

Supplementary Information

Experimental section

Materials. Molybdenum(V) chloride (MoCl_5 , >95%), cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, >98%), urea ($\geq 99.5\%$), potassium hydroxide (KOH, >96%), ethanol ($\geq 99.5\%$), isopropyl alcohol ($\geq 99.5\%$) were purchased from Sigma-Aldrich. Ni foam (0.8 mm, 110 ppi) was purchased from Hefei Kejing Materials Technology. All the chemicals were used without further purification.

Preparation of CoMoC catalyst. CoMoC catalyst was prepared on Ni foam via a soft urea pathway¹. Firstly, MoCl_5 (1 g) was added in ethanol (2 g), the MoCl_5 precursor reacts vigorously with the alcohol and releasing HCl gas. A clear dark-green solution was obtained and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1 g) was then dissolved in it. Then, 3 g solid urea was added slowly to the alcoholic solution, the obtained liquid was stirred for about 2 hours until the urea was completely solubilized and the obtained solution was completely clear. Secondly, Ni foam (1 cm \times 1 cm) was immersed inside the solution and then was put into an tube furnace and treated under N_2 flow at 600 °C for 3 hours, before which a slow heat-up treatment (~ 3 °C per min) was necessary to avoid foaming. The sample was cooled down inside the furnace to room temperature under N_2 atmosphere. After that, the CoMoC catalyst on Ni foam was collected for characterization and electrochemical measurements.

Preparation of Mo_2C catalyst. Mo_2C catalyst was prepared by using only MoCl_5 precursor without $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 2 g solid urea was added instead of 3 g. With other conditions unchanged, the resulting catalyst was obtained, which was then confirmed to be Mo_2C .

Preparation of Co catalyst. Co catalyst was prepared by using only $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1 g) precursor without MoCl_5 , and 1 g solid urea was added instead of 3 g. With other conditions unchanged, the resulting catalyst was obtained, which was then confirmed to be Co.

Characterizations. The morphologies of these catalysts were acquired using a Hitachi FE-SEM S-4800 scanning electron microscope (SEM) operated at 5.0 kV. Transmission electron microscopy (TEM) images, high-resolution transmission

electron microscopy (HRTEM) images and energy-dispersive X-ray spectroscopy (EDS) mapping images were taken on a JEOL JEM-2100F transmission electron microscopy operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI5300 instrument with Mg K α X-ray sources. Powder X-ray diffraction (XRD) patterns were obtained with a MiniFlex600 instrument in Bragg-Brettano mode using 0.02° divergence with a scan rate of 0.1°·s⁻¹.

X-ray absorption spectroscopy measurements. The Mo K-edge and Co K-edge X-ray absorption fine structure (XAFS) measurements were performed on the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF), China. The Mo spectra were recorded from 19.8 to 20.5 keV in fluorescence mode with a step size of 0.5 eV at the near edge, which of Co spectra was 7.5 to 8.2 keV. Standard samples were prepared by placing a small amount of homogenized powder on 3M tape. Ni foam loaded catalysts were used for the measurements.

Faradic efficiency measurement. To quantify the H₂ production, a gas chromatograph (Agilent Technologies 7890B) was used online continuously. The gas chromatograph was equipped with a packed HP-AL/S column, a packed HayeSep Q column and a packed MolSieve 5A column. Nitrogen (Praxair, 99.999%) was used as the carrier gas. Thermal conductivity detector (TCD) was used to quantify H₂ concentration. The gas chromatograph was calibrated using three standard gas with H₂ concentration of 13, 50 and 100 ppm.

Calibration of the reference electrode. We used the Ag/AgCl electrode as the reference electrode, which was calibrated with respect to RHE. The calibrations of reference electrode were conducted in the standard three-electrode system, using Ag/AgCl electrode as reference electrode, Pt foil as the working and counter electrodes. The 1.0 M KOH electrolyte was saturated with ultrahigh purity hydrogen and continuously bubbled with hydrogen during calibrations. LSV was run \pm 100 mV between hydrogen evolution and oxidation, and the potential of zero current was recorded. The potential of zero current was around 1.002 V, resulting in the equation of E(RHE) = E(Ag/AgCl) + 1.002 V. Assuming the pH of 1.0 M KOH is 13.6, the result is the same as the calculated E(RHE) = E(Ag/AgCl) + 0.197 V + 0.0591 \times pH.

Electrochemical measurements. Electrochemical measurements were performed using a three-electrode system connected to an electrochemical workstation (MULTI Autolab M204) at room temperature using 1.0 M KOH aqueous solution as electrolyte. The Ag/AgCl with saturated KCl electrode and graphite rod were used as reference and counter electrodes, respectively. As-prepared catalysts on nickel foam were directly used as working electrode. The linear sweep voltammetry (LSV) measurements were

carried out at a scan rate of 5 mV s^{-1} . The current density was calculated by the total geometric area of Ni foam. The impedance spectra of each electrode were measured in the frequency range between 1 MHz and 100 Hz with a perturbation amplitude of 5 mV at -50 mV vs. RHE . Ag/AgCl potentials were converted to the RHE scale by the equation $E_{(\text{RHE})} = E_{(\text{Ag/AgCl})} + 0.197 \text{ V} + 0.0591 \times \text{pH}$.

Electrochemical active area (ECSA) measurements. we have carried out experiments to determine the ECSA. The Ni foam loaded with catalysts in 1 cm^2 geometrical area was used as the work electrode and 0.1 M KOH was used as the electrolyte. The ECSA of the catalysts were estimated by the double-layer capacitance of the system from CVs at the scan rates of 30, 40, 50, 60, 70 and 80 mV s^{-1} in a non-faradic range. In this work, the potential range is 0.1 to 0.2 V versus RHE. Based on the assumption that the measured current is all attributed to the double layer charging in 0.1 V window at the open circuit potential, the ECSA (cm^2) of the catalyst can be calculated according to the equation:

$$\text{ECSA} = \text{CDL} / C_s = i_c / (v C_s)$$

The CDL is the double layer capacitance (mF), the i_c represents the charging current (mA), v is the scan rate (V s^{-1}) and C_s is the specific capacitance of the catalyst (mF cm^{-2}). The C_s is generally valued as 0.035 mF cm^{-2} in 0.1 M KOH. The calculated ECSA of CoMoC, Mo₂C and Co are 216, 53 and 41 cm^2 , respectively. The much higher ECSA of CoMoC than that of Mo₂C and Co may be a result of both nano-sized morphology and less content of non-HER active species like high valence Mo.

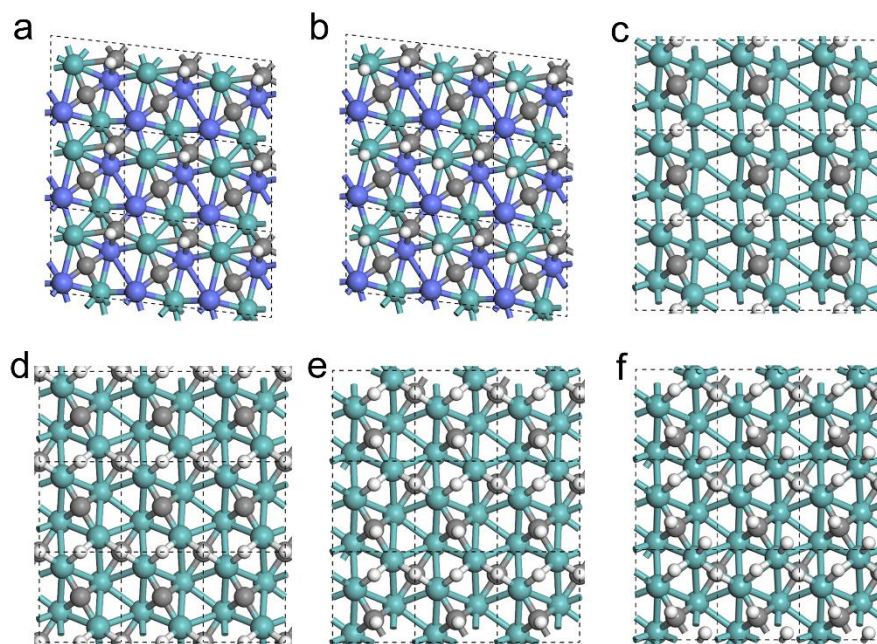


Figure S1. (a, b) The configurations of 16.7% H and 33.3% H coverage on CoMoC-S(110), respectively. (c-f) The configurations of 16.7% H, 33.3% H, 50.0% H and 66.7% H coverage on Mo₂C-S(002), respectively.

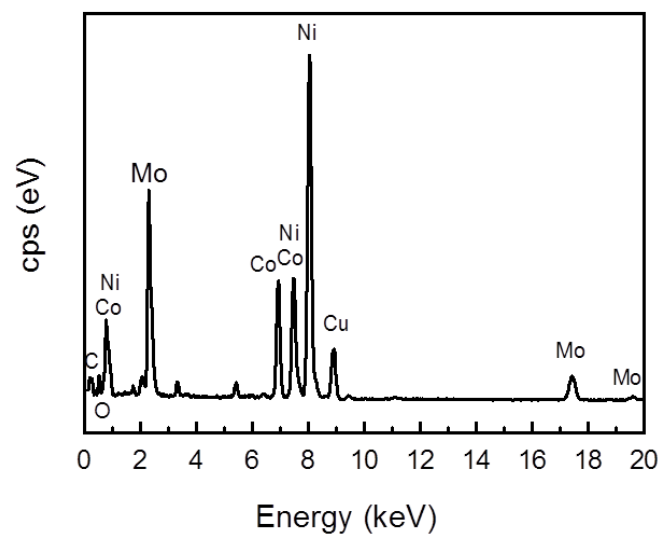


Figure S2. EDS spectrum of CoMoC catalyst.

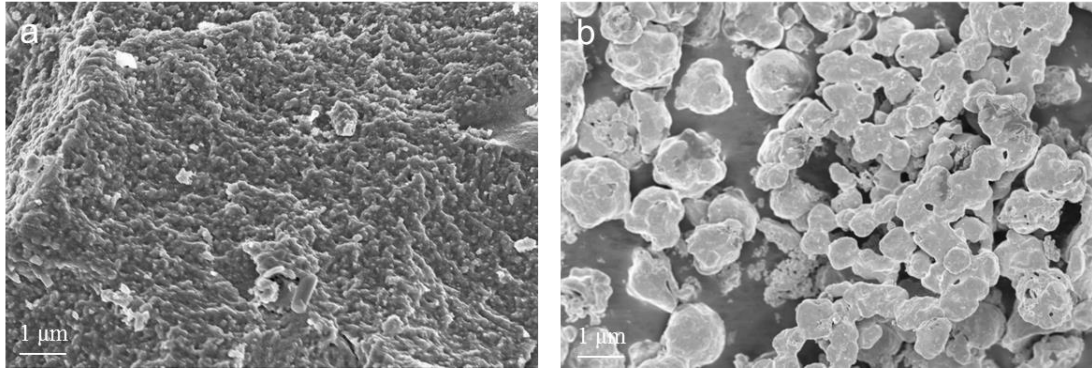


Figure S3. SEM images of (a) Mo₂C and (b) Co.

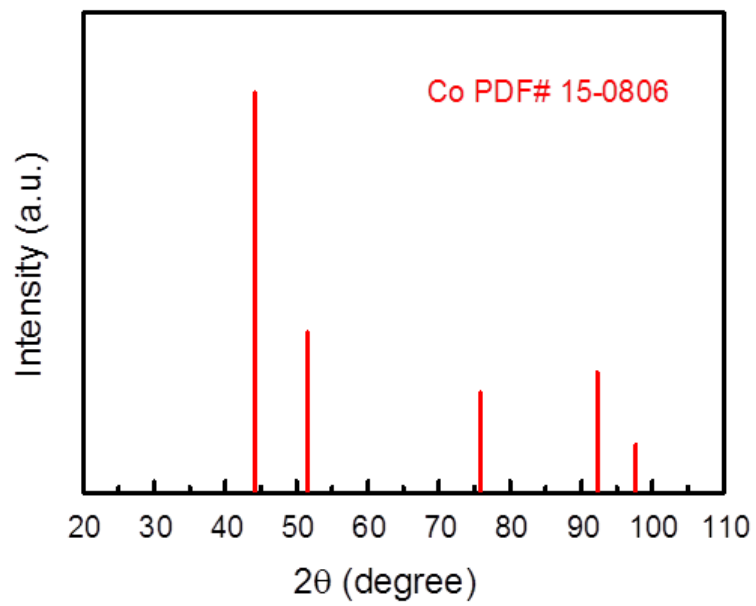


Figure S4. Standard XRD pattern of Co.

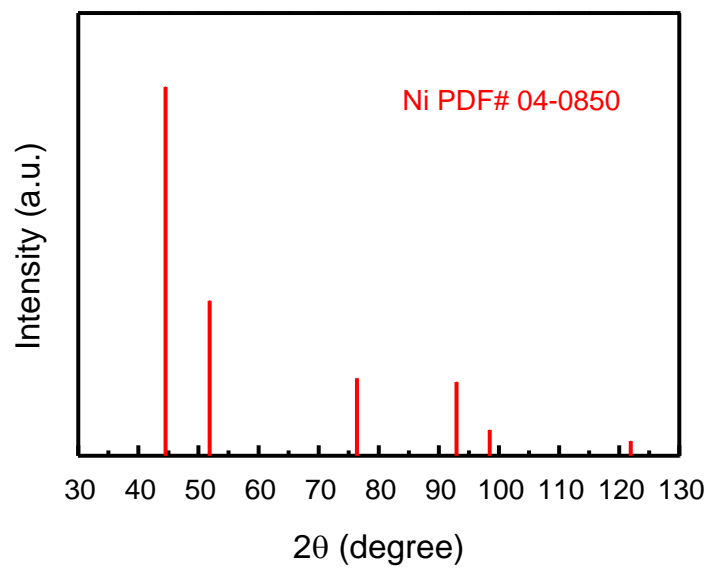


Figure S5. Standard XRD pattern of Ni foam.

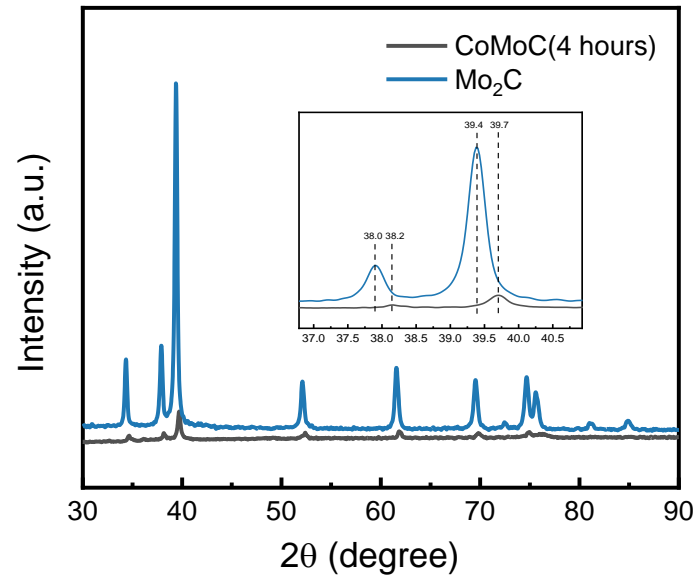


Figure S6. XRD patterns of CoMoC with prolonged annealing time from 3 h to 4 h and Mo₂C.

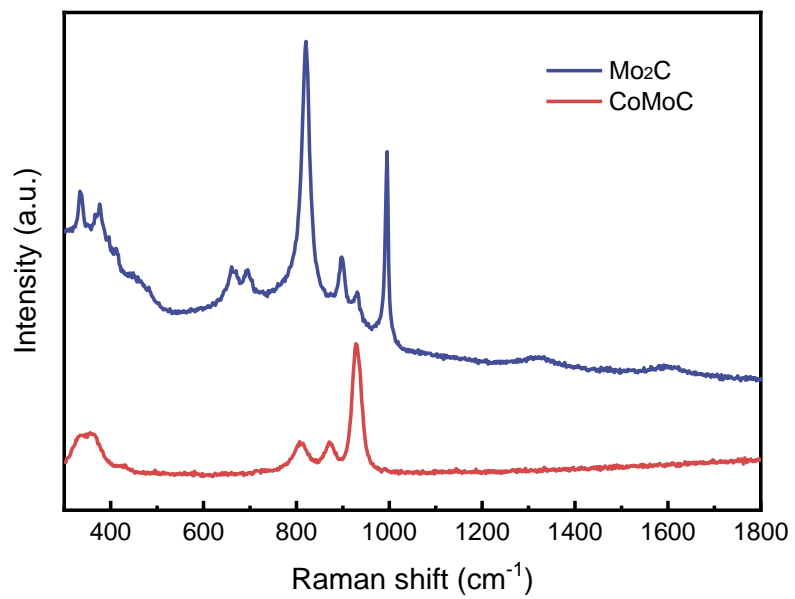


Figure S7. Raman spectra of Mo₂C and CoMoC.

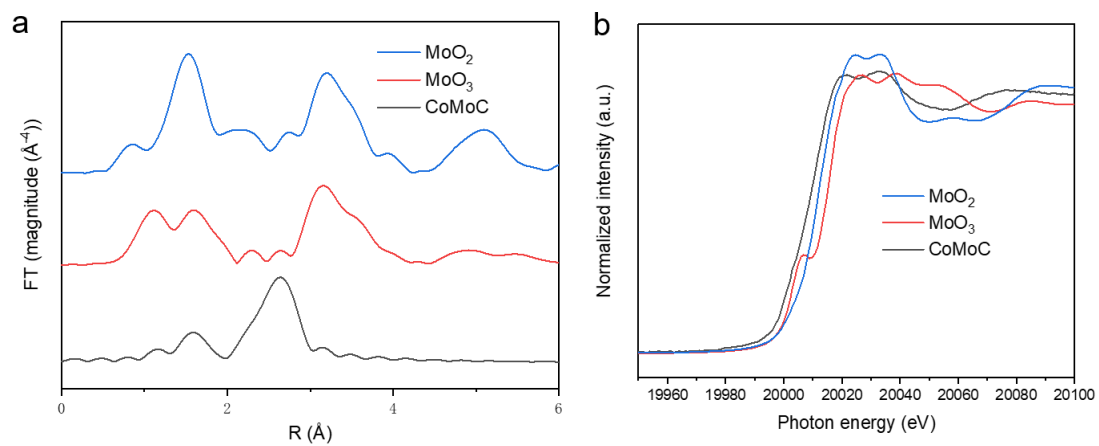


Figure S8. Mo K-edge XAS. (a) k³-weighted EXAFS Fourier transform magnitudes of the samples. (b) XANES of Mo K-edge of the samples.

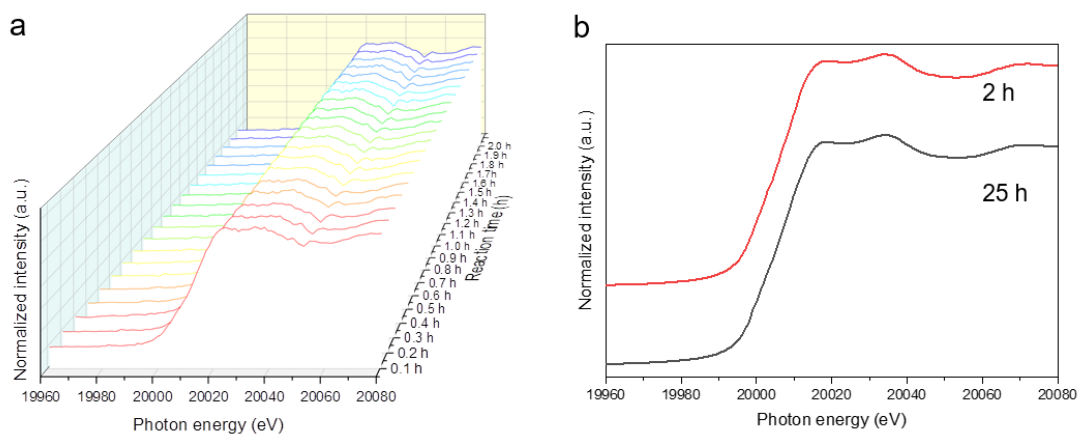


Figure S9. XAS study of Mo in CoMoC catalysts. **(a)** *in-situ* quick X-ray adsorption spectra (QXAFS), and **(b)** the *ex-situ* Mo K-edge XAFS spectra of CoMoC after 2 and 25 h.

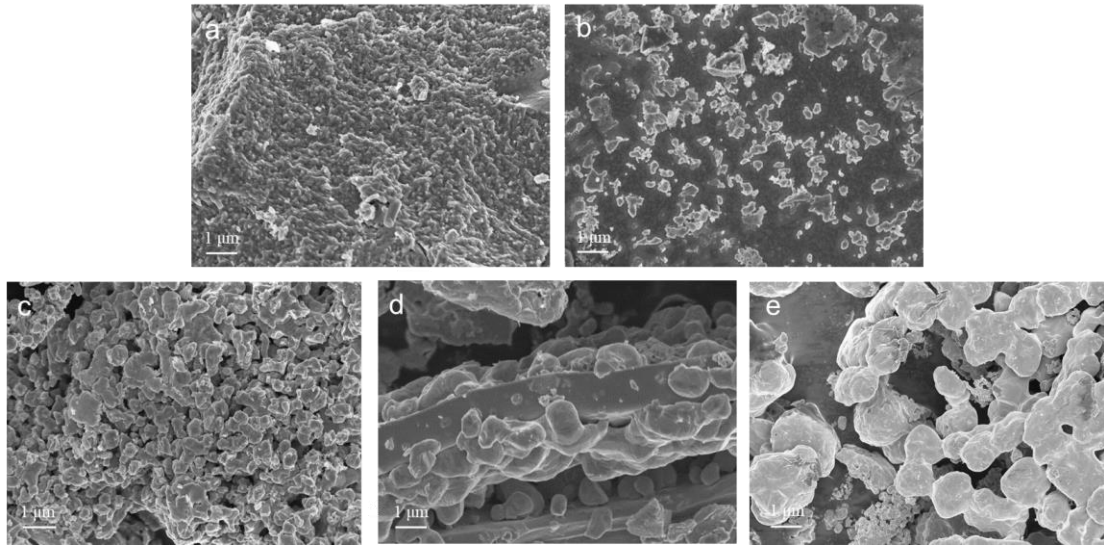


Figure S10. SEM images of the as-prepared bimetallic carbide with different Co/Mo ratio. (a) Co:Mo=0:10. (b) Co:Mo=3:7. (c) Co:Mo=5:5. (d) Co:Mo=7:3 and (e) Co:Mo=10:0.

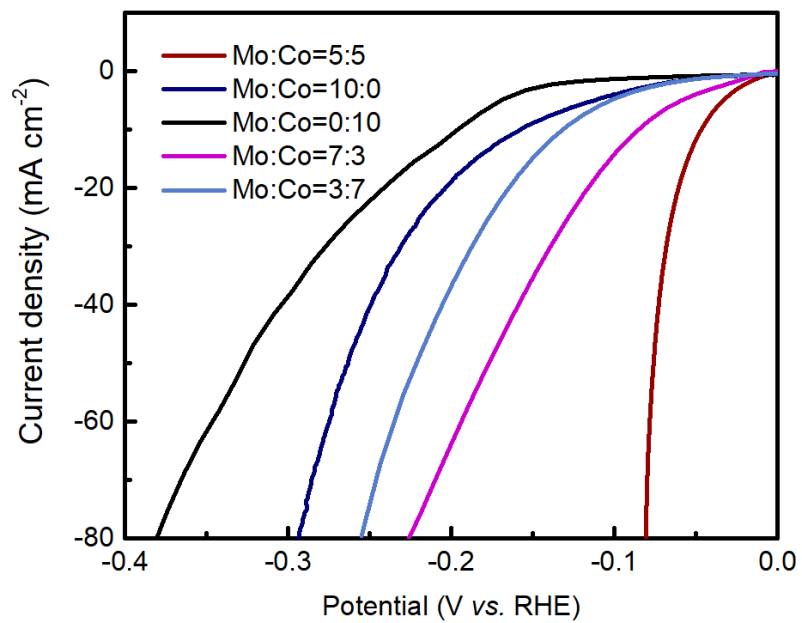


Figure S11. The LSV curves of fabricated catalyst with different Mo/Co ratios.

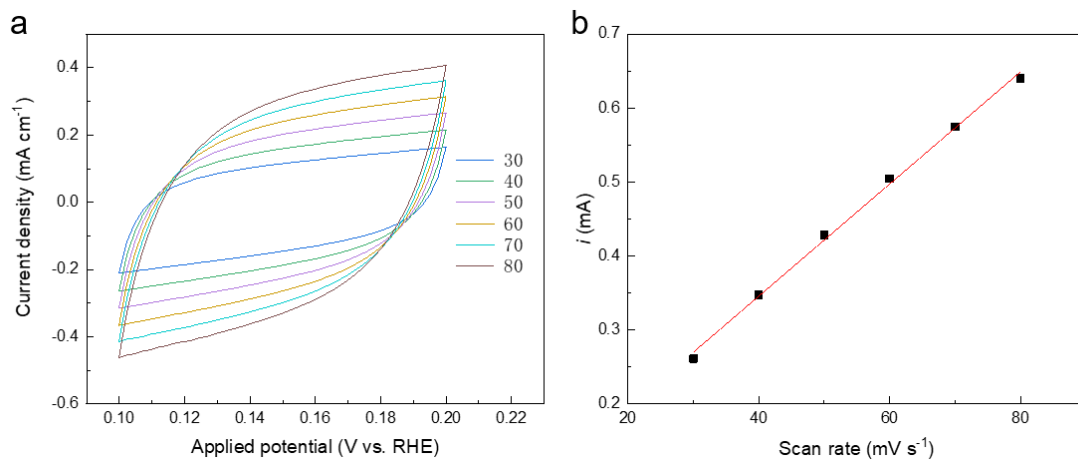


Figure S12. ECSA measurement of CoMoC. **(a)** CV curves of CoMoC with different scan rate in 0.1 M KOH electrolyte. **(b)** Plots of charging current versus scan rate.

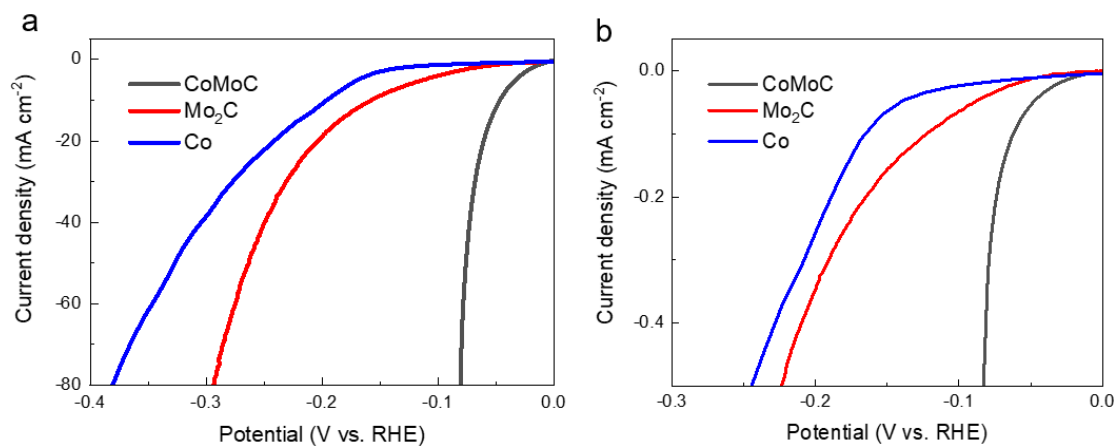


Figure S13. HER performance of the CoMoC catalyst. **(a)** The LSV curves of CoMoC, Mo₂C and Co catalysts normalized using geometric area. **(b)** The LSV curves of CoMoC, Mo₂C and Co catalysts normalized using ECSA.

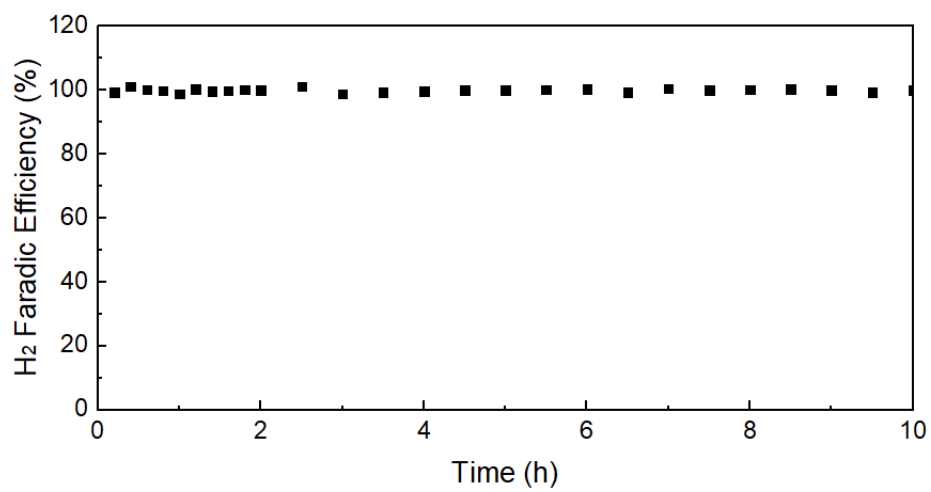


Figure S14. H₂ faradic efficiency versus reaction time.

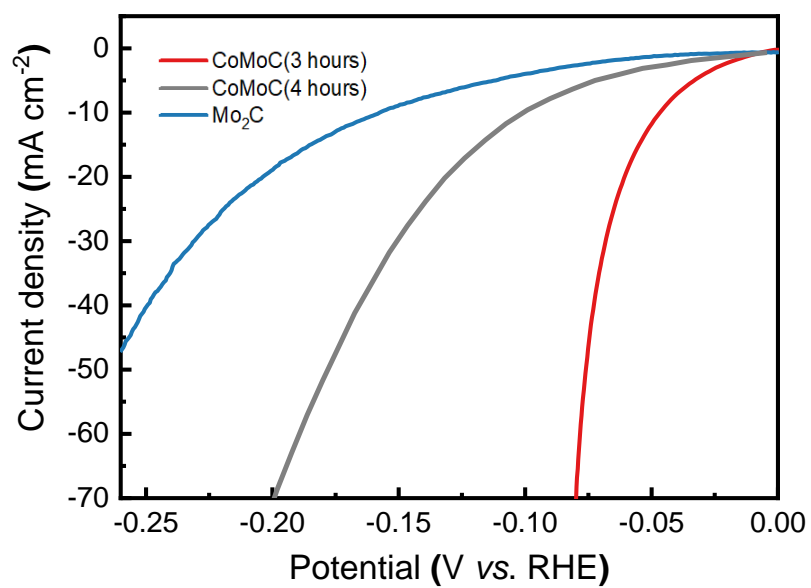


Figure S15. The LSV curves of CoMoC (with annealing time of 3 h), CoMoC (with annealing time of 4 h) and Mo₂C.

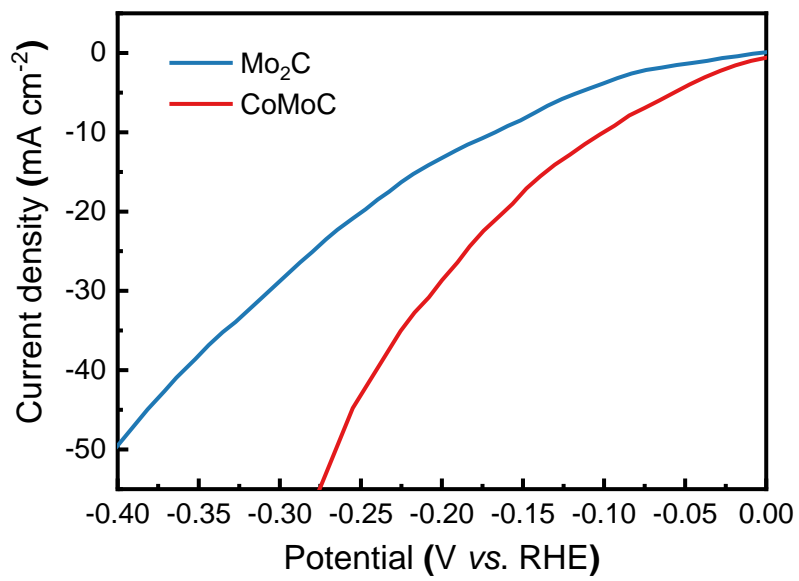


Figure S16. The LSV curves of Mo₂C and CoMoC in 0.5 M H₂SO₄.

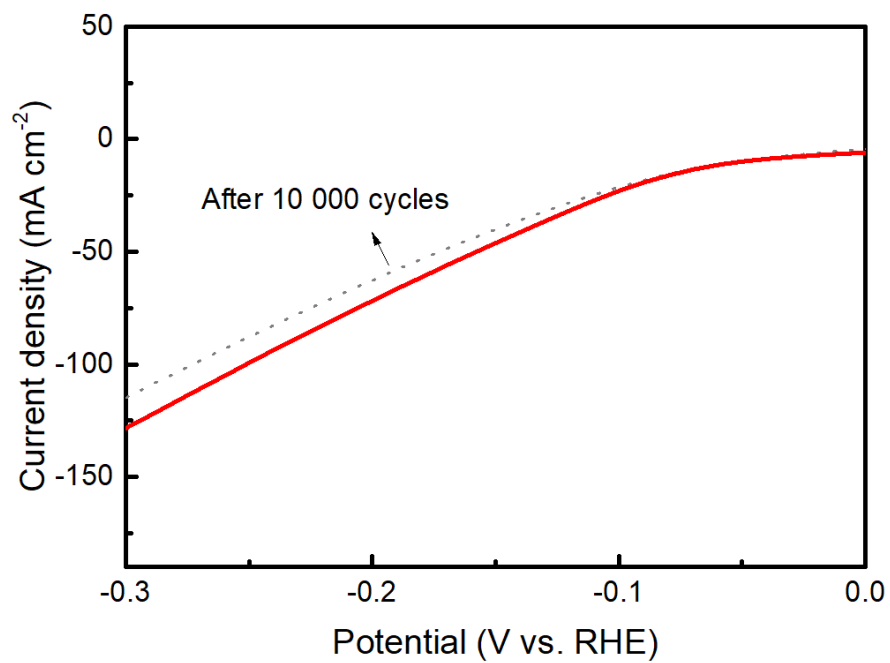


Figure S17. The LSV curves of freshly prepared CoMoC catalysts and after 10 000 cycles.

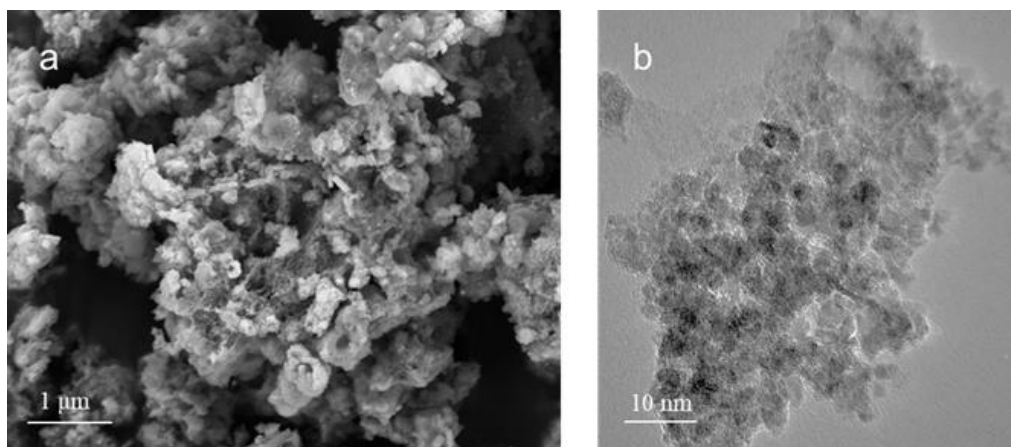


Figure S18. Morphology of CoMoC. (a) SEM and (b) TEM images of CoMoC catalyst after stability test.

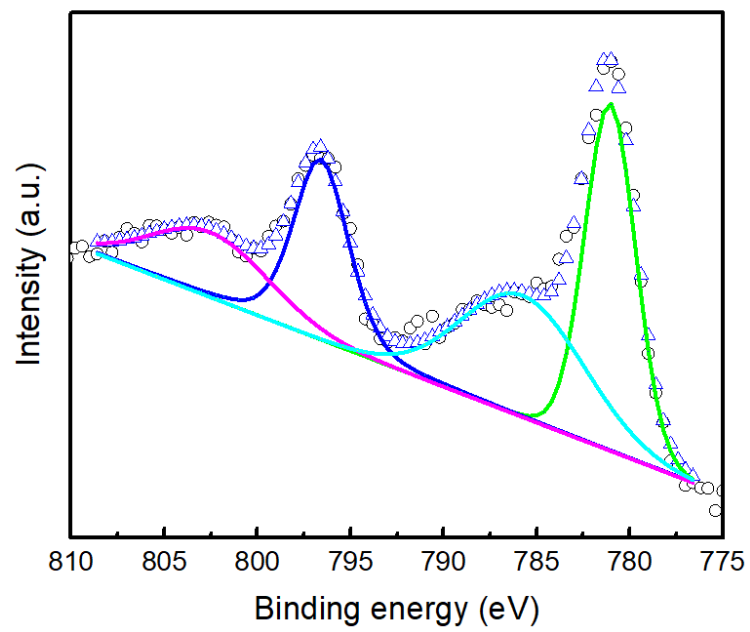


Figure S19. Co 2p XPS data of CoMoC.

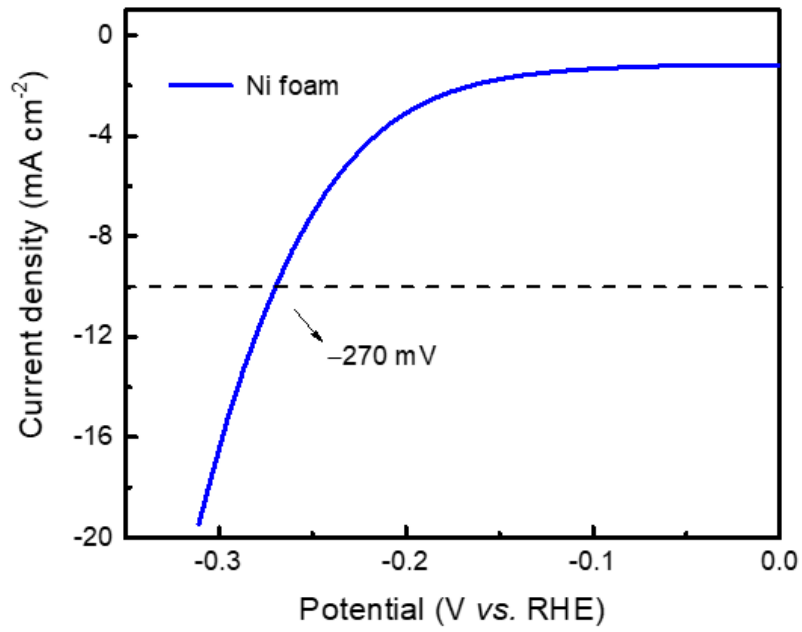


Figure S20. The LSV curve of Ni foam in 1.0 M KOH aqueous solution.

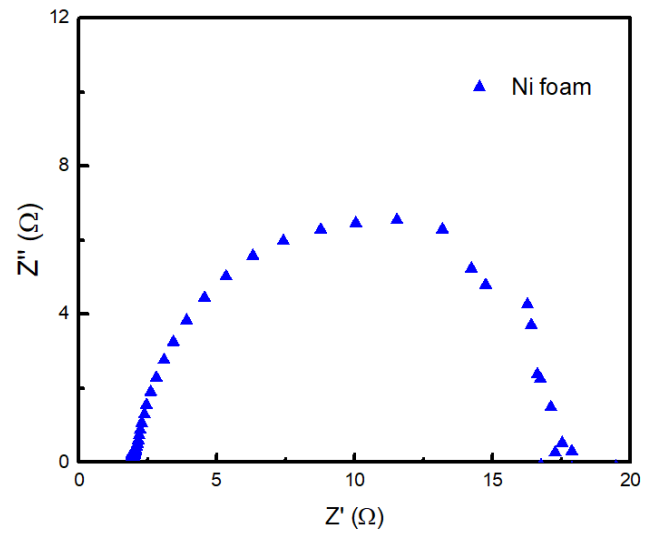


Figure S21. The Nyquist plot of Ni foam.

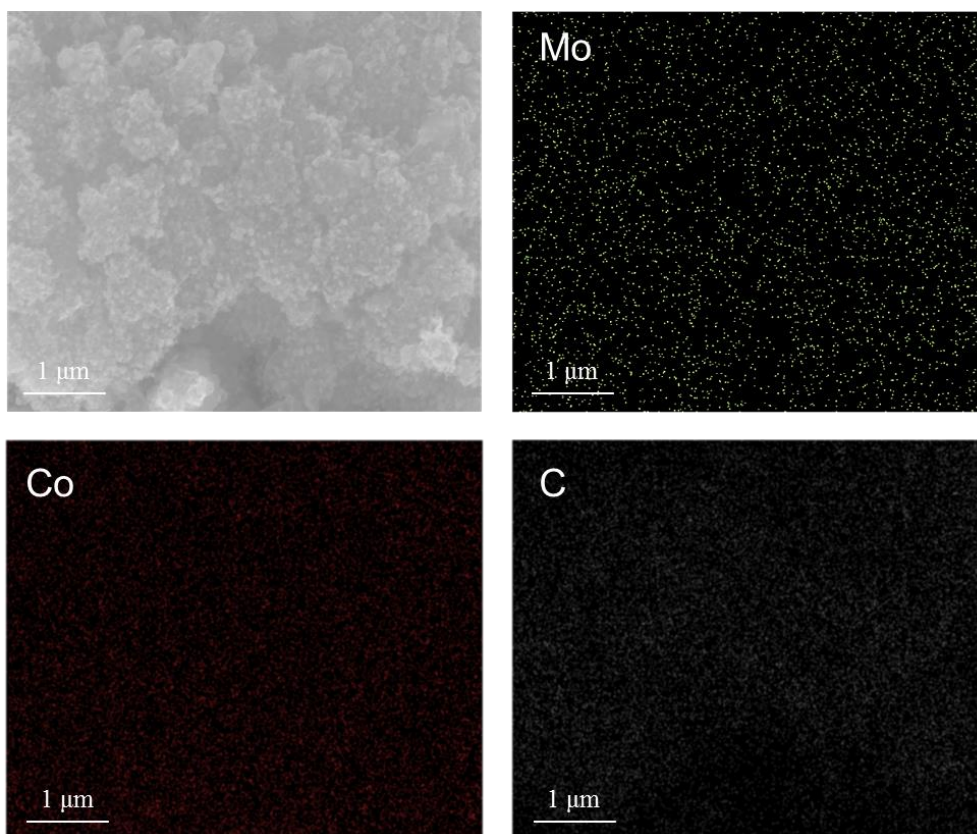


Figure S22. SEM image and corresponding EDS element mappings for Mo, Co and C of CoMoC catalyst.

Table S1. Six low-index surface energy of Mo₂C and CoMoC.

	(100)	(002)	(101)	(102)	(110)	(103)
Mo ₂ C	0.251	0.160	0.245	0.248	0.235	0.254
CoMoC	0.232	0.224	0.215	0.227	0.199	0.222

Table S2. Percentage of C/Co/Mo elements of CoMoC catalyst from EDS.

Elements	wt%	atom%
C	5.96	27.97
N	0.48	1.93
O	0.82	2.89
Co	34.83	33.24
Mo	57.91	33.97

Table S3. The peak fitting results of Mo 4d XPS data of Mo₂C and CoMoC.

Sample	Species	Percentage (%)
Mo ₂ C	Mo ⁰	11.2
	Mo ³⁺	19.0
	Mo ⁴⁺	28.2
	Mo ⁶⁺	41.7
CoMoC	Mo ⁰	26.9
	Mo ³⁺	35.6
	Mo ⁴⁺	15.4
	Mo ⁶⁺	22.1

Table S4. Structure parameters from curve-fitting analysis of the EXAFS experiments.

Sample	Shell	R (Å)	N	ΔE_0 (eV)	σ^2 (10^{-3}Å^2)
CoMoC	Mo-C	2.138	3.09 (± 0.78)	8.48 (± 4.47)	29.98 (± 18.34)
	Mo-Mo	2.948	5.19 (± 0.70)	-3.39 (± 2.87)	3.69 (± 16.97)
Mo ₂ C	Mo-C	2.120	3	7.05 (± 5.38)	7.86 (± 3.64)
	Mo-Mo	2.958	12	-7.61 (± 1.93)	6.22 (± 0.56)

Table S5. ICP-OES results of electrolyte after stability test.

Element	Concentration (mg L ⁻¹)	Dissolved ratio (%)
Co	0.019	0.13
Mo	0.036	0.15

Reference

- 1 C. Giordano, C. Erpen, W. Yao, B. Milke and M. Antonietti, *Chem. Mater.*, 2009, **21**, 5136-5144.