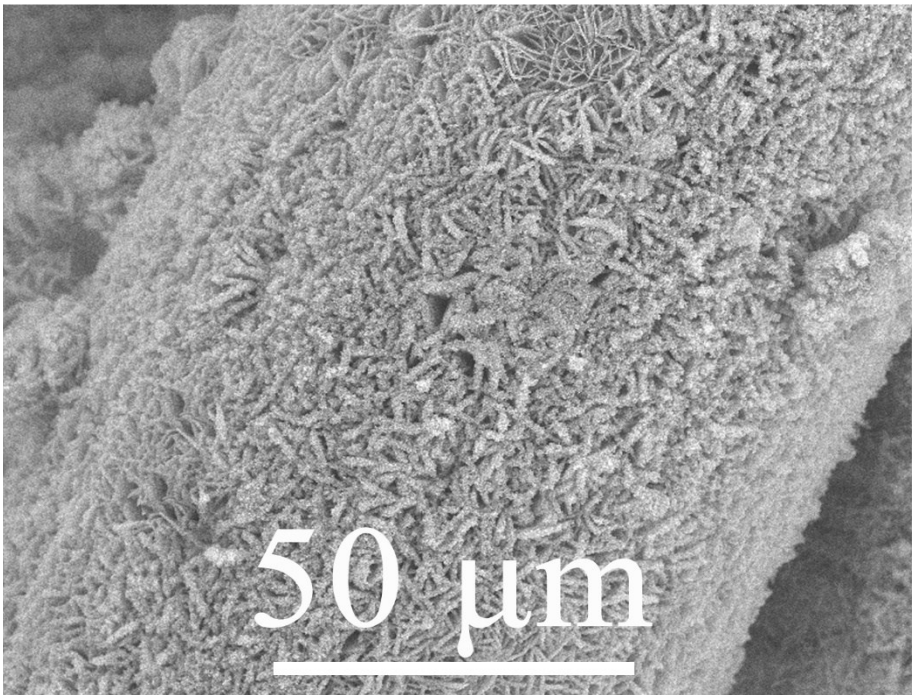

Fig. S10. SEM image of $NiMoS_4$/Ti after long-term stability test.

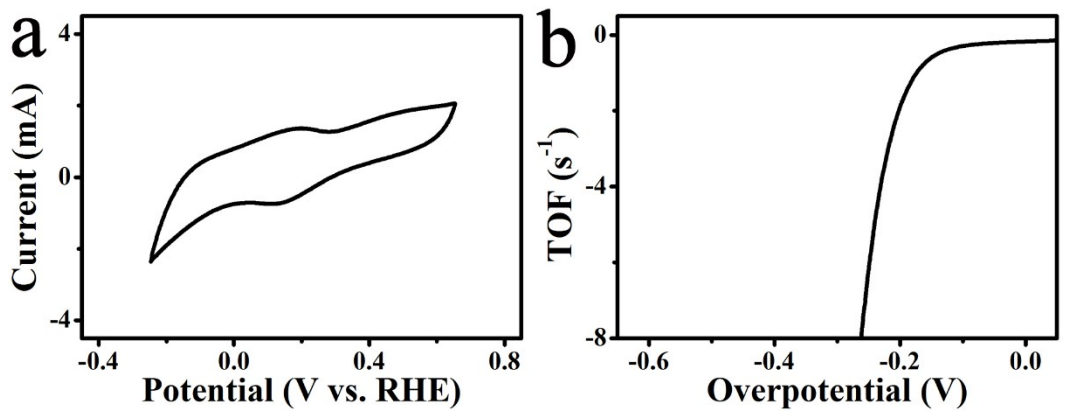

Fig. S11. (a) Cyclic voltammogram of $NiMoS_4$/Ti in PBS with a scan rate of 50 mV s^{-1}. (b) Calculated TOFs for $NiMoS_4$/Ti in 0.1 M KOH.

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