Supporting Information

Multi-interfaces $MoS_2/Ni_3S_4/Mo_2S_3$ composite as efficient electrocatalyst for hydrogen evolution reaction in a wide pH range

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I. Experimental Section

1. Materials and Characterizations

All reagents are commercially available and used as received without further purification. Pattern X-ray diffraction (PXRD) was recorded using a Bruke D8 equipped with Cu-Ka radiation. X-ray photon-electron Spectroscopy (XPS) analysis was performed using a VG ESCALAB MK II spectrophotometer with Mg-Kα radiation (1253.6 eV). Scanning electron microscopy (SEM) test was carried out on a Hitachi S-4800 instrument at an accelerating voltage of 5 kV. The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) was performed on a JEM-F200 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV.

2.Synthesis of $(NH_4)_4[NiH_6Mo_6O_{24}]\cdot 5H_2O$

The $(NH_4)_4[NiH_6Mo_6O_{24}]\cdot 5H_2O$ (abbreviated to $NiMo_6$) was prepared according to a modified published procedure.[1] $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (5.2073 g, 4.2135 mmol) was dissolved in water (80 mL) and then heated to 100°C. $Ni(NO_3)_2\cdot 6H_2O$ (0.6717 g, 2.3099 mmol) was dissolved in water (20 mL), which was added to the above solution with stirring. The mixture was kept heating and stirring to give rise to a blue solution. The crude product was isolated with evaporation and filteration. The light blue targeted product was obtained by recrystallization in hot water (80 °C) two times, then dried under vacuum. The purity of $NiMo_6$ was confirmed with the PXRD. As shown in Fig.S1, the peaks at 8.0°, 11.0°, 12.3°, 15.3°, 16.4°, 17.4°, 23.8°, 28.5°, 29.5°, 32.1°, 33.0° and 34.1°, can be clearly observed, which are assigned to the characteristic peaks of $(NH_4)_4[NiH_6Mo_6O_{24}]\cdot 5H_2O$(PDF# 22-0506).

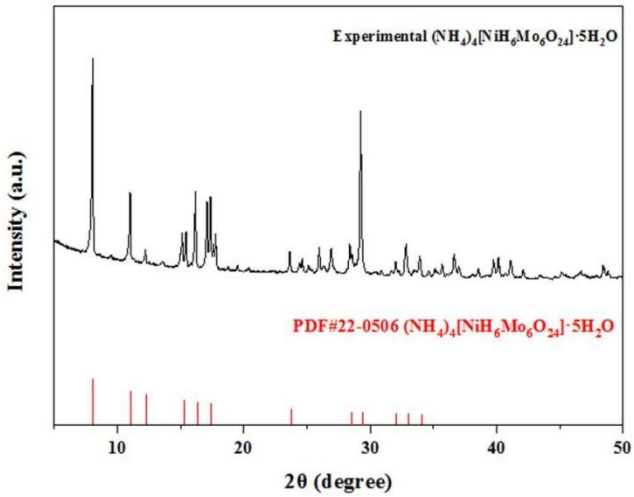

Fig.S1 PXRD patterns of $NiMo_6$.

3. Synthesis of the $MoS_2/Ni_3S_4/Mo_2S_3$/CC-xh (x= 20,24, 28 and 32)

Carbon cloth (CC) was initially pretreated by ethanol, acetone and water ultrasonic for 30 min, respectively, and then transferred into Teflon-lined stainless steel reactor and heated at 100 °C for 2 h in concentrated nitric acid, removing the residual organic species before the experiment.

First, $NiMo_6$ (0.2616 g, 0.2205 mmol), thiourea (TU) (0.3206 g, 4.2118 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.0694 g, 0.2387 mmol) were dissolved in 15 mL water, and then one piece of CC (geometric surface area, 1 × 1.5 cm^2) was put into solution, and sonication for 60 min to form suspension. The suspension was transferred into a 25mL Teflon-lined stainless steel reactor at 200℃ for 20h, 24h, 28h and 32h, respectively, then achieving $MoS_2/Ni_3S_4/Mo_2S_3$/CC-xh (where x is hydrothermal reaction time, x= 20, 24, 28 and 32) , samples were washed by distilled water for several time, followed by drying at 60℃ overnight.

As a contrast, the electrode containing 1 mg cm^{-2} Pt/C on CC was prepared as the following: 5 mg of 20% Pt/C powder was dispersed in 1 mL of solution containing 0.95 mL of ethanol and 50 μL of 0.5 wt% Nafifion. Then the mixture was ultrasonicated for 30 min to generate a homogeneous slurry. Finally, an appropriate amount of Pt/C slurry was daubed uniformly over 1 cm^2 of area on a piece of 1 cm × 2 cm CC and dried at room temperature for 24 h.

4. Synthesis of the MoS_2/Ni_3S_4/CC

$NiMo_6$ (0.2616 g, 0.2205 mmol) and thiourea (TU) (0.3206 g, 4.2118 mmol) were dissolved in 15 mL water, and then one piece of CC (geometric surface area, 1 × 1.5 cm^2) was put into solution, and sonication for 60 min to form suspension. The suspension was transferred into a 25mL Teflon-lined stainless steel reactor at 200℃ for 24h, then achieving samples, which were washed by distilled water for several time, followed by drying at 60℃ overnight.

5. Electrochemical measurements

Both cyclic voltammetry (CV), linear sweep voltammetry (LSV) tests, current density *vs* time (I-t) curves, electrochemically active surface area (ECSA) and Electrochemical Impedance Spectroscopy (EIS) were conducted with a CHI760E workstation in a conventional three electrode system. $MoS_2/Ni_3S_4/Mo_2S_3$/CC-xh series electrodes (S = 1 cm^2) served as the working electrode in electrochemical experiments, and a using Ag/AgCl electrode as the reference electrode. And, graphite rod was considered as counter electrode. All the final potentials were expressed in reference to the reversible hydrogen electrode (RHE) via the Nernst equation: in 0.5 M H_2SO_4, $E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197$. where pH is the pH value of the electrolyte solution. For 0.5 M H_2SO_4 solution,the pH value is 0.3. For 1 M KOH solution, the pH value is 14. Linear sweep voltammetry (LSV) was measured to study the HER performance at the rate of 5 mV s^{-1}. The Tafel data were fitted according to the equation $\eta = b \log(j) + \alpha$ (j: current density, and b:Tafel slope). The durability tests were carried out by repeating the potential at a scan rate of 100 mV s^{-1} for 1000 cycles. All current densities are the ratios of currents and geometric areas of working electrodes. The ECSA was elucidated by measuring double layer capacitance (C_{dl}) of cyclic voltammetry (CV) at non-Faradaic potentials (0.115-0.215 V in 0.5 M H_2SO_4 *vs* RHE and scan rates from 2 to 12 mV s^{-1}, 0.52-0.62V in 1.0 M KOH versus RHE and scan rates from 6 to 36 mV s^{-1}, respectively) recorded at different scan rates. Electrochemical Impedance Spectroscopy (EIS) measurement was measured in the frequency range of 0.01Hz-100 kHz.

II Supplementary Structural Section

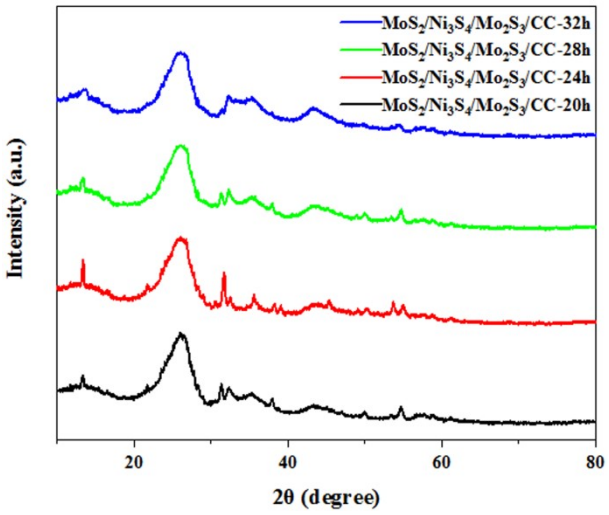

Fig.S2 PXRD of $MoS_2/Ni_3S_4/Mo_2S_3$/CC-xh (x = 20, 24, 28 and 32 h)

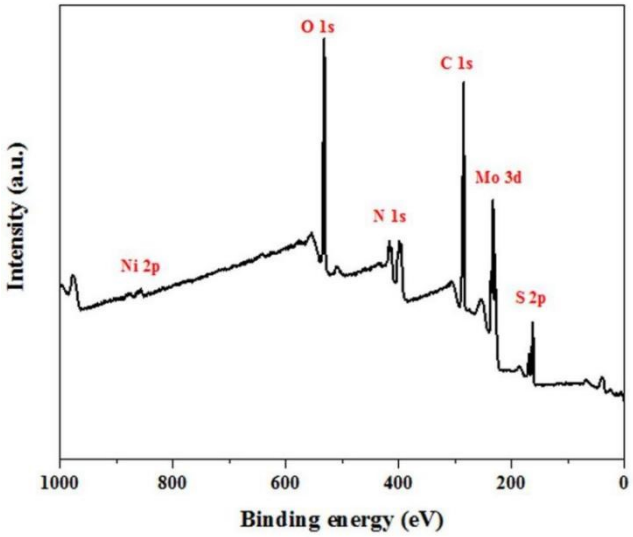

Fig.S3 XPS spectrum of $MoS_2/Ni_3S_4/Mo_2S_3$/CC-24h

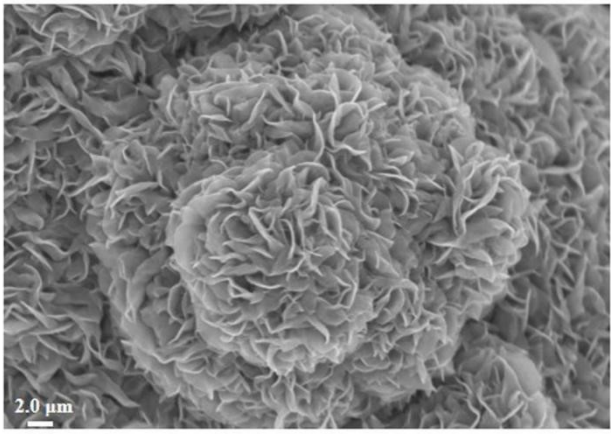

Fig.S4 SEM image of MoS_2 and Ni_3S_4 nanosheets

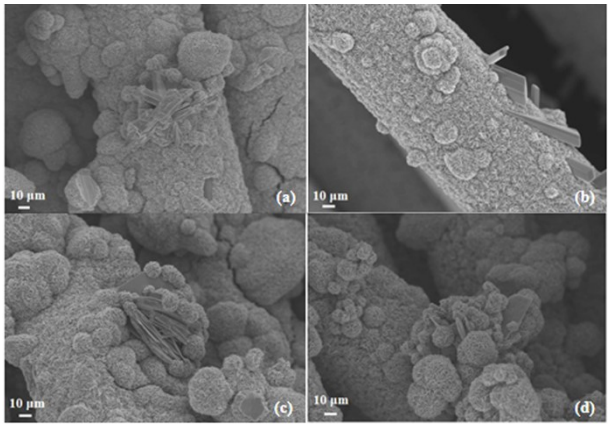

Fig.S5 SEM images of $MoS_2/Ni_3S_4/Mo_2S_3$/CC-xh (a) 20h; (b) 24h; (c) 28h and (d) 32h

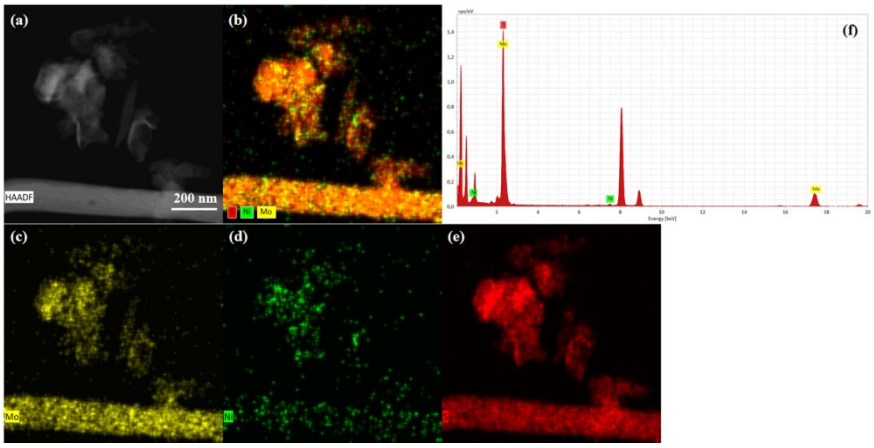

Fig.S6 (a-e)The EDS mapping; (f)the EDS microanalysis of $MoS_2/Ni_3S_4/Mo_2S_3$/CC-24h

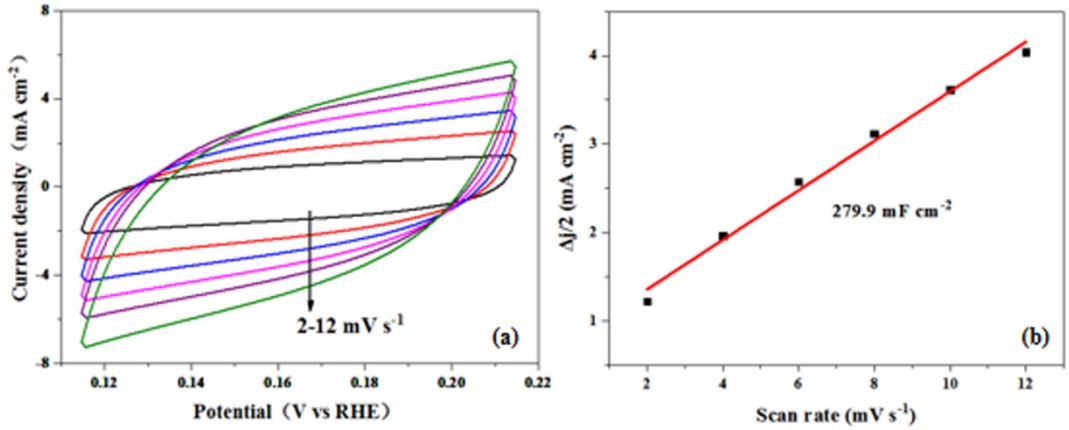

Fig.S7 (a) CV curves between the potential of 0.115-0.215 V; (b) C_{dl} according to the CV curves for $MoS_2/Ni_3S_4/Mo_2S_3$/CC-20h in 0.5 M H_2SO_4 solution.

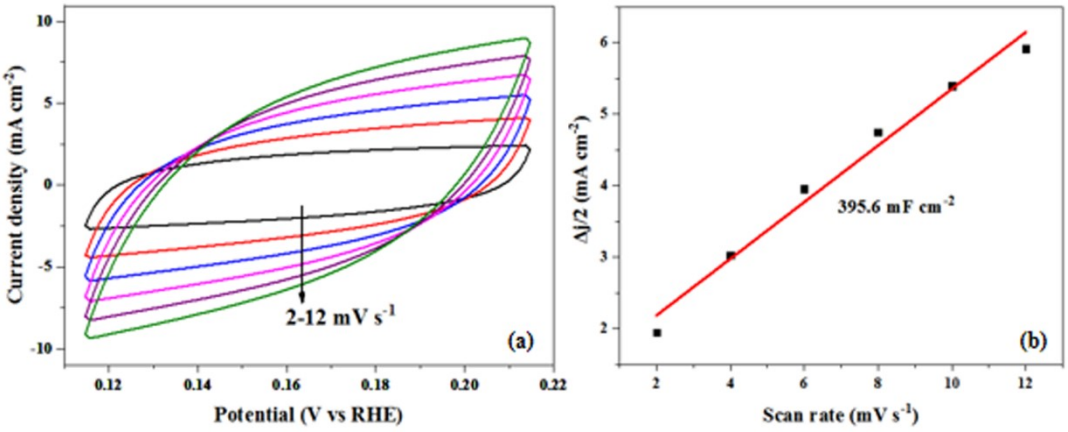

Fig.S8 (a) CV curves between the potential of 0.115-0.215 V; (b) C_{dl} according to the CV curves for $MoS_2/Ni_3S_4/Mo_2S_3$/CC-24h in 0.5 M H_2SO_4 solution.

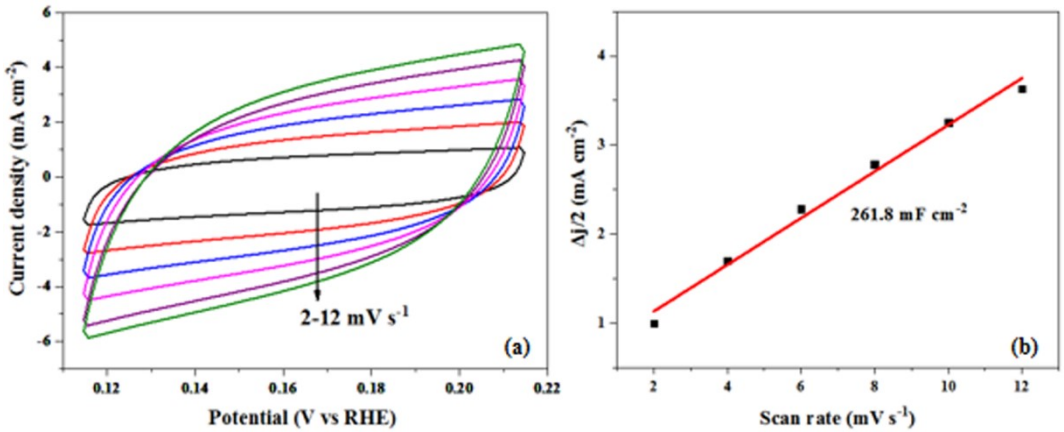

Fig.S9 (a) CV curves between the potential of 0.115-0.215 V; (b) C_{dl} according to the CV curves for $MoS_2/Ni_3S_4/Mo_2S_3$/CC-28h in 0.5 M H_2SO_4 solution.

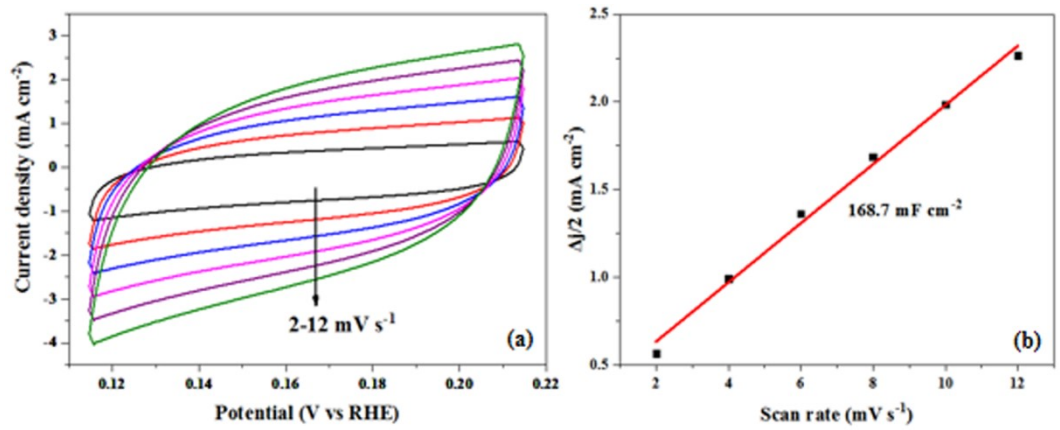

Fig.S10 (a) CV curves between the potential of 0.115-0.215 V; (b) C_{dl} according to the CV curves for $MoS_2/Ni_3S_4/Mo_2S_3$/CC-32h in 0.5 M H_2SO_4 solution.

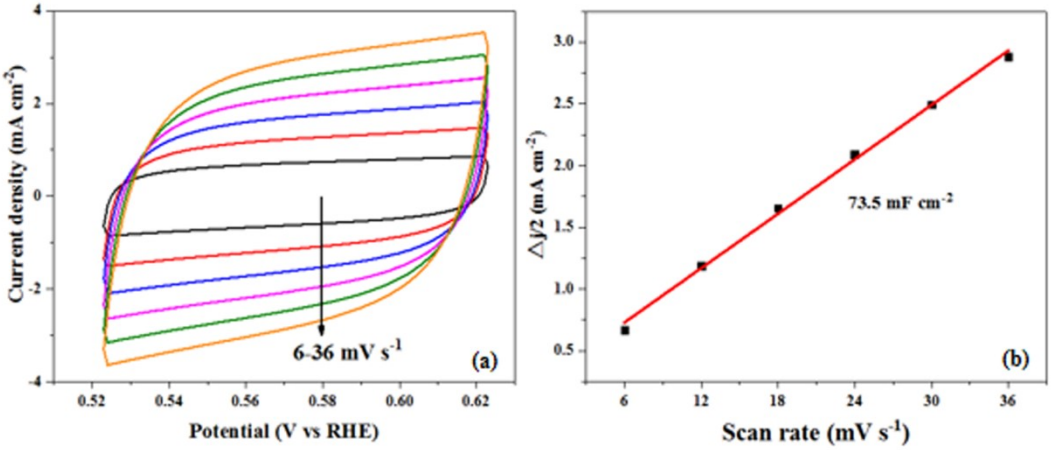

Fig.S11 (a) CV curves between the potential of 0.52-0.62 V; (b) C_{dl} according to the CV curves for $MoS_2/Ni_3S_4/Mo_2S_3$/CC-20h in 1 M KOH solution.

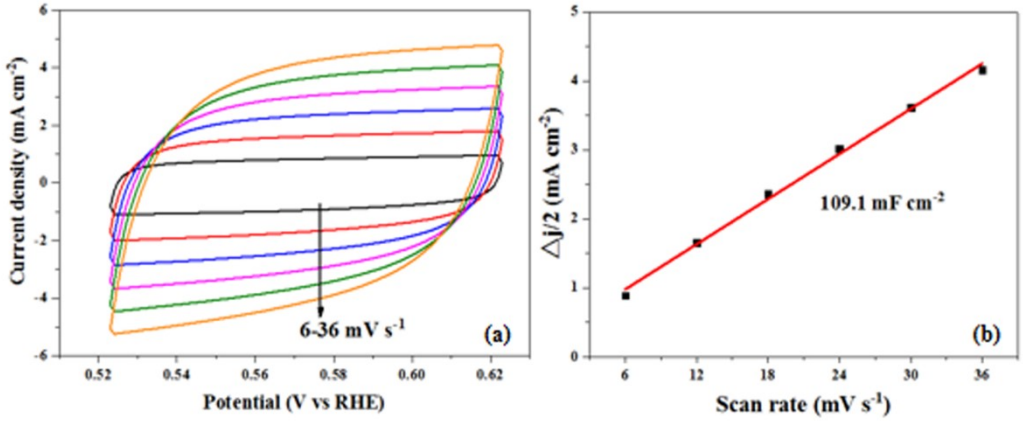

Fig.S12 (a) CV curves between the potential of 0.52-0.62 V; (b) C_{dl} according to the CV curves for $MoS_2/Ni_3S_4/Mo_2S_3$/CC-24h in 1 M KOH solution.

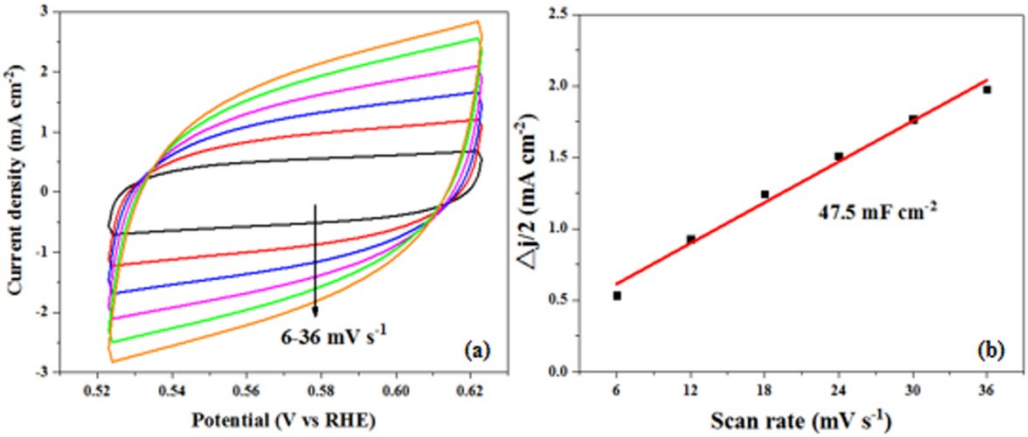

Fig.S13 (a) CV curves between the potential of 0.52-0.62 V; (b) C_{dl} according to the CV curves for $MoS_2/Ni_3S_4/Mo_2S_3$/CC-28h in 1 M KOH solution.

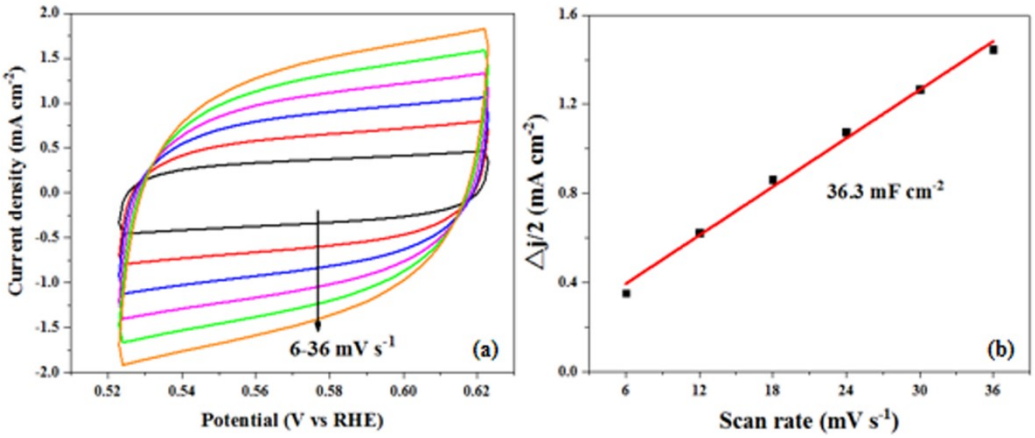

Fig.S14 (a) CV curves between the potential of 0.52-0.62 V; (b) C_{dl} according to the CV curves for $MoS_2/Ni_3S_4/Mo_2S_3$/CC-32h in 1 M KOH solution.

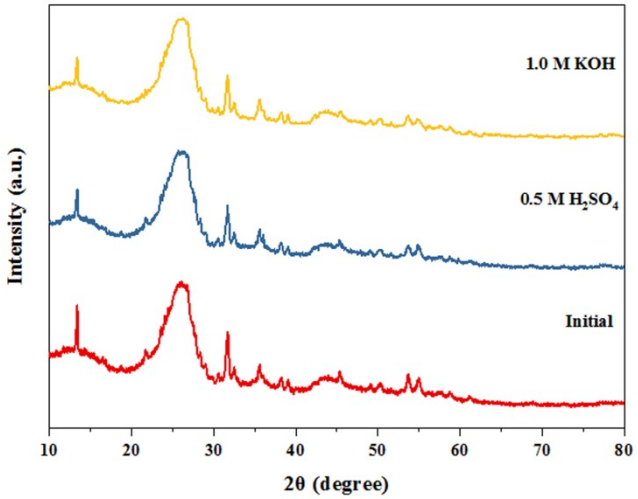

Fig.S15 PXRD pattern of $MoS_2/Ni_3S_4/Mo_2S_3$/CC-24h after various electrochemistry measurements in 0.5 M H_2SO_4 and 1.0 M KOH electrolytes.

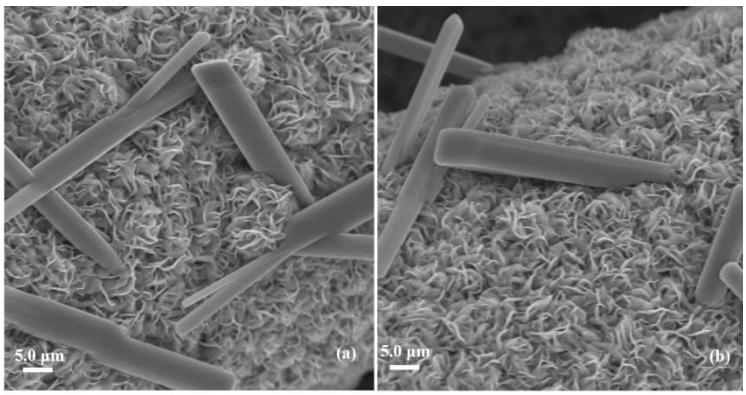

Fig.S16 The SEM images of $MoS_2/Ni_3S_4/Mo_2S_3$/CC-24h after various electrochemical tests in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH solution.

Table S1. Comparison of HER performance of similar composite catalysts in 0.5 M H_2SO_4 and 1.0 M KOH electrolytes.

Catalyst	Counter electrode	Electrolyte	η_{10} (mV *vs.* RHE)	Tafel slops (mV dec^{-1})	References
$MoS_{2x}Se_{2(1-x)}$	graphite rod	0.5 M H_2SO_4	188	43	2
Se-MoS_2-NF	graphite rod	0.5 M H_2SO_4	132	75	3
S-vacancy MoS_2	Pt	0.5 M H_2SO_4	131	48	4
MoS_2@CoS_2	graphite rod	0.5 M H_2SO_4	96	60	5
Co-1T-MoS_2	graphite rod	0.5 M H_2SO_4	84	47	6
MoS_2/CoS_2-10	graphite rod	0.5 M H_2SO_4	69	62	7
Rh-MoS_2	graphite rod	0.5M H_2SO_4	67	54	8
Co-MoS_2	graphite rod	0.5M H_2SO_4	56	32	9
NiO@1T-MoS_2	graphite rod	0.5M H_2SO_4	46	52	10
MoS_2/Ni_3S_4/Mo_2S_3/CC	graphite rod	0.5 M H_2SO_4	38	84	This work
1T–2H MoS_2	graphite rod	1.0 M KOH	290	65	11
NiS_2/MoS_2	Pt wire	1.0 M KOH	148	70	12
Ni_3S_4–MoS_2	Pt	1.0 M KOH	116	81	13
MoS_2/Ni_3S_2	Pt rod	1.0 M KOH	110	83	14
MoS_2-Ni_3S_2 (UR-2)/NF	graphite rod	1.0 M KOH	98	74.8	15
MoS_2-Ni_3S_2 HNRs/NF	graphite rod	1.0 M KOH	98	61	16
Ni_3S_2@MoS_2/FeOOH	graphite rod	1.0 M KOH	95	85	17
MoS_2/NiS	graphite rod	1.0 M KOH	92	113	18
MoS_2/NiS/MoO_3	graphite rod	1.0 M KOH	91	55	19
MoS_2/Ni_3S_4/Mo_2S_3/CC	graphite rod	1.0 M KOH	51	83	This work

Supplementary References

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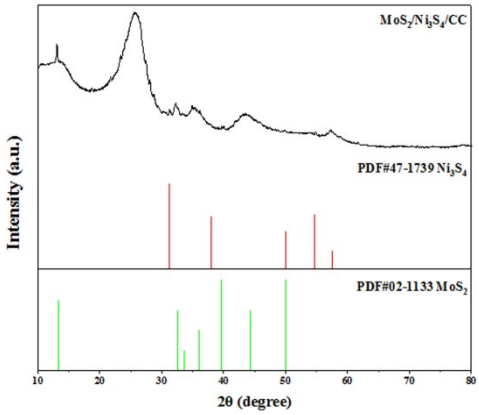

Fig.S17 PXRD patterns of MoS_2/Ni_3S_4/CC, Ni_3S_4 and MoS_2.

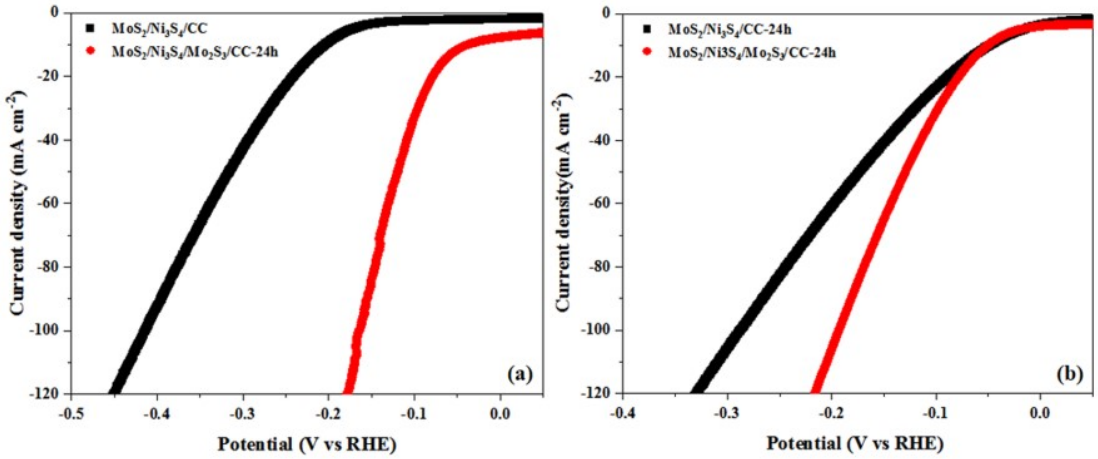

Fig.S18 The polarization curves of MoS_2/Ni_3S_4/CC and $MoS_2/Ni_3S_4/Mo_2S_3$/CC-24h (a) in 0.5 M H_2SO_4 electrolyte and (b) 1.0 M KOH electrolyte.

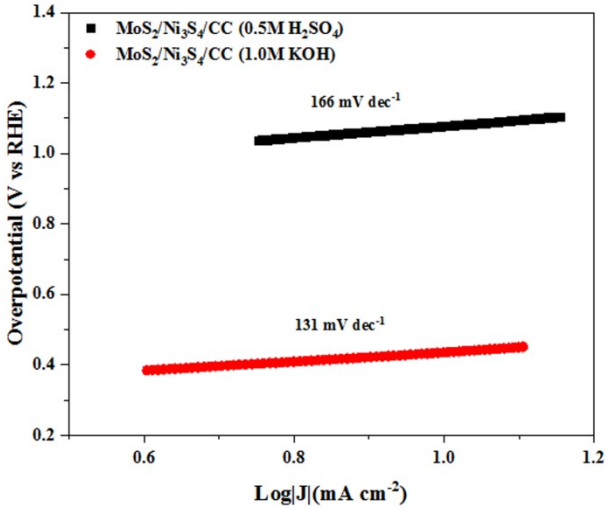

Fig.S19 The Tafel plots ofMoS_2/Ni_3S_4/CC in 0.5 M H_2SO_4 and 1.0 M KOH electrolytes.

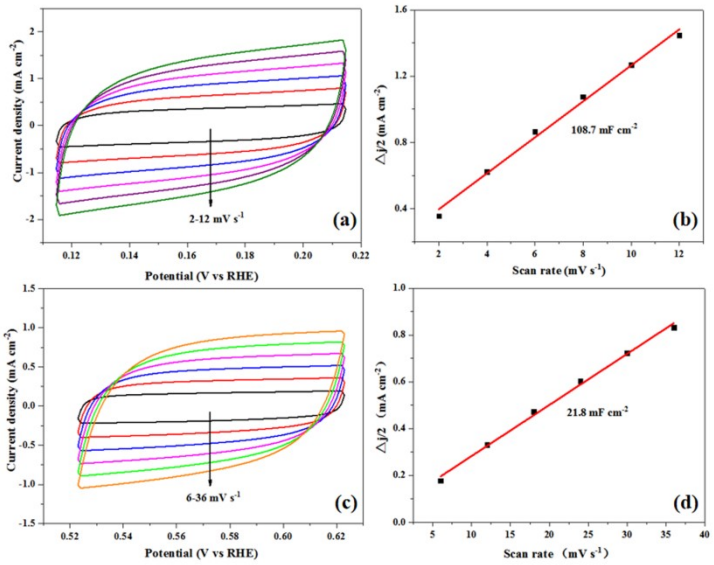

Fig.S20 (a) CV curves between the potential of 0.115- 0.215 V; (b) C_{dl} according to the CV curves for MoS_2/Ni_3S_4/CC in 0.5 M H_2SO_4 solution; (c) CV curves between the potential of 0.52-0.62 V; (d) C_{dl} according to the CV curves for MoS_2/Ni_3S_4/CC in 1 M KOH solution.