

Supporting Information

Enhancing electrocatalytic activity for hydrogen evolution by strongly coupled molybdenum nitride@nitrogen-doped carbon porous nano octahedrons

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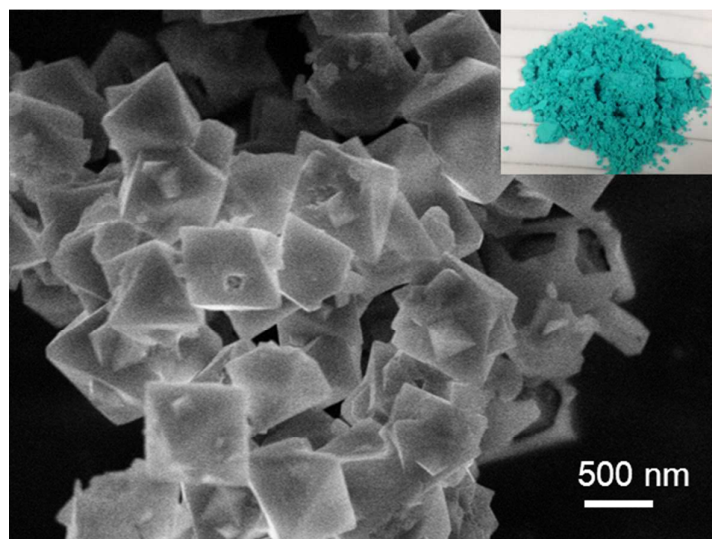


Figure S1. FESEM image (inset: digital photo) of the as-prepared NENU-5 nano-octahedrons.

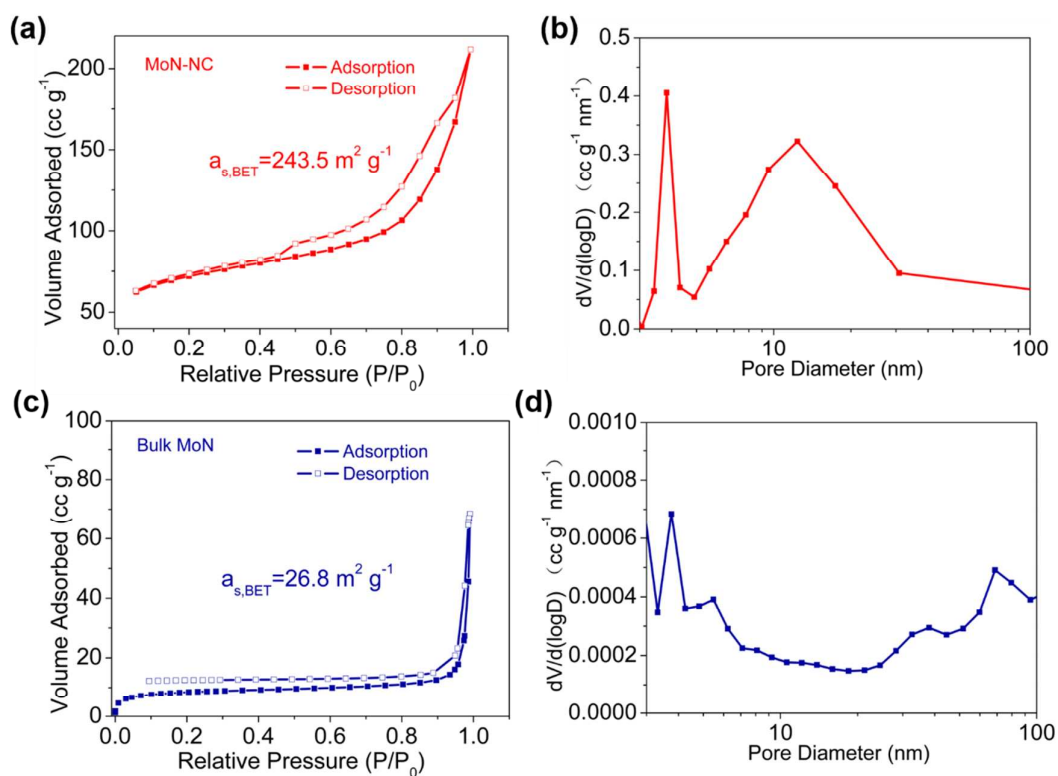


Figure S2. The N₂ sorption isotherms and the corresponding pore diameter distributions of (a, b) MoN-NC nano-octahedrons and (c, d) bulk MoN.

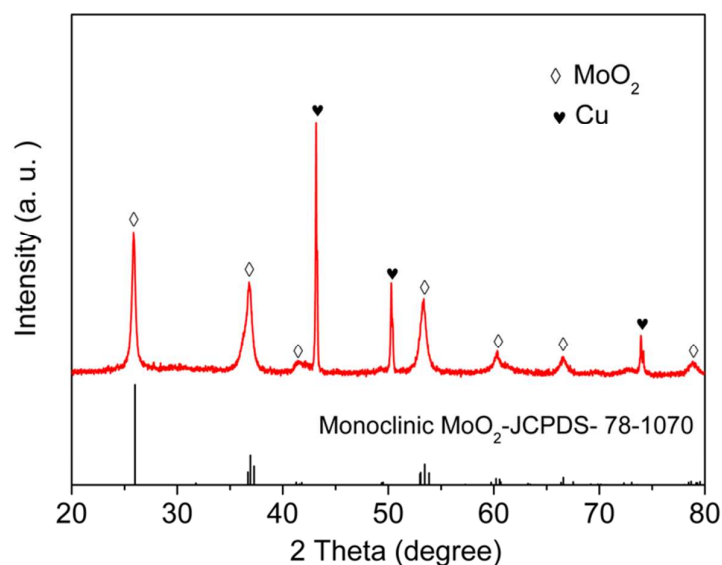


Figure S3. XRD pattern of the composite after the first thermal treatment of NENU-5.

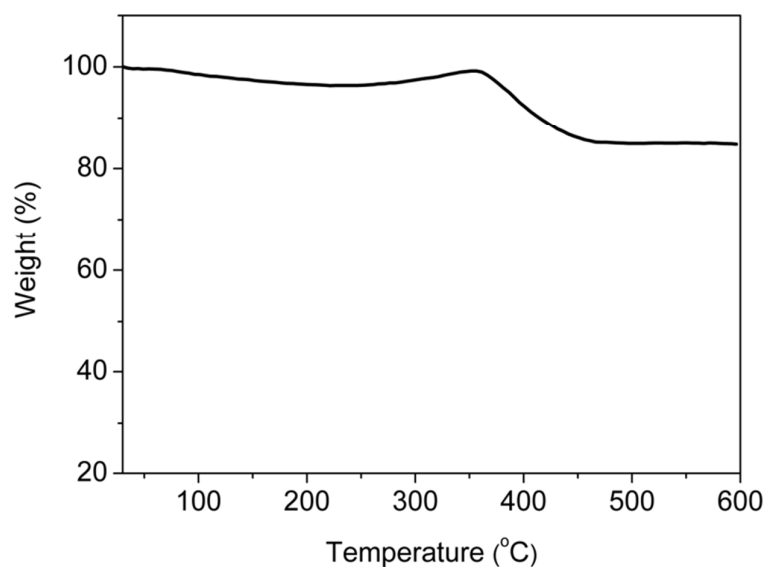


Figure S4. TGA curve of the MoN-NC nano-octahedrons.

The thermogravimetric (TG) result of the MoN-NC nano-octahedrons is shown in Fig. S2. Clearly, the weight loss before 200 °C comes from absorbed moisture (3.4 wt%). The weight change between 200 and 500 °C is due to both the gradual oxidation of MoN to MoO₃, and the combustion of carbon. Over 500 °C, the weight remains constant. Assuming that the sample converts to only MoO₃ after heating to 600 °C with remaining weight of 84.7 wt%, the carbon content is calculate to be 32.0 wt%.

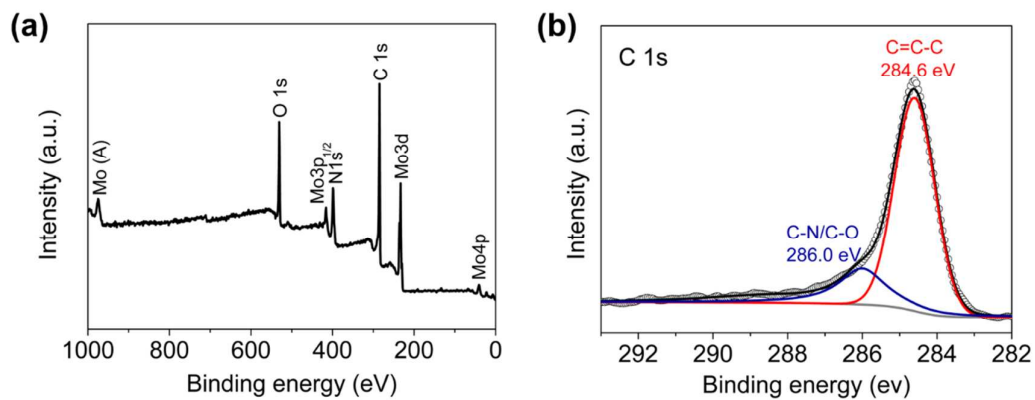


Figure S5. (a) Survey XPS spectrum of the MoN-NC nano-octahedrons. (b) high-resolution XPS spectrum of C 1s.

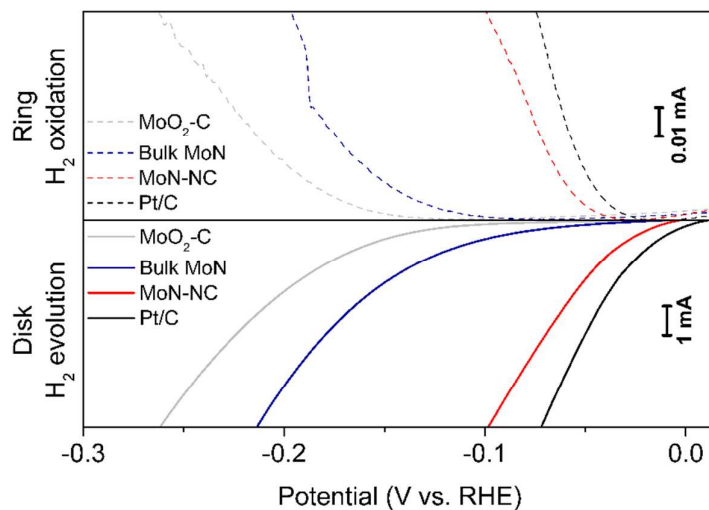


Figure S6. RRDE measurements of H₂ evolution on different catalyst-modified electrodes. The potential of the Pt-ring electrode was kept at 0.7 V for oxidation of the H₂ produced from the catalysts on the disk electrode.

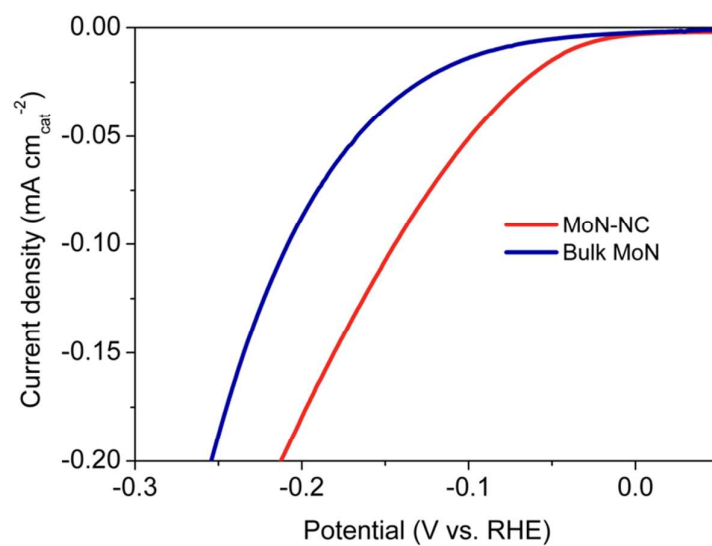


Figure S7. Polarization curves (normalized by the specific surface area) for the MoN-NC and the bulk MoN catalysts recorded in 0.5 M H_2SO_4 .

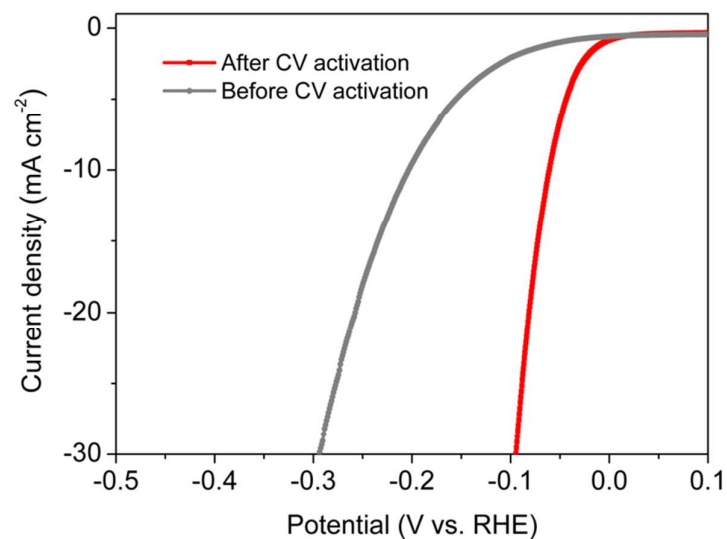


Figure S8. Polarization curves of the MoN-NC nano-octahedrons catalyst before and after CV activation.

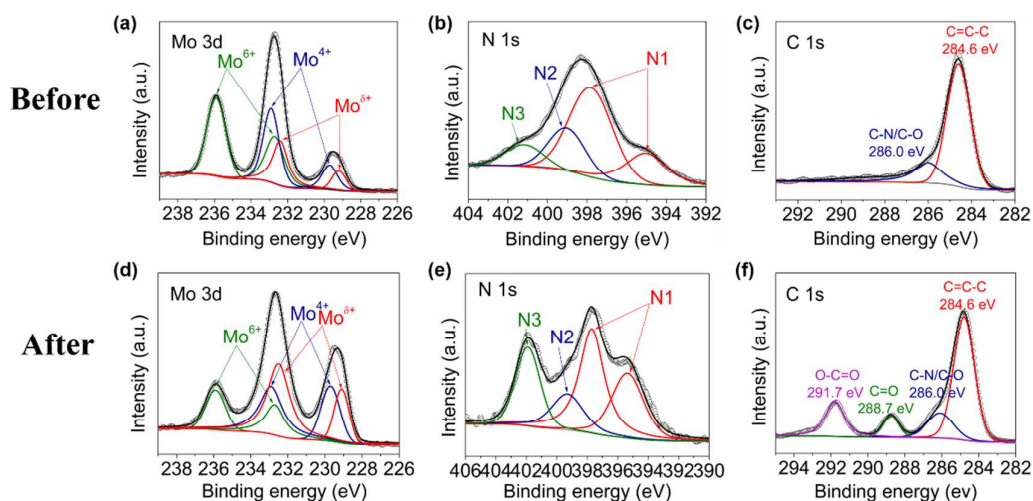


Figure S9. XPS spectra of the MoN-NC nano-octahedrons (a, b, c) before and (d, e, f) after the activation process.

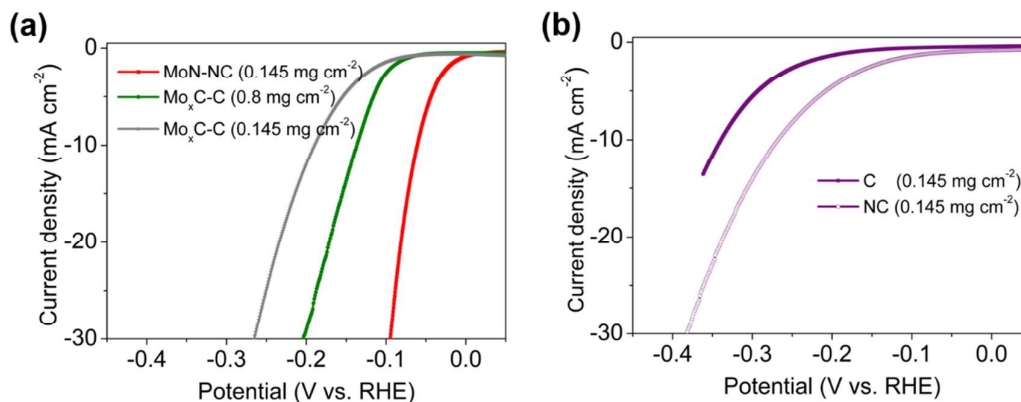


Figure S10. Polarization curves (iR-compensated) in 0.5 M H_2SO_4 of the (a) MoN-NC nano-octahedrons (0.145 mg cm^{-2}) and $\text{MoC}_x\text{-C}$ nano-octahedrons (0.145 mg cm^{-2} , 0.8 mg cm^{-2}); (b) the blank carbon before and after nitrogen doping (0.145 mg cm^{-2}).

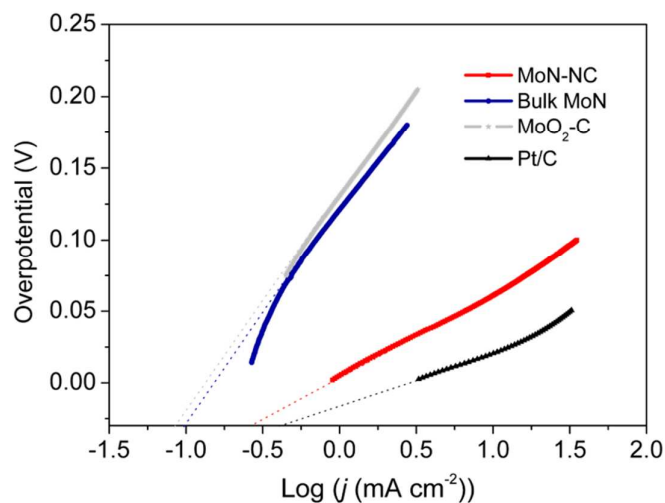


Figure S11. Calculated exchange current densities of the four samples by applying extrapolation method to the Tafel plots.

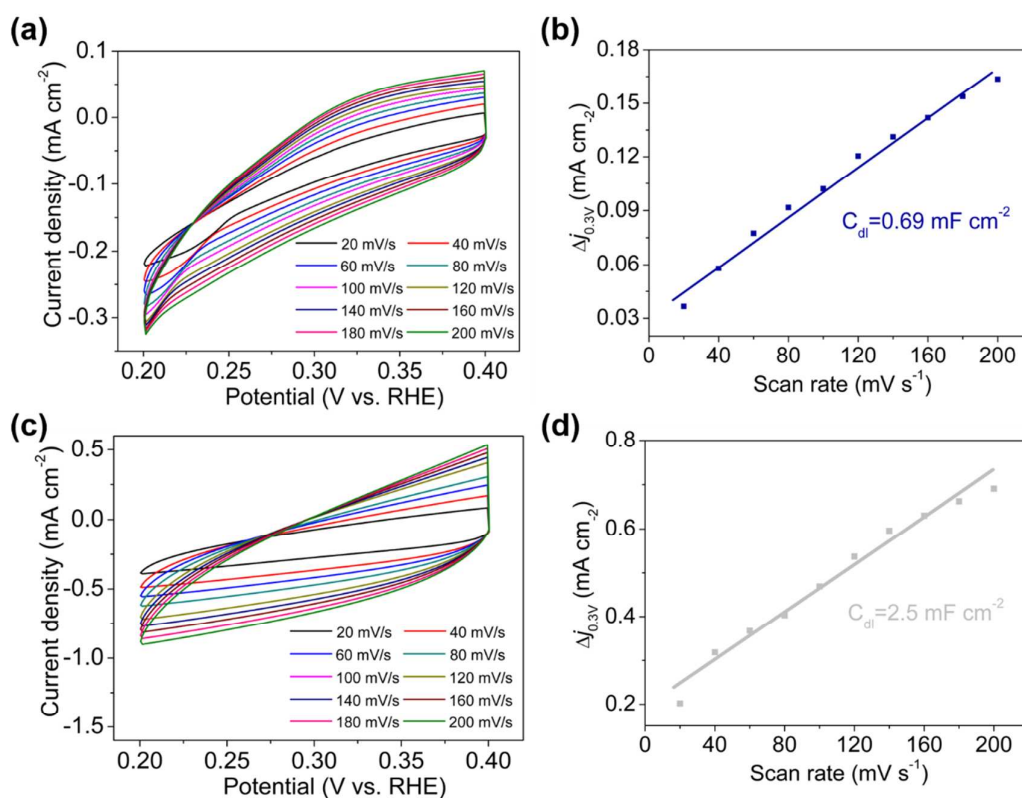


Figure S12. Electrochemical CV scans recorded for (a) bulk MoN and (c) intermediate MoO₂-C catalysts at different potential scanning rates from 20 to 200 mV s⁻¹ in the potential range of 0.2-0.4 V. Linear fitting of the capacitive currents versus CV scan rates for (b) bulk MoN and (d) intermediate MoO₂-C.

Table S1 Comparison of electrocatalytic HER activity in acidic conditions (0.5 M H₂SO₄) for MoN-NC nano-octahedrons with some of the most active non-precious HER catalysts ever reported.

Catalyst	Loading (mg cm ⁻²)	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	j_0 (mA cm ⁻²)	Referenc e
MoN-NC nanooctahedrons	0.145	62	54	0.778	This work
Mo _x C nanooctahedrons	0.8	142	53	0.023	[1]
Mo _x C-Ni@NCV	1.1	68	45	0.95	[2]
CoPS NP S	0.36	48	56	0.984	[3]
SCEIN/SWNT	0.18	77	40	0.19	[4]
Mo ₂ C/CNT-graphene	0.65	130	58	0.062	[5]
MoP S	0.17	64	50	0.2	[6]
P-WN/rGO	0.337	85	54	0.35	[7]
CoP nanoparticles	2	75	50	0.14	[8]
MoDCA-5	0.25	78	41	0.178	[9]
MoCN NPs	0.4	140	46	---	[10]
Metallic WO ₂ -carbon	0.35	58	46	0.64	[11]
β -Mo ₂ C/rGO	0.47	109	66.4	0.037	[12]
MoP	0.39	150	54	0.086	[13]
WS ₂ nanosheets	1	142	70	---	[14]
Co ₂ P nanorods	1.02	134	51.7	0.025	[15]
Ni ₂ P nanoparticles	1	100	46	0.033	[16]
CoSe ₂ on carbon fiber	2.2	137	40	0.0049	[17]

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