Electronic Supplementary Material

Small-sized Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C for efficient alkaline and acidic hydrogen evolution reaction by an anchoring calcination strategy

Jianxia Gu (✉)[1], Ying Zhu[2], Haiyan Zheng[2], Chunyi Sun (✉)[2], Zhongmin Su[2]

1 Department of Chemistry, Xinzhou Normal University, Xinzhou, China

2 School of Chemistry, Northeast Normal University, Changchun, China

E-mails: gujx349@nenu.edu.cn (Gu J), suncy009@nenu.edu.cn (Sun C)

Experimental section

Material characterization

X-ray diffraction (XRD) patterns were recorded by a Siemens D5005 diffractometer with CuKα (λ = 1.5418Å). Raman spectrum was recorded on a Raman spectrometer (JY, Labram HR 800). Scanning electron microscopy (SEM, Hitachi, SU-70) and transmission electron microscopy (TEM, JEOL, JEM-2100F) were utilized to obtain the morphology and the structure of the samples. N_2 sorption experiments were performed on automatic volumetric adsorption equipment (Belsorp mini II). X-ray photoelectron spectroscopy (XPS) measurements were measured on a KRATOS Axis ultra DLD X-ray photoelectron spectrometer with a monochromatized Mg Ka X-ray source (hn = 1283.3 eV).

Synthesis of NiCo-LDH

$CoCl_2 \cdot 6H_2O$ (6 mmol), urea (18 mmol) and $NiCl_2 \cdot 6H_2O$ (3 mmol) were dissolved in the deionized water of 60 mL and stirred for 0.5 h, and then the obtained solution was transferred to a Teflon-lined stainless steel vessel (100 mL) and heated to 120°C for 8 h. After the vessel is lowered to room temperature, the product is centrifuged, washed twice with deionized water, and then cleaned once with anhydrous ethanol. Then, the final purple solid of NiCo-LDH was obtained successfully after drying in vacuum at 60°C for 8 h.

Synthesis of Mo_2C@C

1 g PEI and 0.2 g PMo_{12} were mixed in a small beacher containing 5 mL deionized water and stirred at room

temperature for 0.5 h, then heated and stirred until the gel state, then poured into a porcelain boat while hot and continued to heat until dried, and cooled to room temperature to obtain the precursor. Then the porcelain boat was placed in the center of a tubular furnace with N_2 acting as a protective gas. The temperature was raised to 900°C (5°C/min) and maintained for 120 min. The natural cooling to room temperature resulted in the black sample Mo_2C@C.

Synthesis of Ni-Co@C

1 g PEI and 0.2 g NiCo-LDH were mixed evenly in a small beaker containing 5 mL of deionized water, and then stirred at room temperature for 0.5 h, then heated while stirring to gel state, poured into the porcelain boat while hot and heated until evaporated dry, cooled to room temperature to obtain the precursor. Then place the porcelain boat in the center of the tubular furnace, N_2 acts as a protective gas, rises from room temperature to 900 °C (5°C/min) and maintains it for 120 minutes, then naturally cools to room temperature to obtain a black sample Ni-Co@C .

Synthesis of C

1 g PEI was mixed evenly in a small beaker containing 5 mL of deionized water, and then stirred at room temperature for 0.5 h, then heated while stirring to gel state, poured into the porcelain boat while hot and continued to be heated until evaporated dry, and cooled to room temperature to obtain the precursor. Then place the porcelain boat in the center of the tubular furnace, with N_2 serving as a protective gas, and raise the room temperature to 900 °C (5 °C/min) for 120 minutes. Cool naturally to room temperature to obtain a black sample called C.

Electrochemical testing

All electrochemical tests were completed in a three-electrode system on the CHI760e electrochemical workstation. Among them, saturated Ag/AgCl electrode and carbon rod are used as reference electrode and counter electrode, respectively. Accurately weighed 5 mg of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C was ultrasonically dispersed in ethanol (200 μL), ultrapure water (200 μL) and naphthol solution (0.5%, 100 μL). Then, added 6 μL of obtained dispersion liquid on a glassy carbon electrode (GCE, r=1.5 mm), dried at room temperature, and used for HER testing ($0.85\ mg/cm^2$). The tested potentials need to convert into reversible hydrogen potentials (RHE) according to the Nernst equation ($E_{RHE}=E_{Ag/AgCl}+0.059\ pH+0.197$). Prepare 20% commercial Pt/C, Mo_2C@C, Ni-Co@C and C modified GCE and test under the same conditions for

comparison. All LSV curves were measured at room temperature in a nitrogen atmosphere of 0.5 M H_2SO_4 and 1 M KOH at a sweep rate of 5 mV s^{-1} and no iR-correction was performed in any of the tests. To activate the catalyst, the catalyst was subjected to 20 cyclic voltammetry cycles at a sweep rate of 100 mV s^{-1} before measuring the electrochemical tests of HER. The catalysts were subjected to cyclic voltammetry tests at sweep rates of 20, 40, 60, 80, and 100 mV s^{-1}, respectively. Impedance testing is conducted in the range of 0.1~100000 Hz with an amplitude of 5 mV.

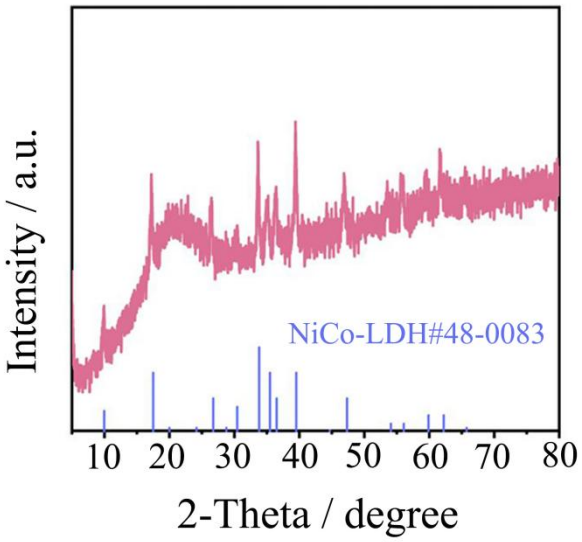

Fig. S1 The XRD of NiCo-LDH.

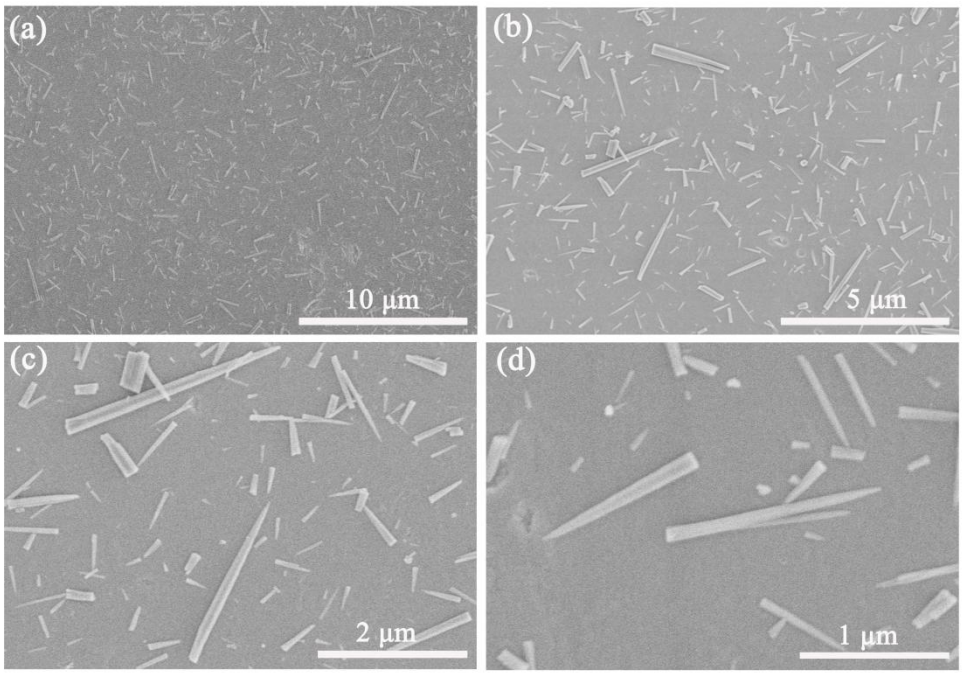

Fig. S2 The SEM diagrams with different multiples of NiCo-LDH.

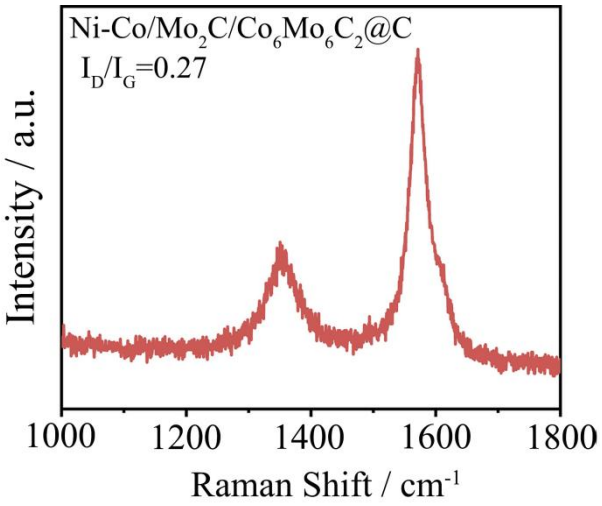

Fig. S3 The Raman spectrum of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C.

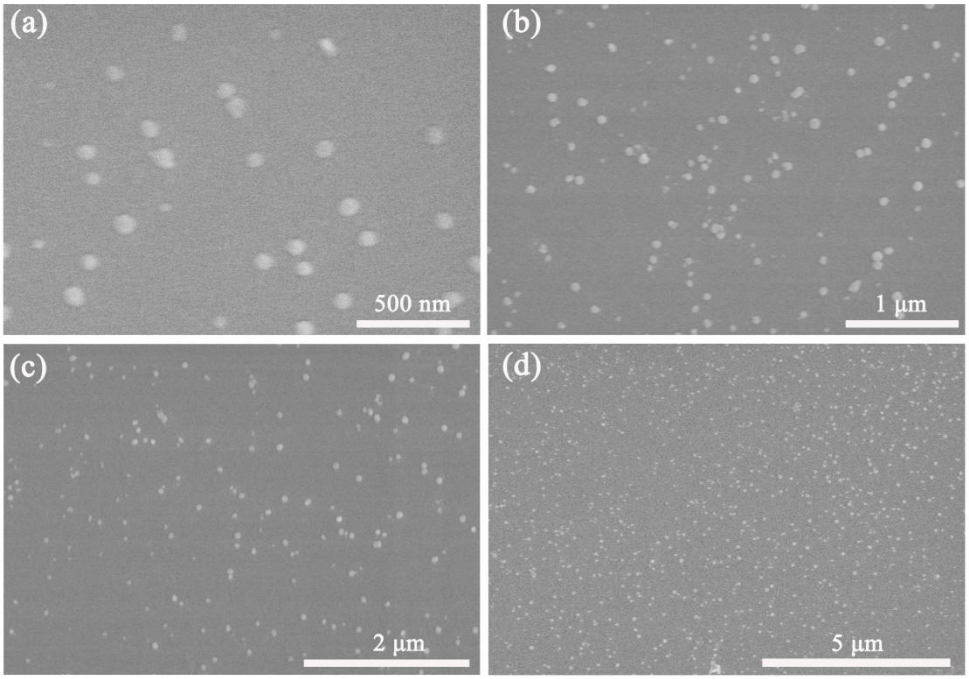

Fig. S4 The SEM diagrams with different multiples of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C.

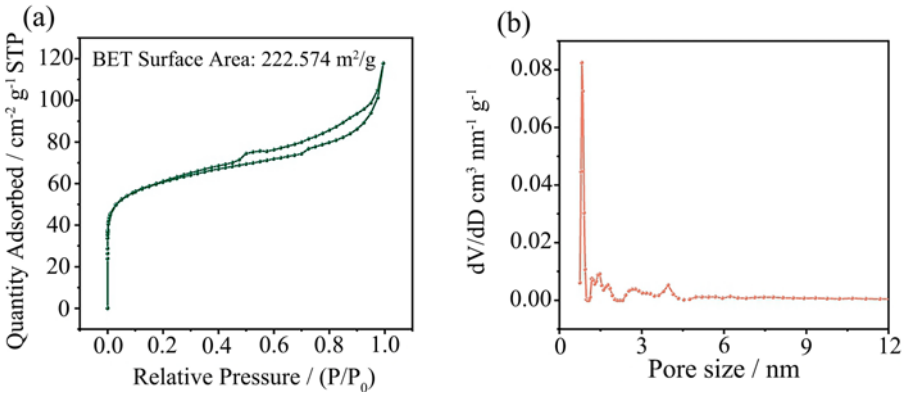

Fig. S5 The N_2 adsorption-desorption curve (a) and pore size distribution (b) of Ni-

Co/Mo_2C/$Co_6Mo_6C_2$@C.

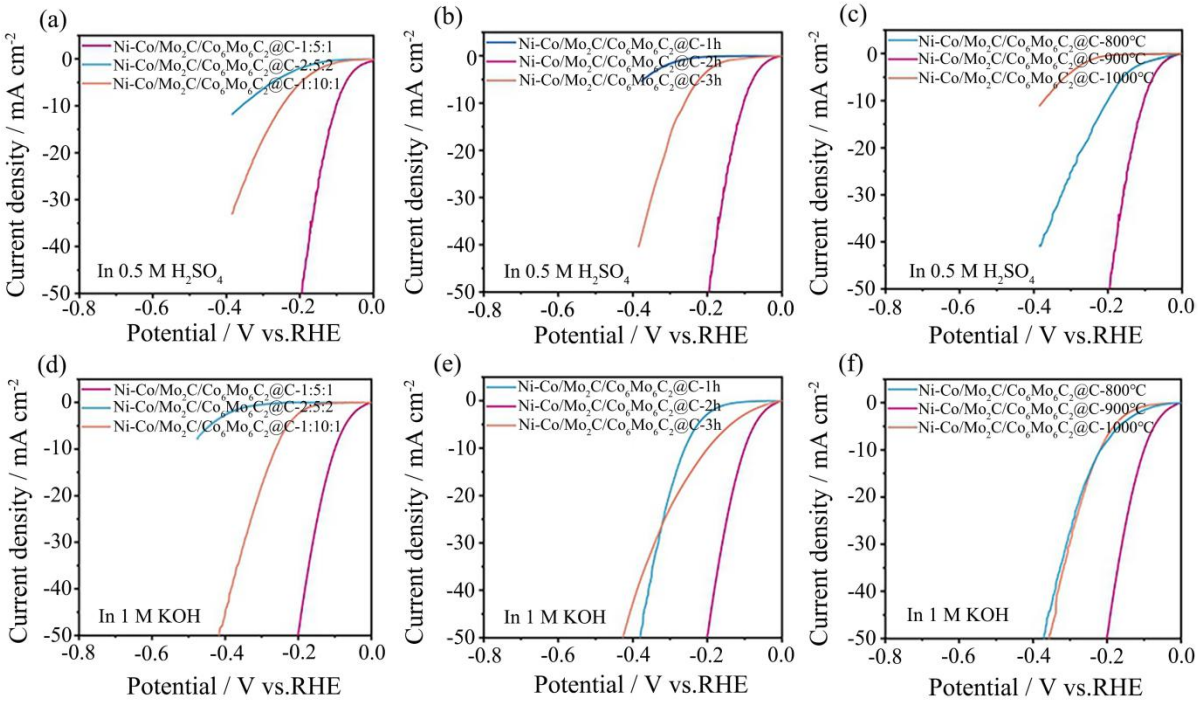

Fig. S6 Polarization curves of HER for different synthesis conditions of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C in the 0.5 M H_2SO_4 and 1 M KOH: (a, d) Addition ratio of NiCo-LDH, PEI and PMo_{12}, (b, e) Calcination time, (c, f) Calcination temperatures.

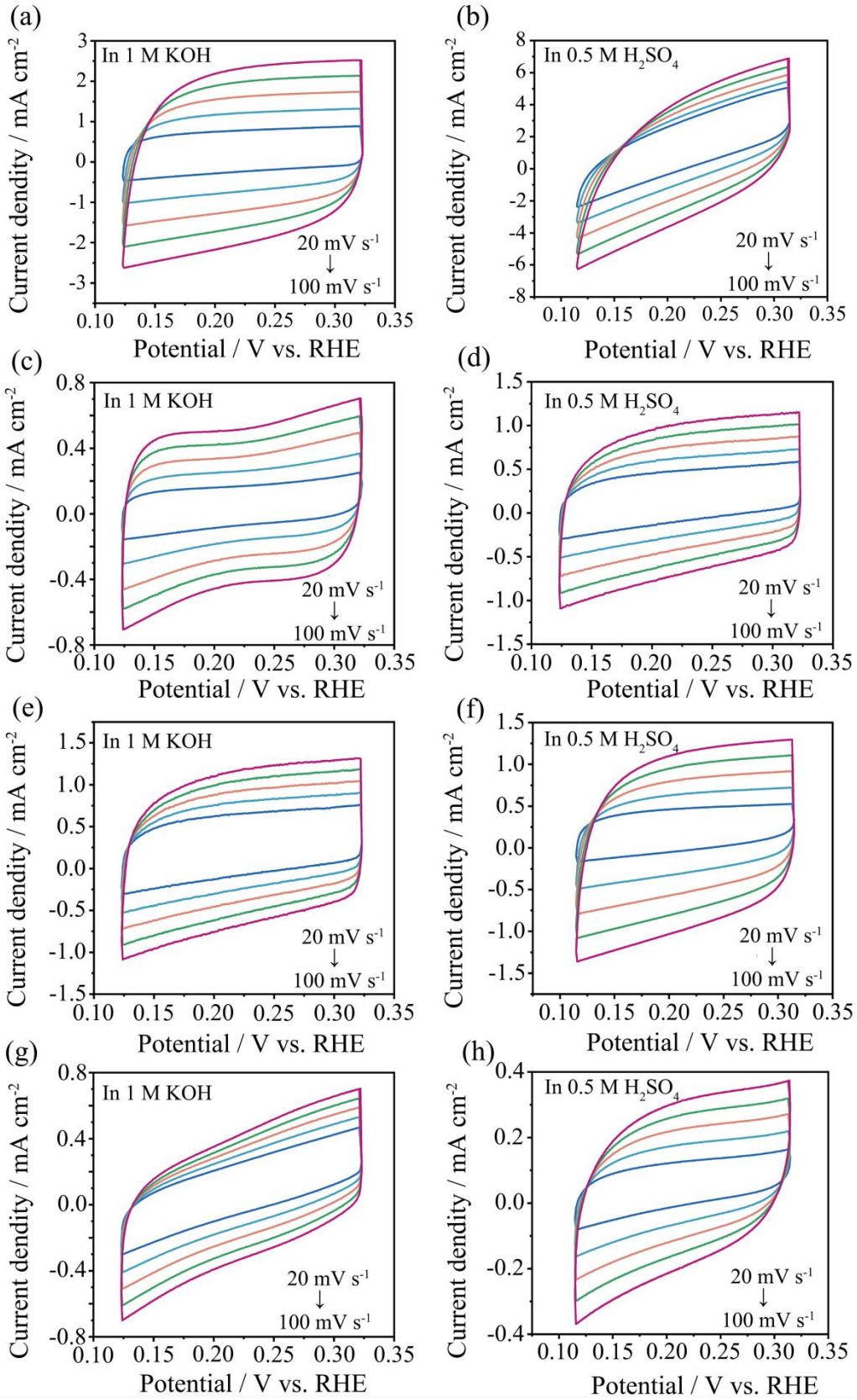

Fig. S7 CV curves of (a, b) Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C, (c, d) Mo_2C@C, (e, f) Ni-Co@C and (g, h) C at different scan rates (20~100mV s^{-1}) in alkaline and acidic atmospheres.

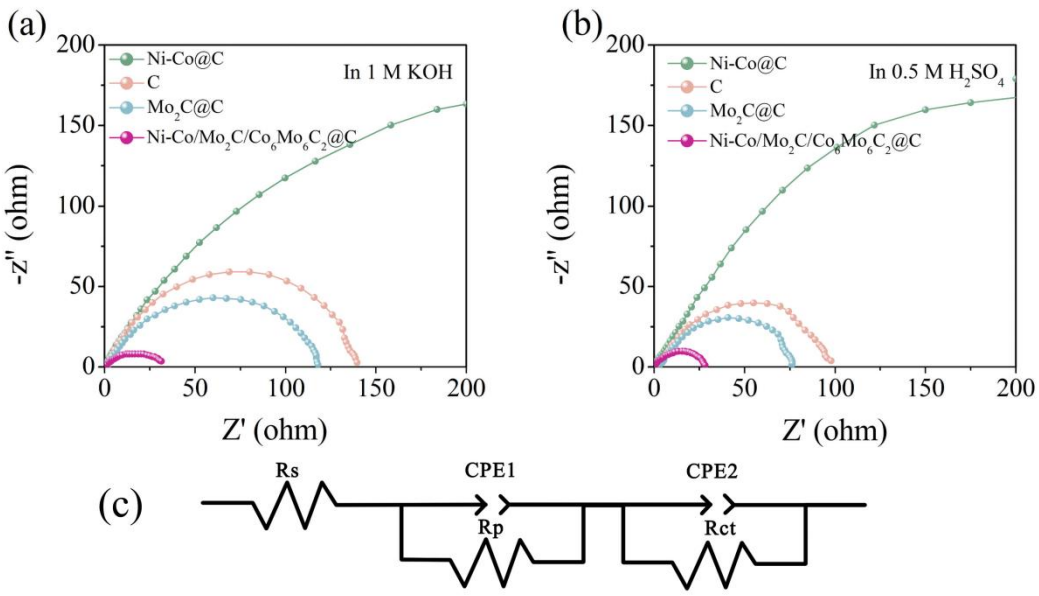

Fig. S8 Nyquist diagrams of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C, Mo_2C@C, Ni-Co@C in (a) 1 M KOH and (b) 0.5 M H_2SO_4, respectively, (c) Corresponding fitted circuit diagram.

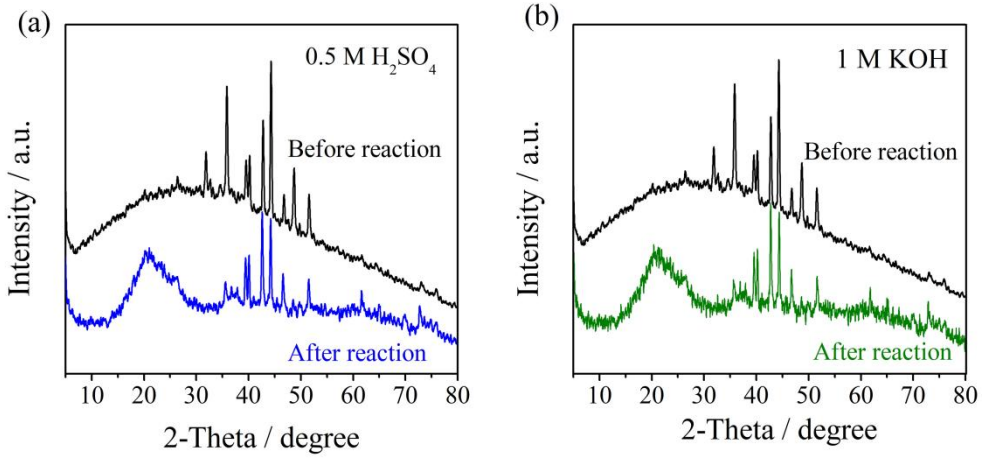

Fig. S9 The XRD of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C after 2000 cycle tests under acidic (a) and alkaline (b) conditions.

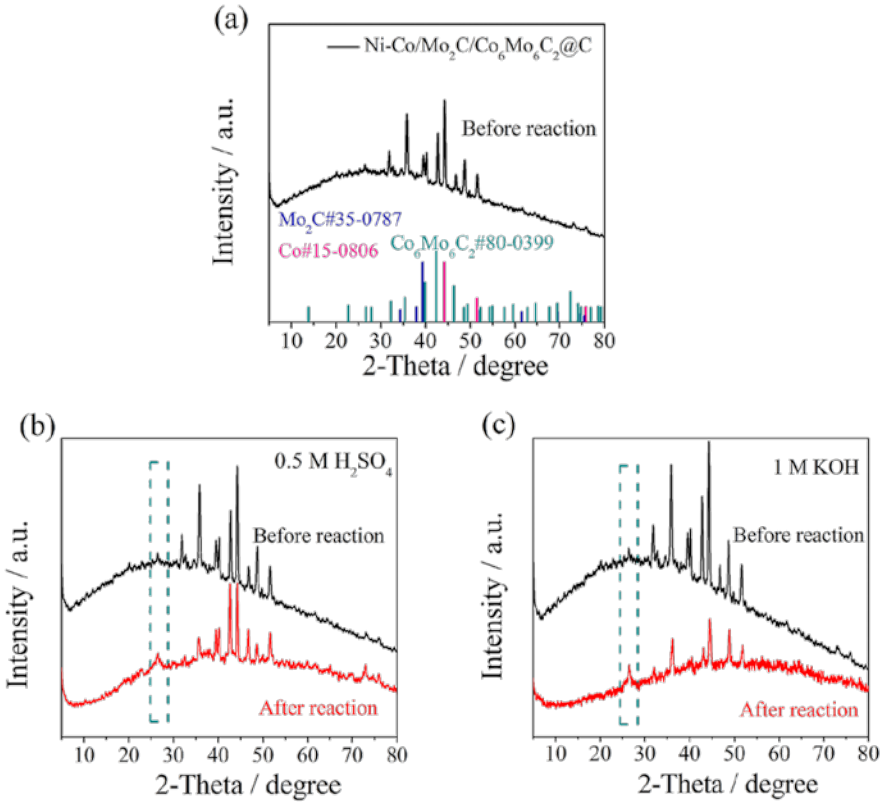

Fig. S10 (a) XRD of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C before HER. XRD of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C after HER in 0.5 M H_2SO_4 (b) and 1 M KOH (c).

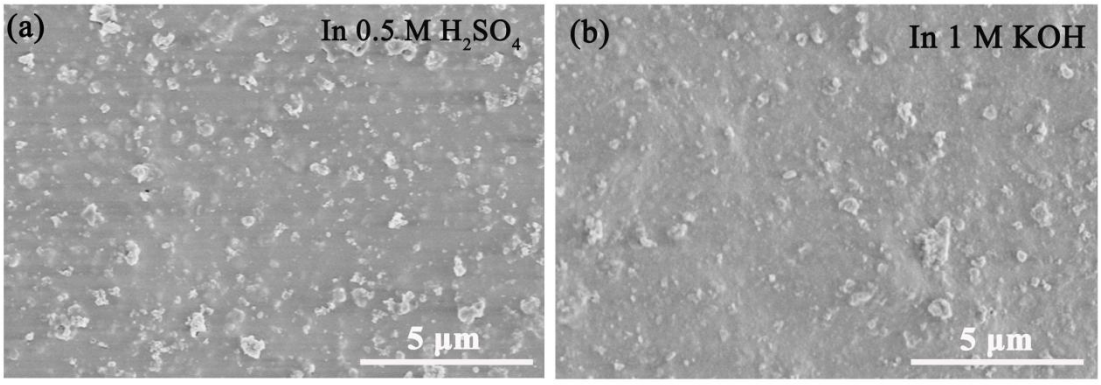

Fig. S11 SEM of Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C after HER in the 0.5 M H_2SO_4 (a) and 1 M KOH (b).

Table S1 The comparison of HER performance for some reported transition-based catalysts in acidic and alkaline solutions.

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Electrode materials	Electrolyte	Overpotential (mV, 10 mA cm^{-2})	Tafel slope (mV $decade^{-1}$)	Refs
PVA-Mo_2C/Mo_2N	0.5 M H_2SO_4	132	51.8	[1]
	1 M KOH	142	50.4	
Mo_2N/CoS_2	0.5 M H_2SO_4	85	66.46	[2]
	1 M KOH	105	65.53	
Mo_2N-Mo_2C/HGr	0.5 M H_2SO_4	157	55	[3]
	1 M KOH	154	68	
Mo_2C/C-0.5	0.5 M H_2SO_4	198	79	[4]
	1 M KOH	164	66	
Ni-Mo_2C-0.67	0.5 M H_2SO_4	165	54.1	[5]
	1 M KOH	151	50.9	
MoS_2/NLG-3	0.5 M H_2SO_4	110	50.1	[6]
	1 M KOH	145	105.8	
Co/β-Mo_2C@N-CNTs	-	-	-	[7]
	1 M KOH	170	92	
MoS_2/Co-N-CN_2	0.5 M H_2SO_4	180	74	[8]
	-	-	-	
MCNTs@Cu@MoS_2	1 M H_2SO_4	225	81	[9]
	-	-	-	
N-Cu-MoC	-	-	-	[10]
	1 M KOH	158	64.7	
MoC/Mo_2C (II)	0.5 M H_2SO_4	153	72.9	[11]
	1 M KOH	112	69	
Co/MoN/NC	1M KOH	29	89.28	[12]
$MoS_2/Co_{1-x}S$@C	-	-	-	[13]
	1M KOH	135	106.0	
Ni-Co/Mo_2C/$Co_6Mo_6C_2$@C	0.5 M H_2SO_4	102.3	82.49	This work
	1 M KOH	95	99.92	

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