Supporting Information

Synergistic Improvement of pH-Universal Hydrogen Evolution through B, N Dual-Doped Mo_2C

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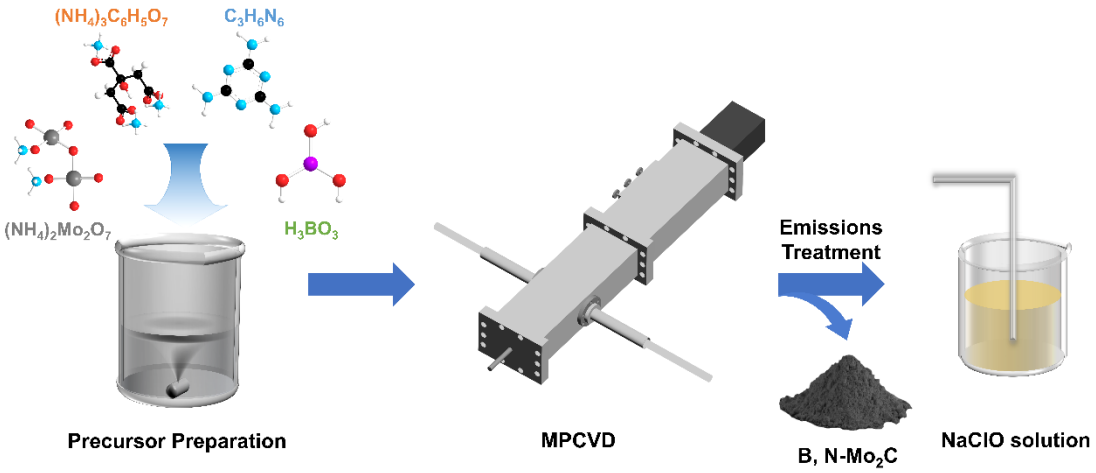

Fig. S1 Reaction flowchart of the experiment.

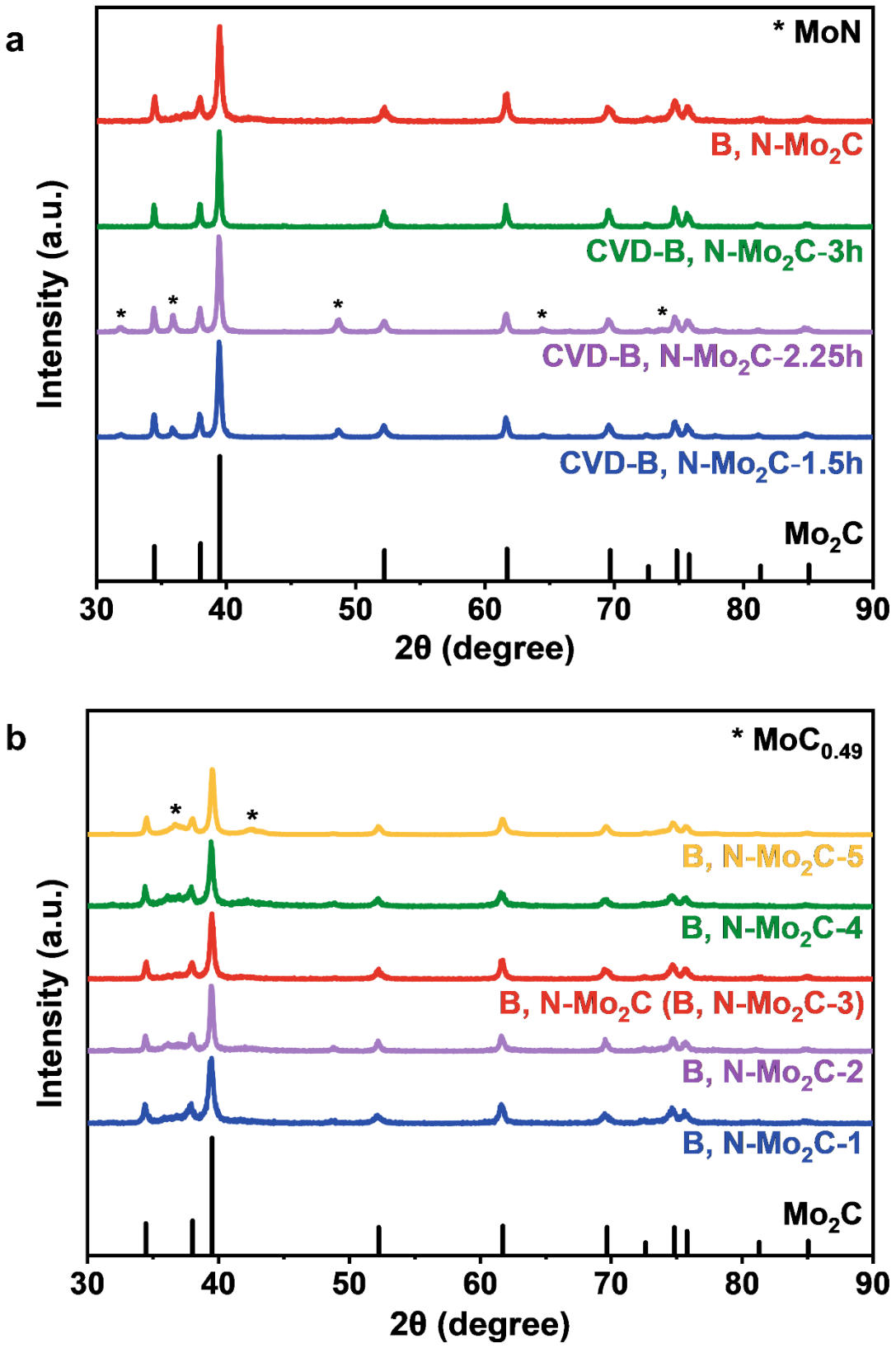

Fig. S2 XRD patterns of (a) CVD-B, N-Mo_2C-1.5h, CVD-B, N-Mo_2C-2.25h, CVD-B, N-Mo_2C-3h, and B, N-Mo_2C. (b) B, N-Mo_2C-X (X stands for the ratio of boric acid dosage).

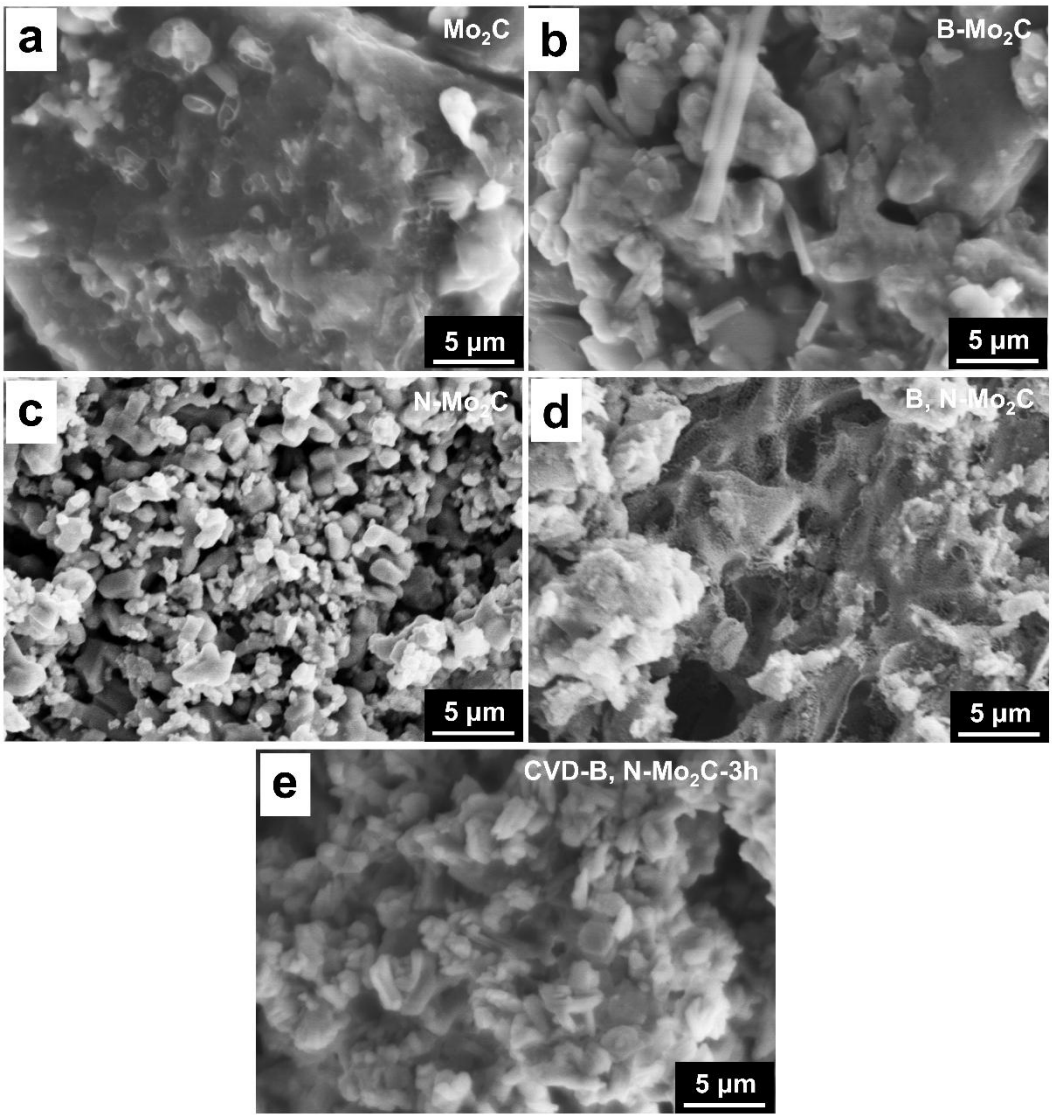

Fig. S3 SEM image of (a) Mo_2C, (b) B-Mo_2C, (c) N-Mo_2C, (d) B, N-Mo_2C, and (e) CVD-B, N-Mo_2C-3h.

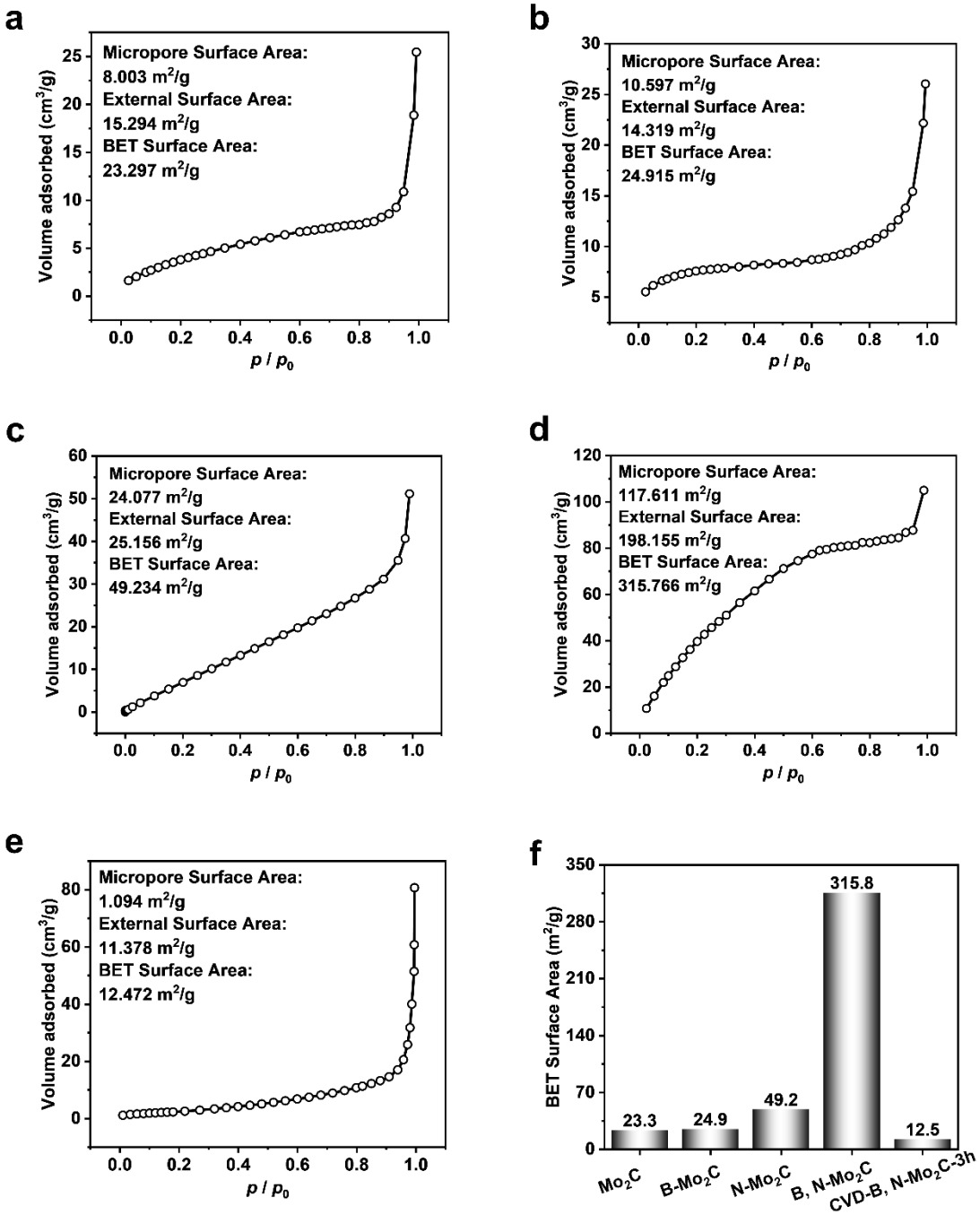

Fig. S4 N_2 adsorption isotherms of (a) Mo_2C, (b) B-Mo_2C, (c) N-Mo_2C, (d) B, N-Mo_2C, (e) CVD-B, N-Mo_2C-3h, and (f) BET surface area.

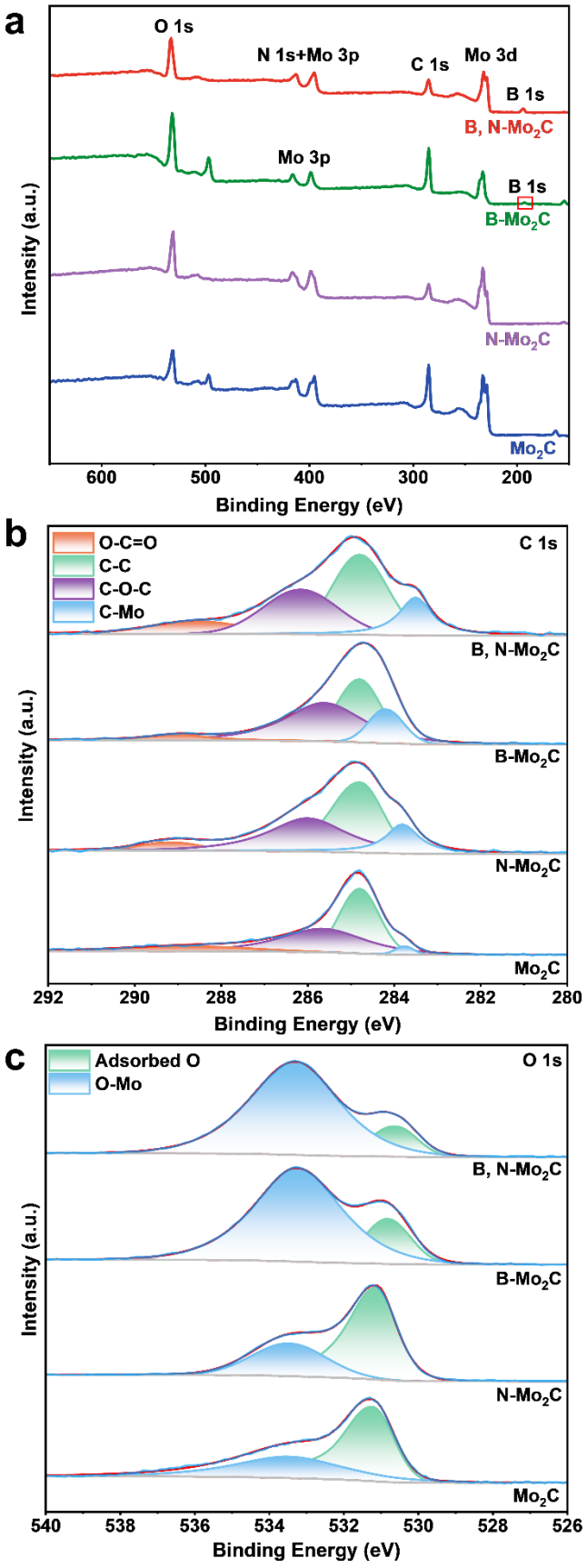

Fig. S5 High-resolution XPS spectra. (a) survey spectra, (b) C 1s and (c) O 1s spectra of Mo_2C, N-Mo_2C, B-Mo_2C, and B, N-Mo_2C.

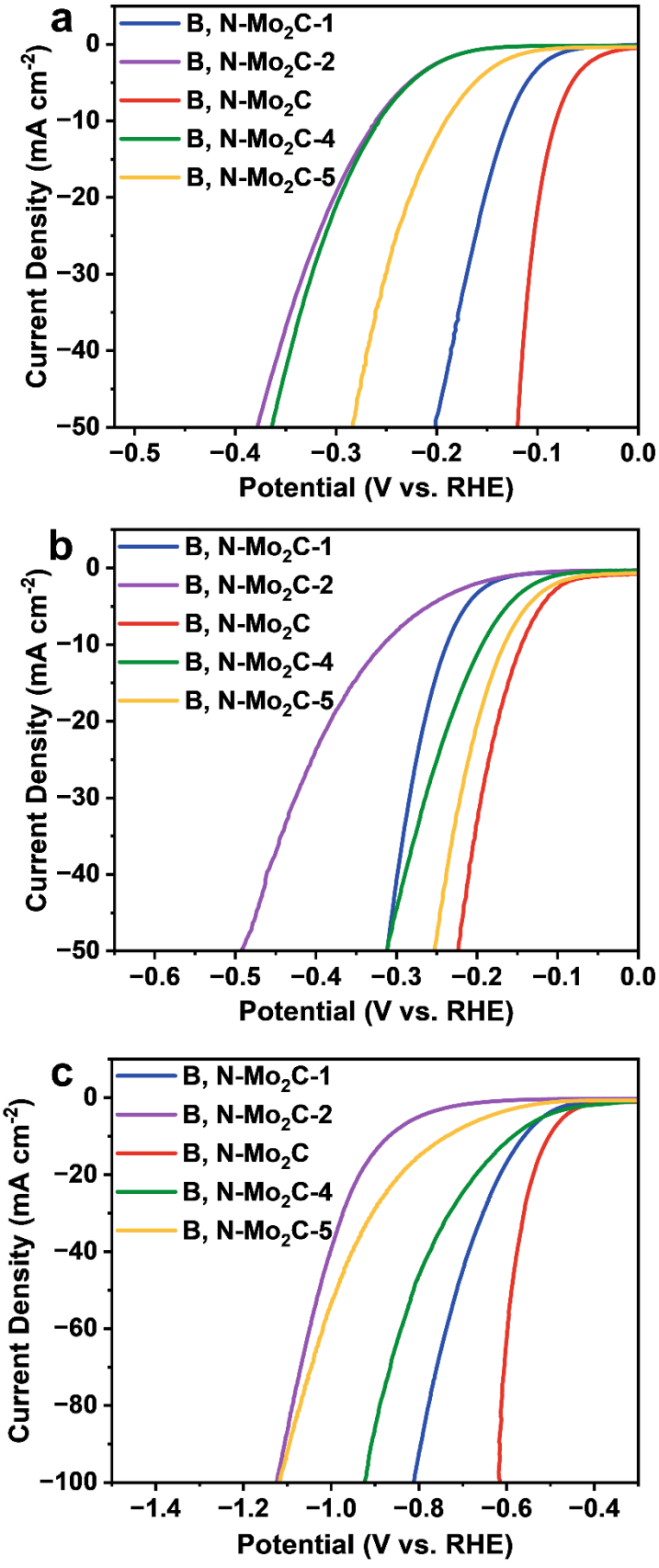

Fig. S6 HER performance of different samples in Polarization curves. (a) 1.0 M KOH, (b) 0.5 M H_2SO_4, and (c) 0.5 M Na_2SO_4.

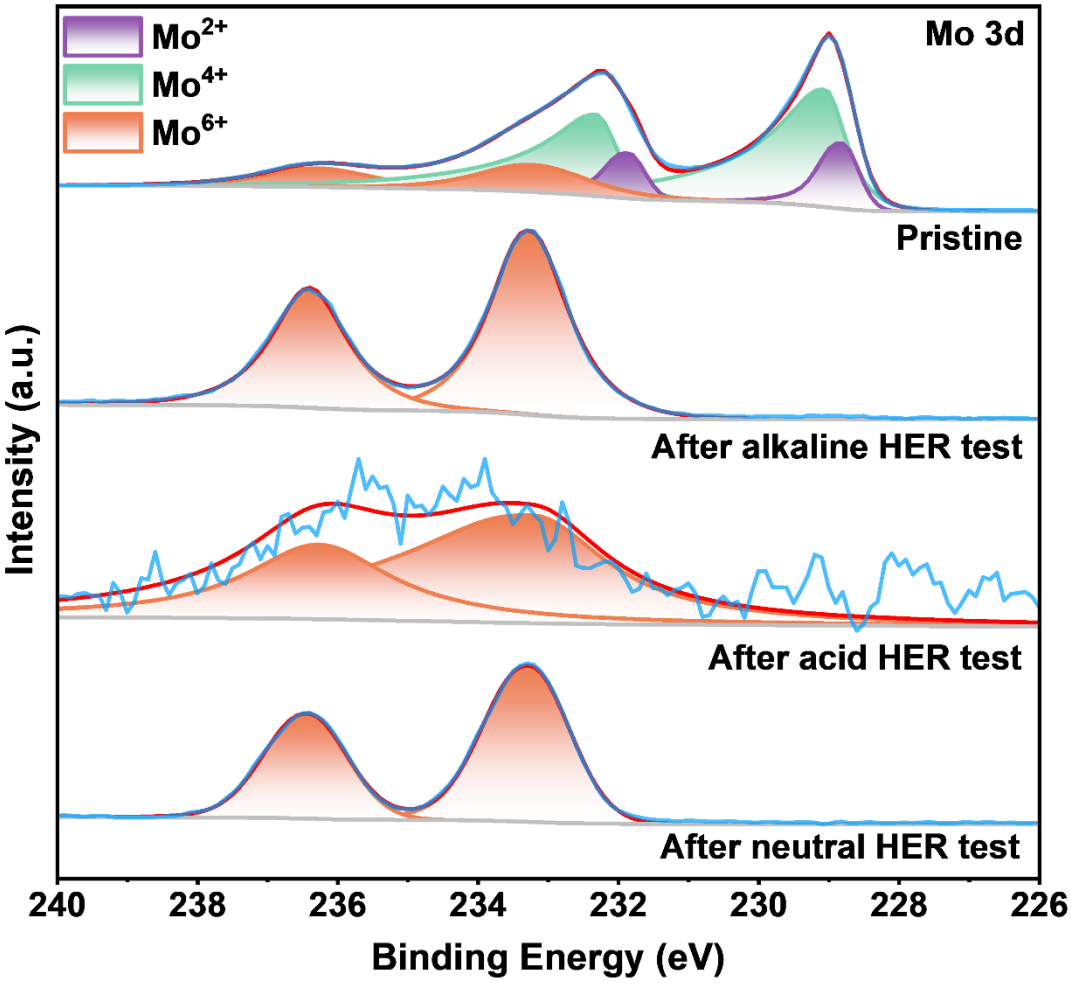

Fig. S7 XPS spectra of Mo 3d in B, N-Mo_2C before and after HER test in different environments.

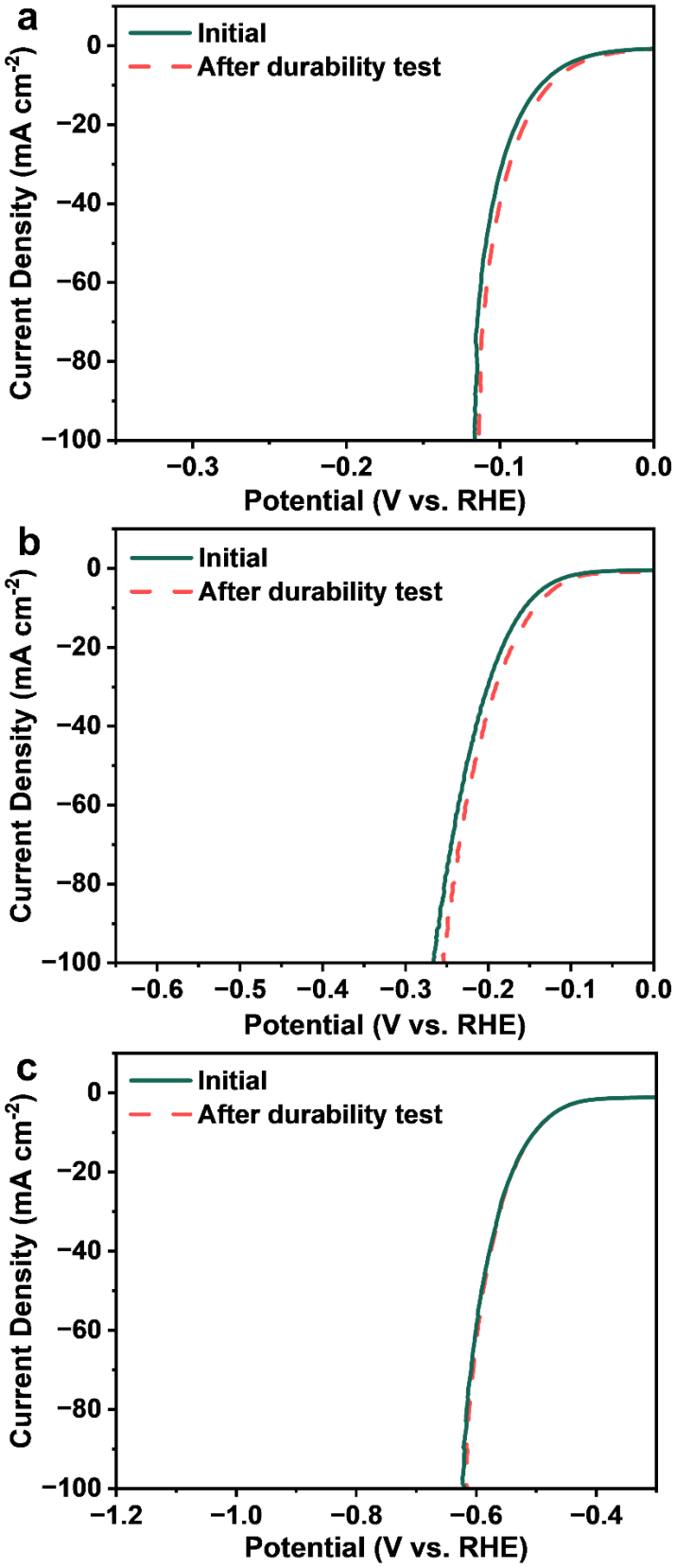

Fig. S8 Polarization curves of B, N-Mo_2C before and after I-t durability tests in (a) 1.0 M KOH, (b) 0.5 M H_2SO_4, and (c) 0.5 M Na_2SO_4.

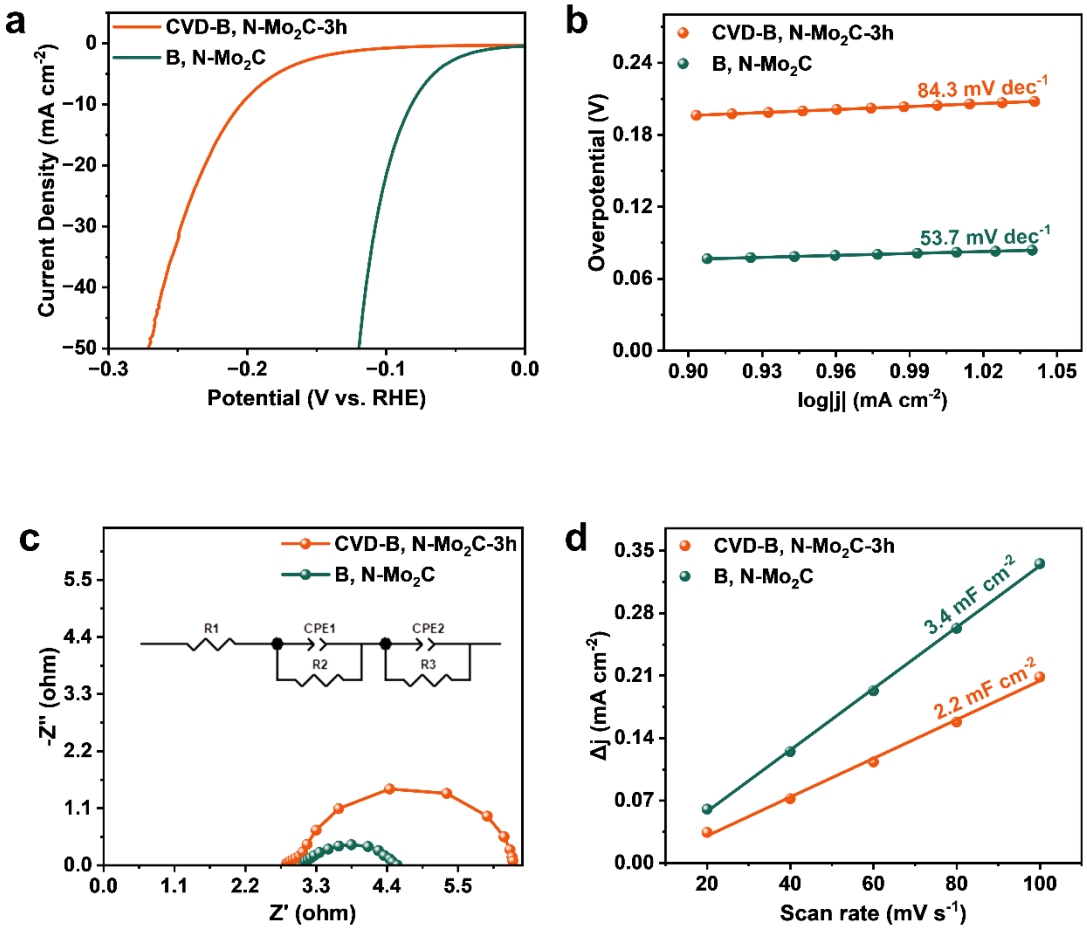

Fig. S9 HER performance of different samples in 1.0 M KOH. (a) Polarization curves, (b) Tafel plots, (c) Nyquist plots collected at the overpotential of 100 mV, and (d) Capacitive currents as a function of scan rates with various rates from 20 to 100 mV s^{-1}.

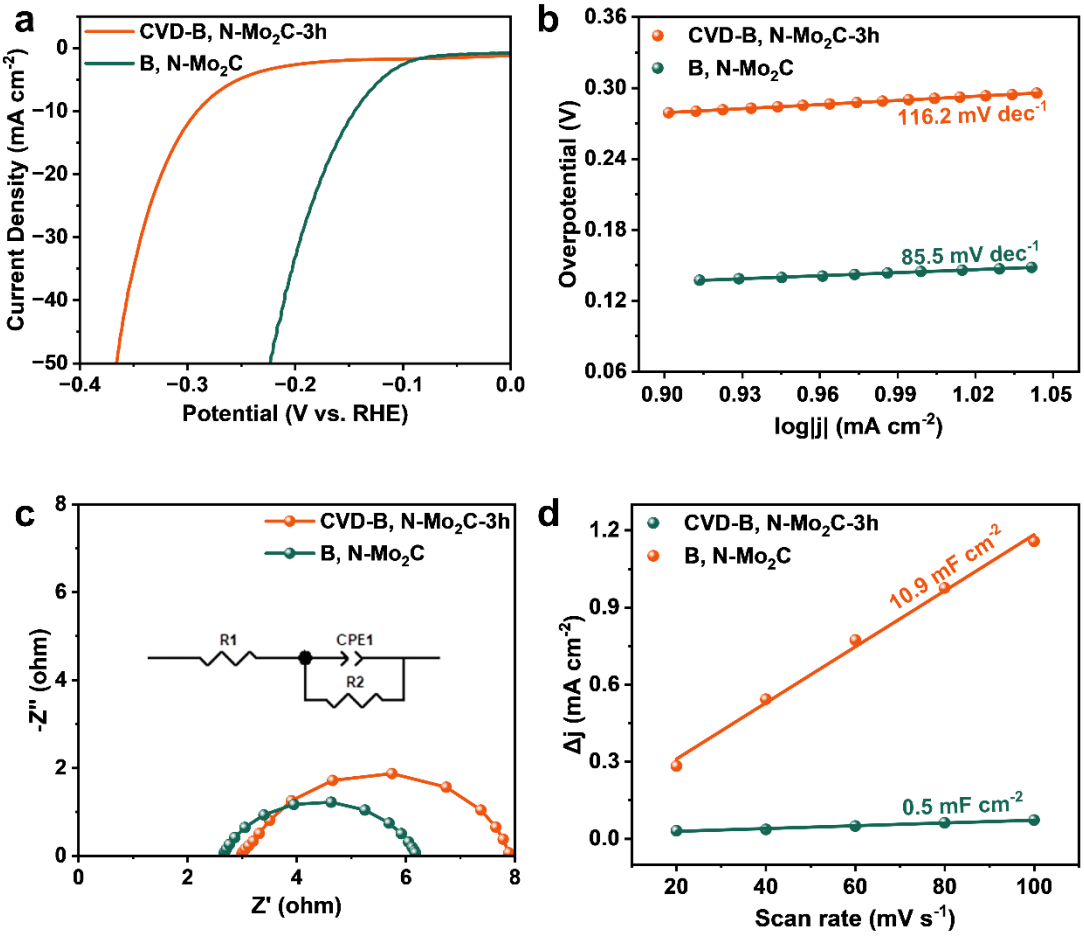

Fig. S10 HER performance of different samples in 0.5 M H_2SO_4. (a) Polarization curves, (b) Tafel plots, (c) Nyquist plots collected at the overpotential of 200 mV, and (d) Capacitive currents as a function of scan rates with various rates from 20 to 100 mV s^{-1}.

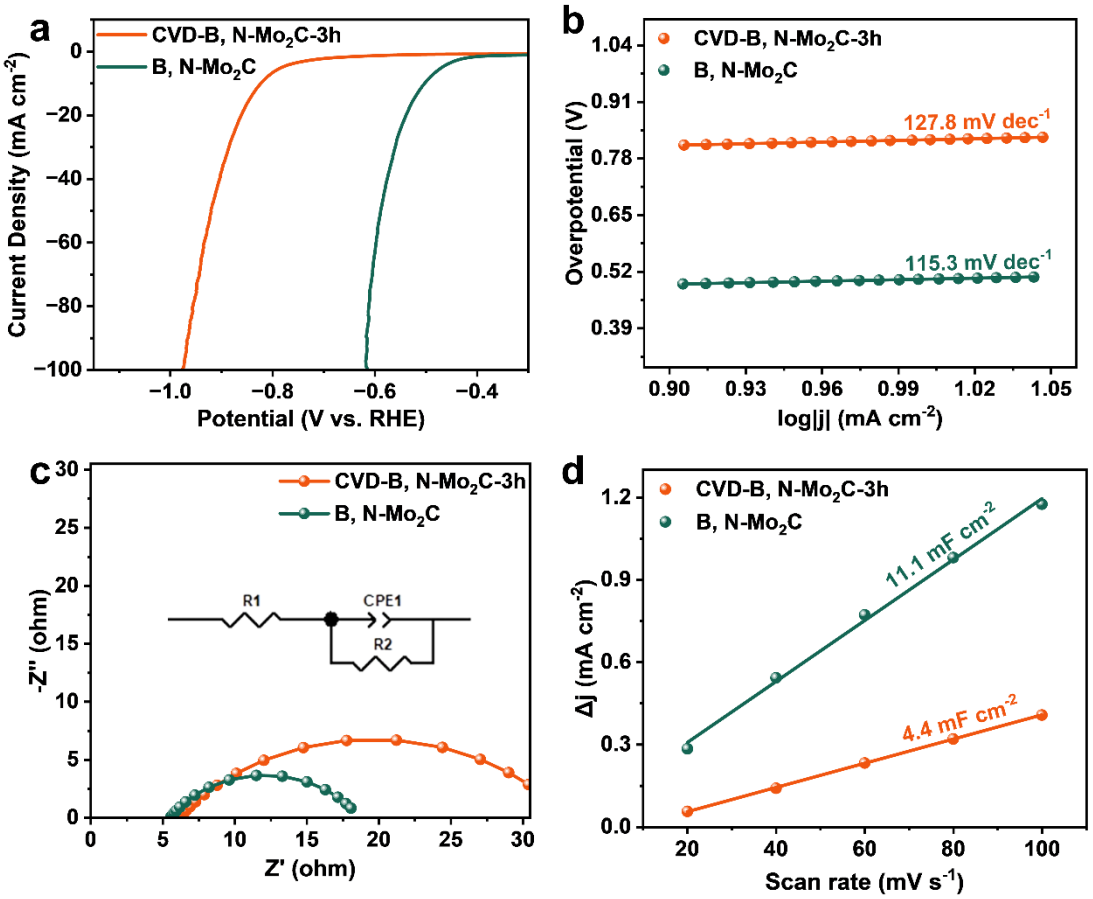

Fig. S11 HER performance of different samples in 0.5 M Na_2SO_4. (a) Polarization curves, (b) Tafel plots, (c) Nyquist plots collected at the overpotential of 600 mV, and (d) Capacitive currents as a function of scan rates with various rates from 20 to 100 mV s^{-1}.

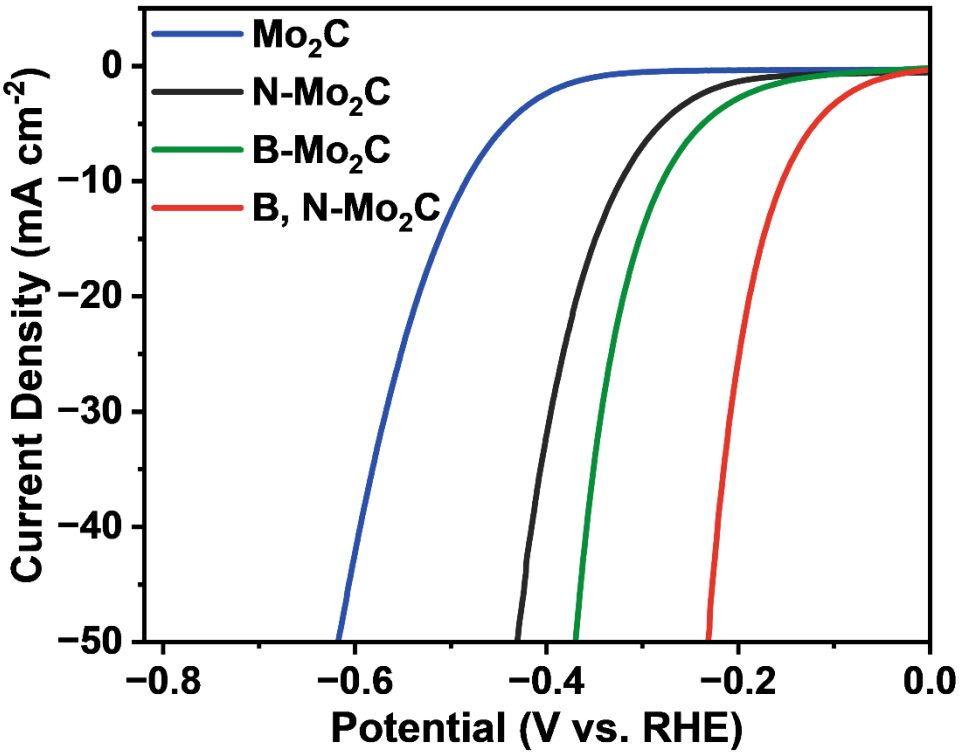

Fig. S12 HER performance of different samples in 0.5 M H_2SO_4. (The counter electrode is a carbon rod.)

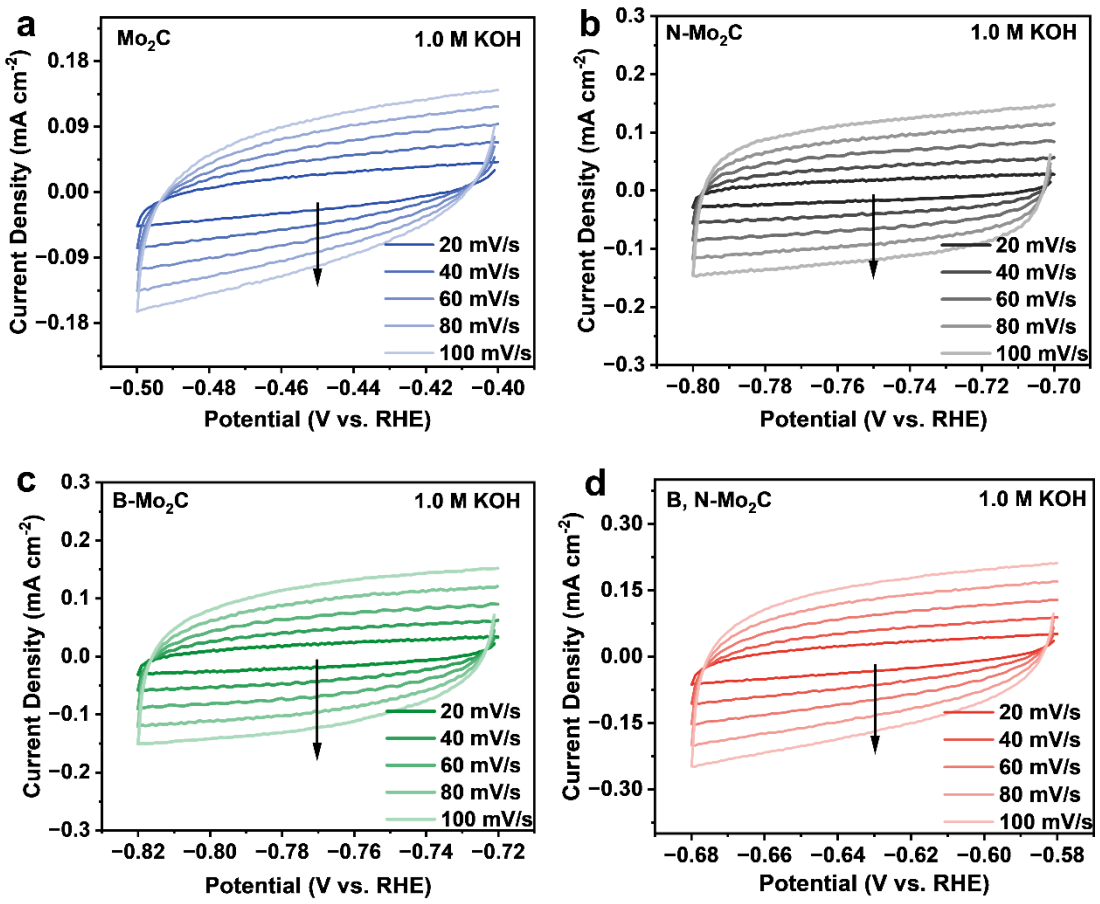

Fig. S13 (a-d) Cyclic voltammetry curves for Mo_2C, N-Mo_2C, B-Mo_2C, and B, N-Mo_2C at different scan rates for HER in 1.0 M KOH (20-100 mV s^{-1}).

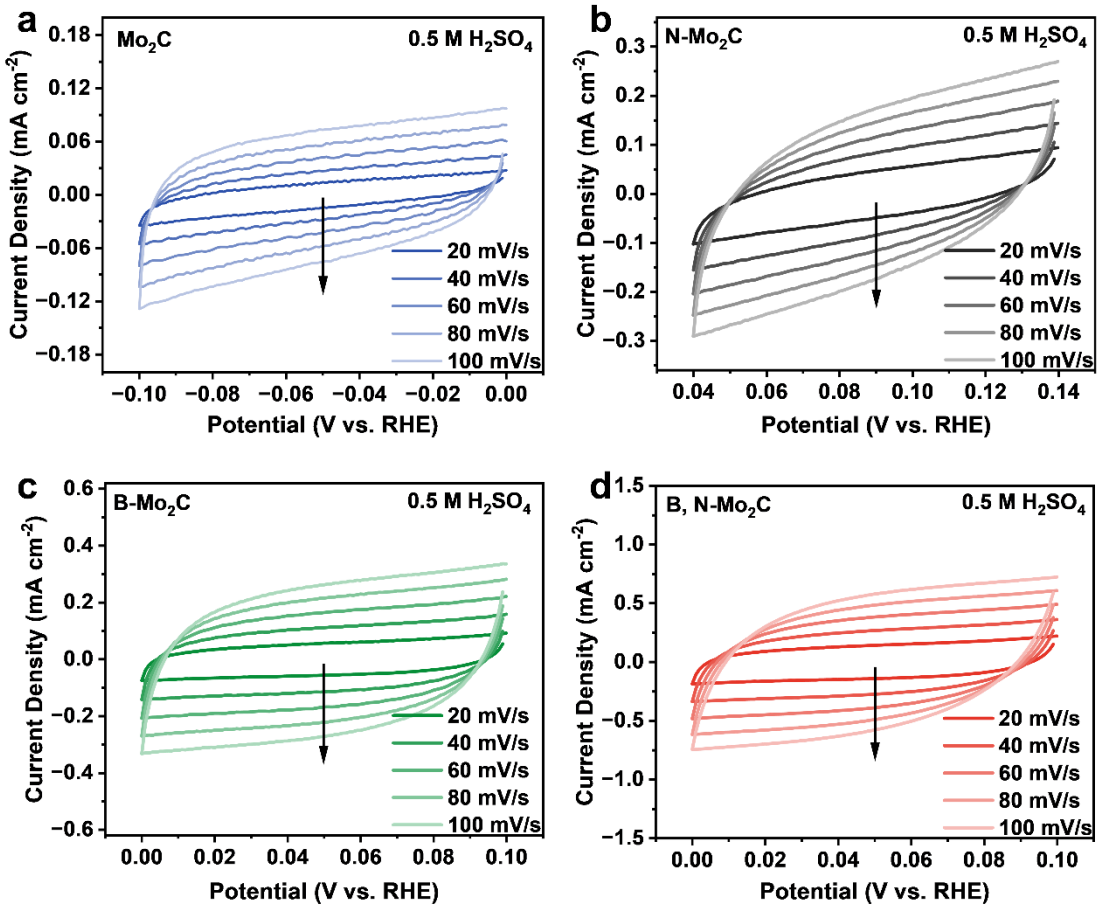

Fig. S14 (a-d) Cyclic voltammetry curves for Mo_2C, N-Mo_2C, B-Mo_2C, and B, N-Mo_2C at different scan rates for HER in 0.5 M H_2SO_4 (20-100 mV s^{-1}).

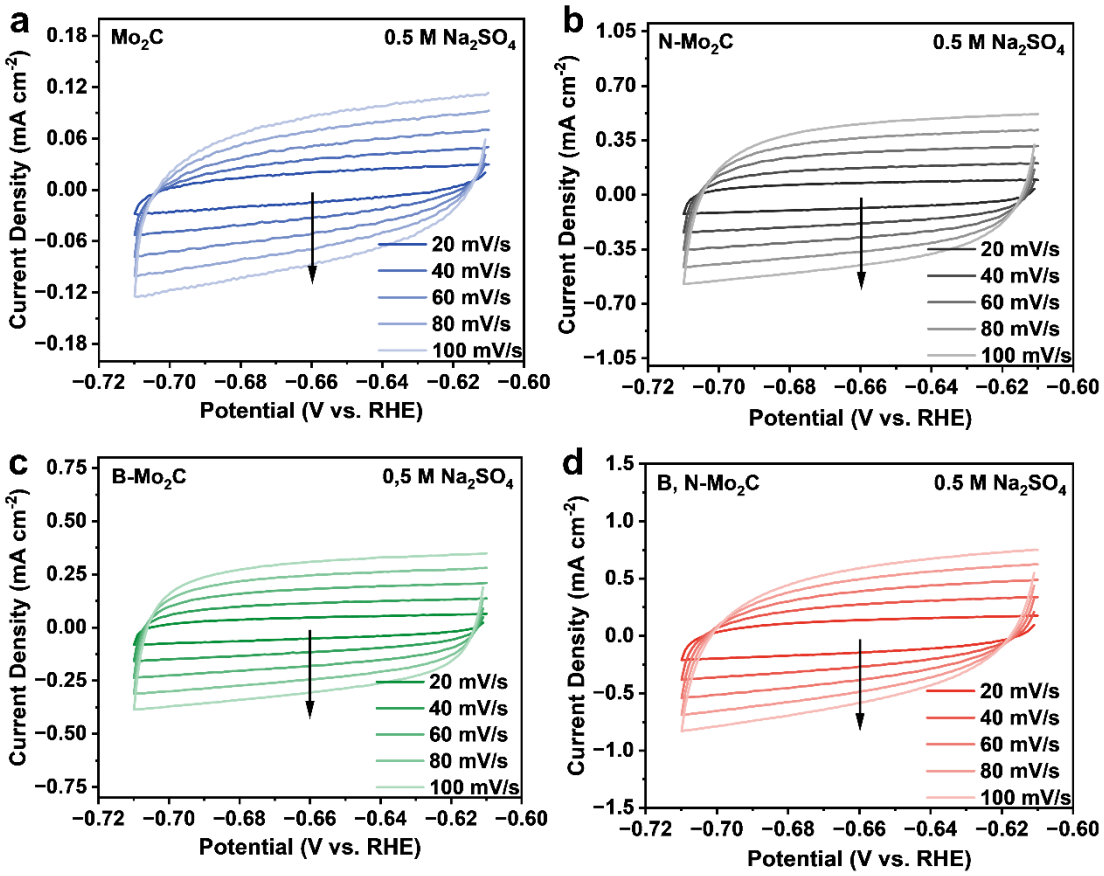

Fig. S15 (a-d) Cyclic voltammetry curves for Mo_2C, N-Mo_2C, B-Mo_2C, and B, N-Mo_2C at different scan rates for HER in 0.5 M Na_2SO_4 (20-100 mV s^{-1}).

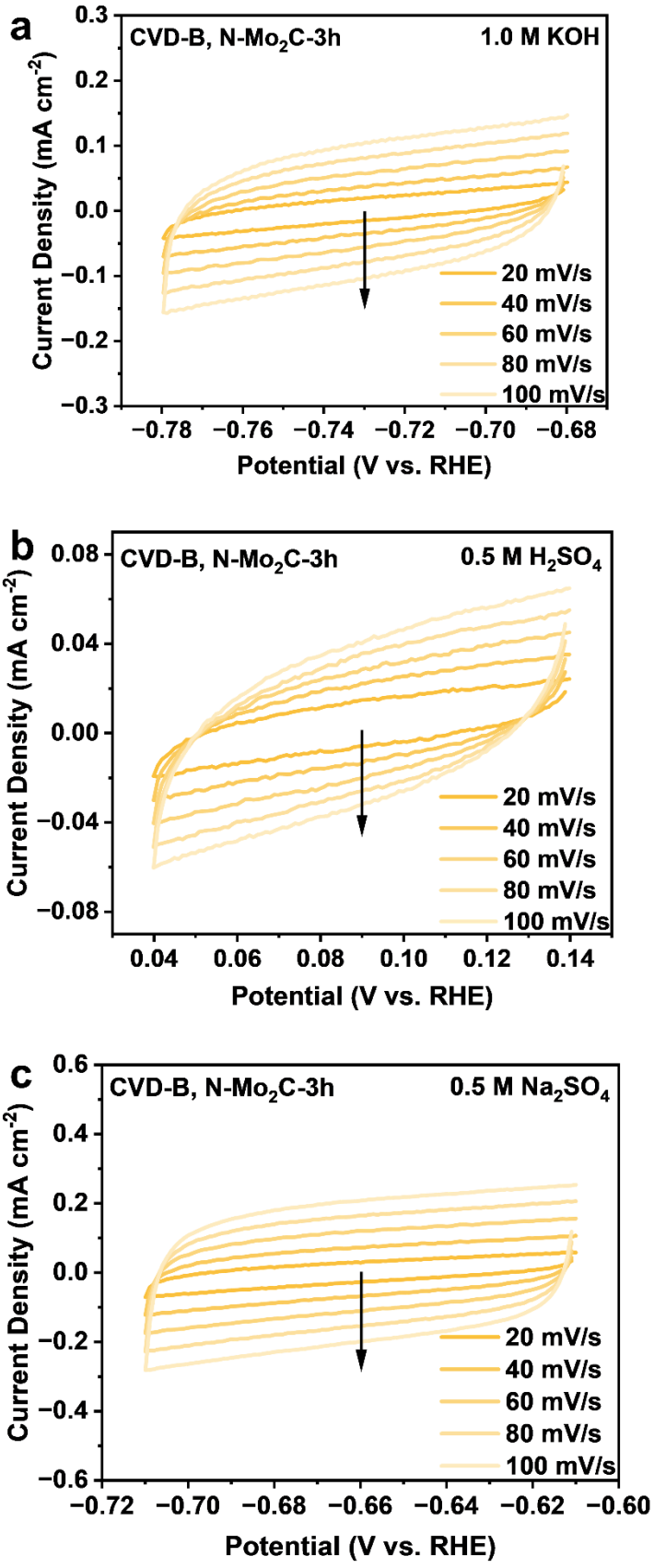

Fig. S16 (a-c) Cyclic voltammetry curves for CVD-B, N-Mo_2C-3h at different pH for HER in 1.0 M KOH, 0.5 M H_2SO_4, and 0.5 M Na_2SO_4 (20-100 mV s^{-1}).

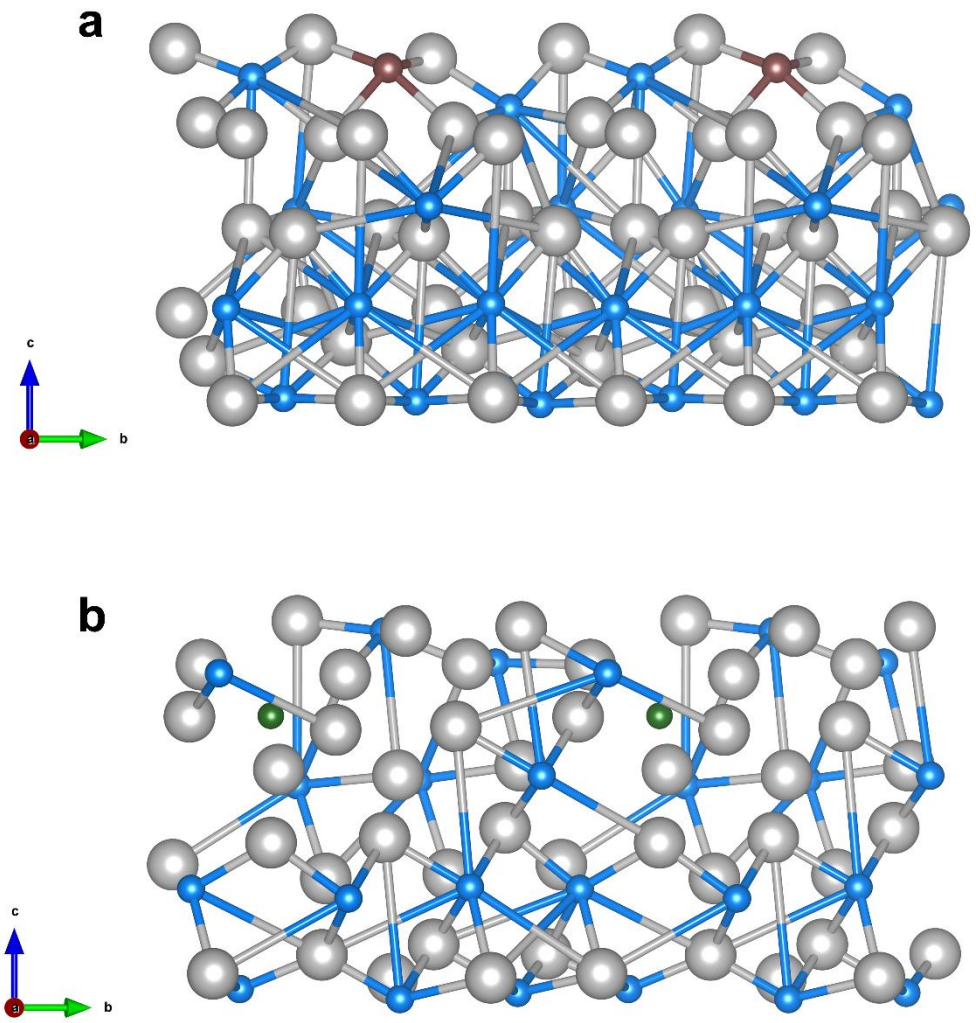

Fig. S17 Optimized geometric structures of (a) N-Mo_2C and (b) B-Mo_2C.

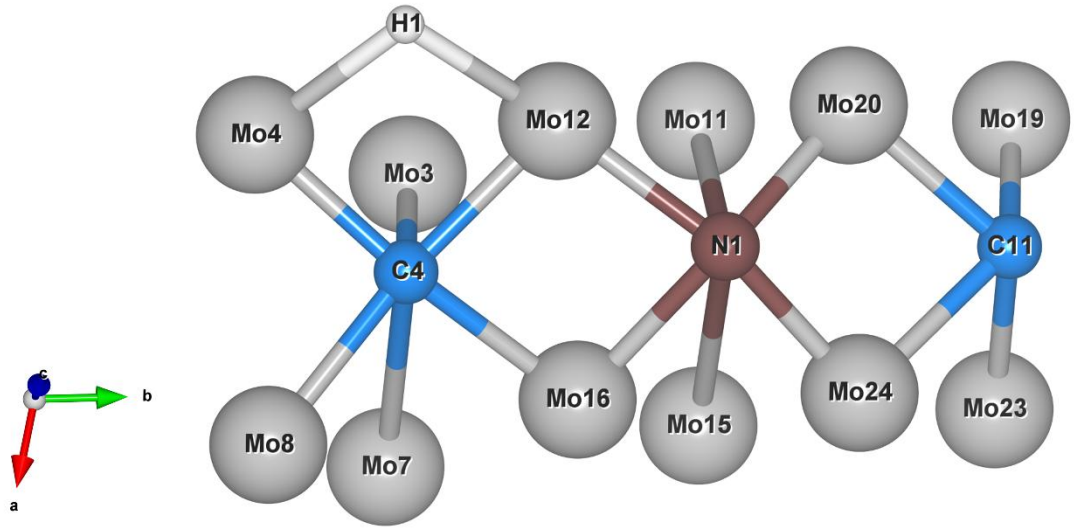

Figure S18 H^* adsorption of N-Mo_2C.

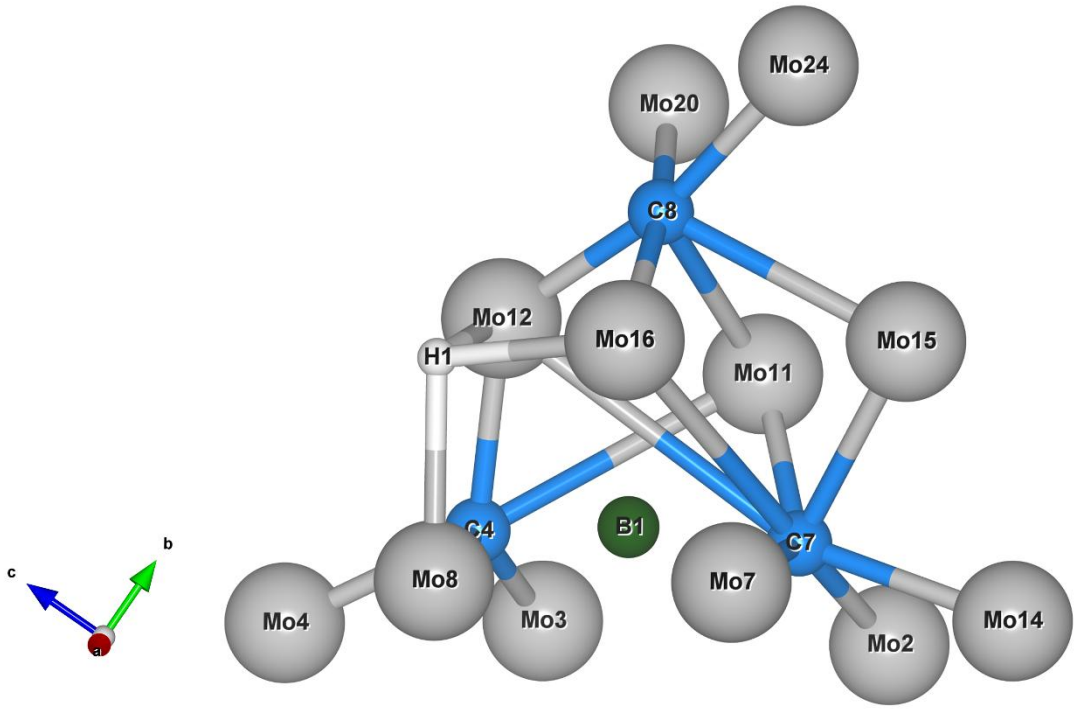

Fig. S19 H^* adsorption of B-Mo_2C.

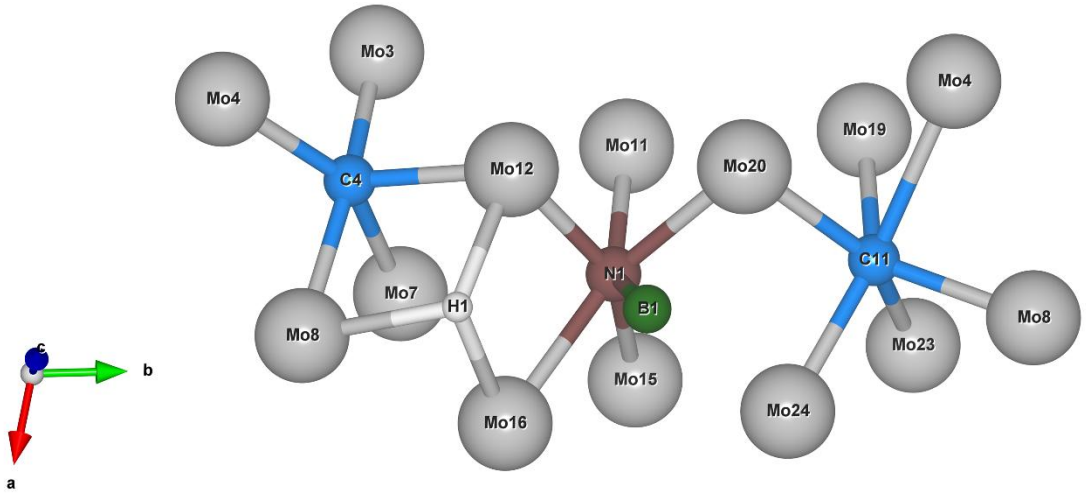

Fig. S20 H^* adsorption of B, N-Mo_2C.

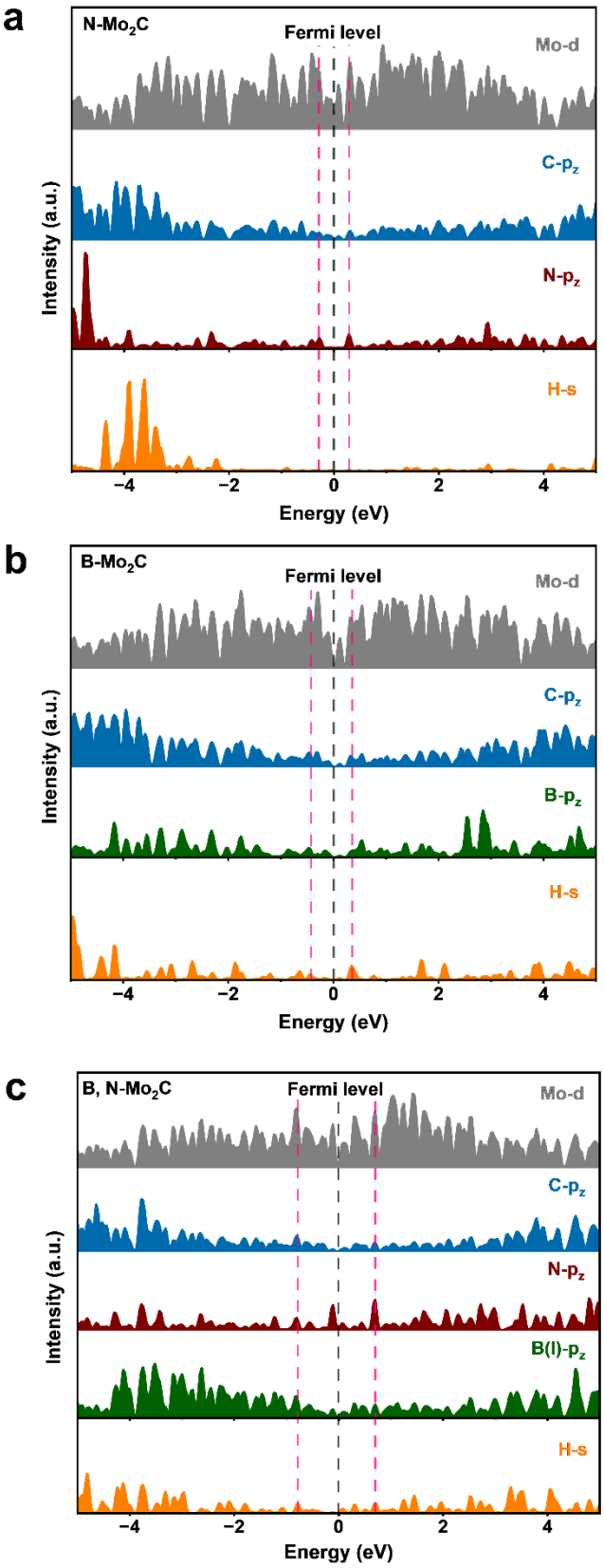

Fig. S21 PDOS of Mo, C, B, N and H atoms in the (a) N-Mo_2C, (b) B-Mo_2C, and (c) B, N-Mo_2C structure after adsorption.

Table S1 Comparison of time and drug costs of B, N-Mo_2C with other reported Boron and Nitrogen co-doped Mo_2C-based electrocatalysts.

Catalysts	Time	Drug costs(￥)	Reference
B, N-Mo_2C	**1 h**	**0.231**	**This work**
Mo_2C@BCN	7.5 h	2876.3184	1
B, N-Mo_2C/NPNC	5.8 h	2.152	2

Table S2 Comparison of productivity of B, N-Mo_2C produced through the different equipment and different time. (Product yield was obtained by calculating the mass ratio of the obtained products to the reactants.)

Equipment	Time	Quality before reaction	Quality after reaction	Product yield
MPCVD	**1 h**	**0.2 g**	**0.0636 g**	**31.8 %**
CVD	1.5 h	0.2 g	0.0649 g	32.5 %
CVD	2.25 h	0.2 g	0.0616 g	30.8 %
CVD	**3 h**	**0.2 g**	**0.0572 g**	**28.6 %**

Table S3 Mass percentage of elements tested by energy dispersive spectrometer (EDS).

	Mo	C	B	N
Mo_2C	29.48%	70.52%		
N-Mo_2C	49.55%	47.83%		2.62%
B-Mo_2C	18.48%	75.80%	5.72%	
B, N-Mo_2C	46.37%	44.35%	6.82%	2.46%

Table S4 EIS parameters of different catalysts for HER.

		Mo_2C	N-Mo_2C	B-Mo_2C	B, N-Mo_2C	CVD-B, N-Mo_2C-3h
pH=14	$R_s(\Omega)$	2.88	3.14	2.55	3.11	2.82
	$R_{ct}(\Omega)$	18.02	5.17	3.00	1.45	3.22
pH=0	$R_s(\Omega)$	2.43	2.55	2.70	2.64	2.98
	$R_{ct}(\Omega)$	403.30	5.52	16.77	3.57	4.70
pH=7	$R_s(\Omega)$	5.84	6.26	5.91	5.53	6.14
	$R_{ct}(\Omega)$	131.50	63.44	73.14	13.13	26.97

Table S5 Bader charge analysis before and after H^* adsorption in N-Mo_2C.

Atomic number	Bader charge before adsorption	Bader charge after adsorption	Net charge
Mo_3	13.516	13.473	-0.043
Mo_4	13.484	13.330	-0.155
Mo_7	13.612	13.588	-0.024
Mo_8	13.446	13.437	-0.010
Mo_{11}	13.510	13.515	0.005
Mo_{12}	13.414	13.244	-0.170
Mo_{15}	13.538	13.544	0.006
Mo_{16}	13.461	13.439	-0.022
Mo_{19}	13.406	13.423	0.017
Mo_{20}	13.584	13.486	-0.098
Mo_{23}	13.410	13.399	-0.010
Mo_{24}	13.422	13.434	0.011
C_4	5.232	5.206	-0.027
C_{11}	5.291	5.324	0.033
N	6.247	6.284	0.037
H	1	1.472	0.472

Table S6 Bader charges analysis before and after H^* adsorption in B-Mo_2C.

Atomic number	Bader charge before adsorption	Bader charge after adsorption	Net charge
Mo_2	13.269	13.274	0.004
Mo_3	13.575	13.597	0.023
Mo_4	13.594	13.572	-0.021
Mo_7	13.770	13.716	-0.054
Mo_8	13.491	13.407	-0.084
Mo_{11}	13.402	13.383	-0.020
Mo_{12}	13.440	13.269	-0.171
Mo_{14}	13.465	13.473	0.008
Mo_{15}	13.501	13.474	-0.027
Mo_{16}	13.594	13.494	-0.100
Mo_{20}	13.521	13.602	0.082
Mo_{24}	13.396	13.425	0.029
C_4	5.450	5.499	0.049
C_7	5.543	5.600	0.057
C_8	5.220	5.238	0.018
B	2.419	2.207	-0.212
H	1	1.438	0.438

Table S7 Bader charges analysis before and after H^* adsorption in B, N-Mo_2C.

Atomic number	Bader charge before adsorption	Bader charge after adsorption	Net charge
Mo_3	13.400	13.381	-0.019
Mo_4	13.741	13.724	-0.017
Mo_7	13.153	13.133	-0.020
Mo_8	13.548	13.476	-0.072
Mo_{11}	13.241	13.228	-0.013
Mo_{12}	13.329	13.244	-0.086
Mo_{15}	13.232	13.231	-0.001
Mo_{16}	13.582	13.502	-0.080
Mo_{19}	13.170	13.141	-0.028
Mo_{20}	13.426	13.431	0.005
Mo_{23}	13.269	13.290	0.020
Mo_{24}	13.378	13.412	0.035
C_4	5.327	5.285	-0.042
C_{11}	5.256	5.257	0.001
N	6.513	6.514	0.001
B_1	3.137	3.075	-0.062
H	1	1.379	0.379

References

1. S. Wu, M. Chen, W. Wang, J. Zhou, X. Tang, D. Zhou and C. Liu, *Carbon*, 2021, **171**, 385-394.
2. C. He, Y. Cai, Z. Ma, X. Zhong, H. Wang, Q. Li and Y. Huang, *ACS Appl. Nano Mater.*, 2021, **4**, 8897-8905.