Supplementary Materials

A Highly Active Porous Mo_2C-Mo_2N Heterostructure on Carbon Nanowalls/Diamond for a High-current Hydrogen Evolution Reaction

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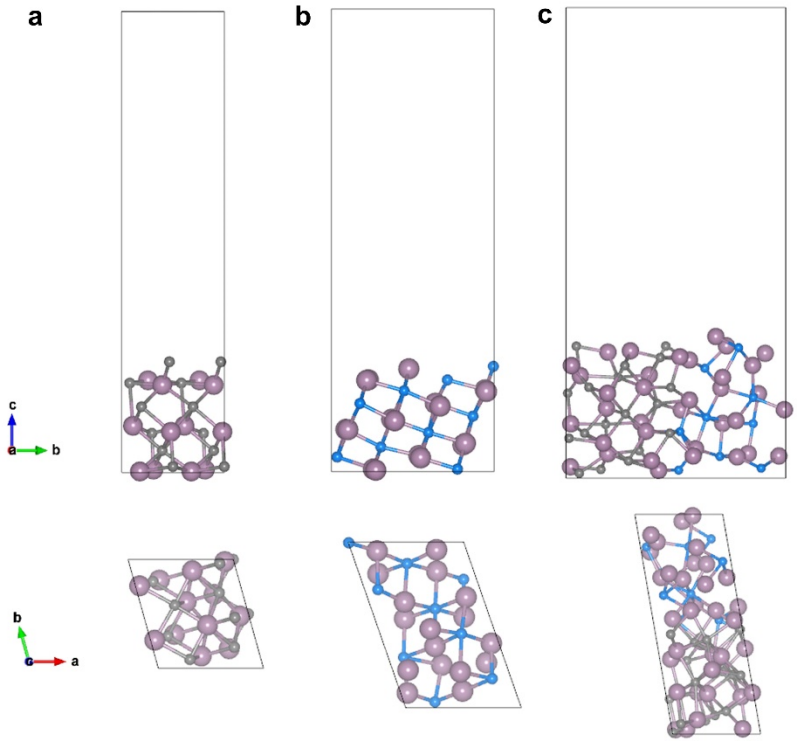

Figure S1. Side view (upper panel) and top view (lower panel) for the super cells of (a) Mo_2C (101), (b) Mo_2N (111), and (c) Mo_2C (101)-Mo_2N (111) heterostructure.

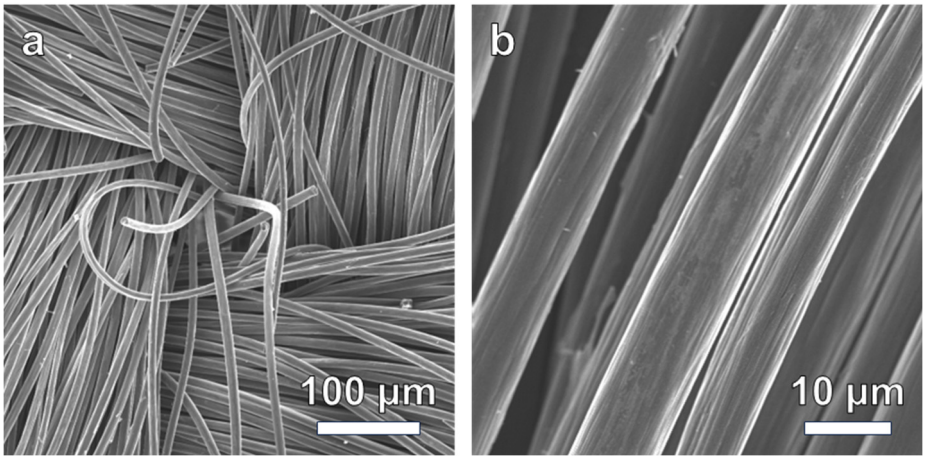

Figure S2. (a) Low-magnification and (b) high-magnification SEM images of CC.

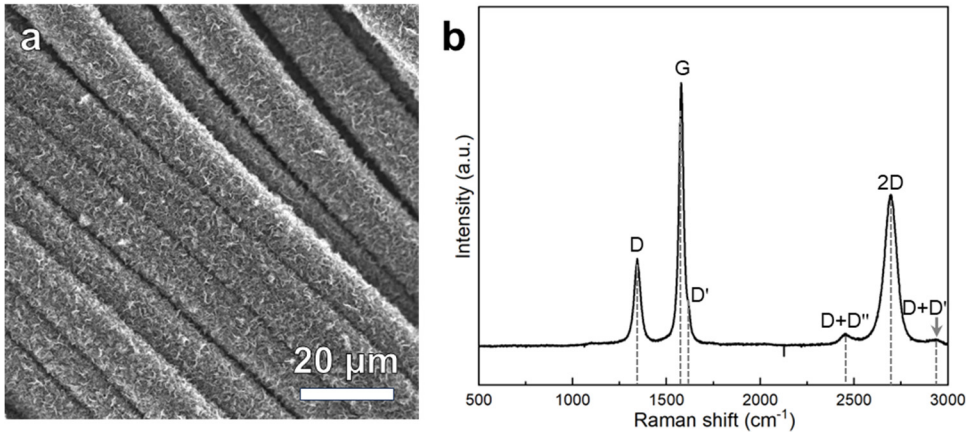

Figure S3. (a) SEM image and (b) Raman spectrum of the pristine CNW/D-coated CC.

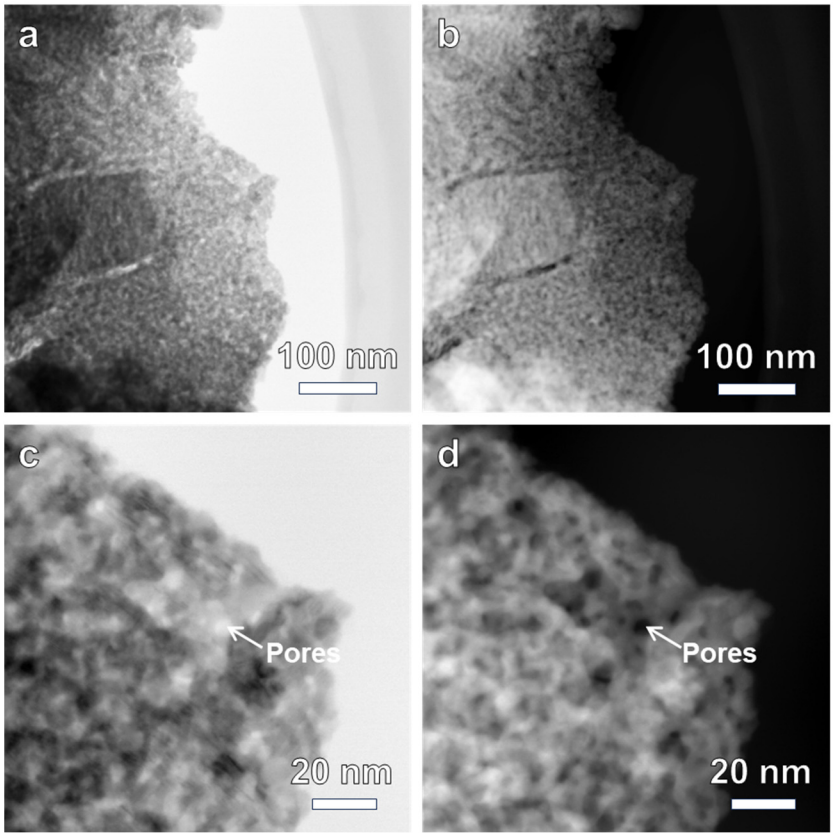

Figure S4. (a,c) Bright-field and (b,d) corresponding HAADF TEM images of Mo_2C-Mo_2N@CNWs/D.

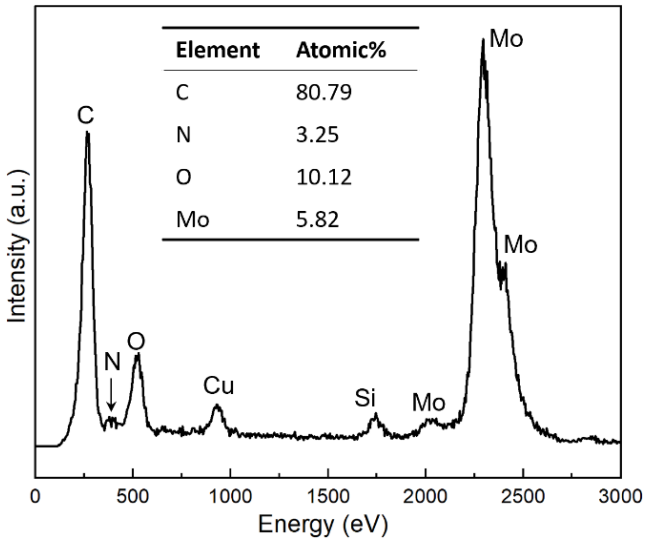

Figure S5. EDS spectrum of Mo_2C-Mo_2N@CNWs/D.

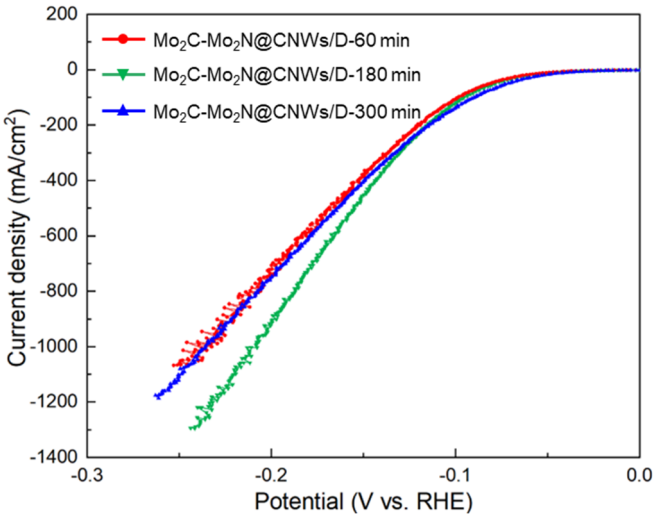

Figure S6. Polarization curves of Mo_2C-Mo_2N@CNWs/D prepared at 700 ºC with the annealing time of 60, 180, and 300 min.

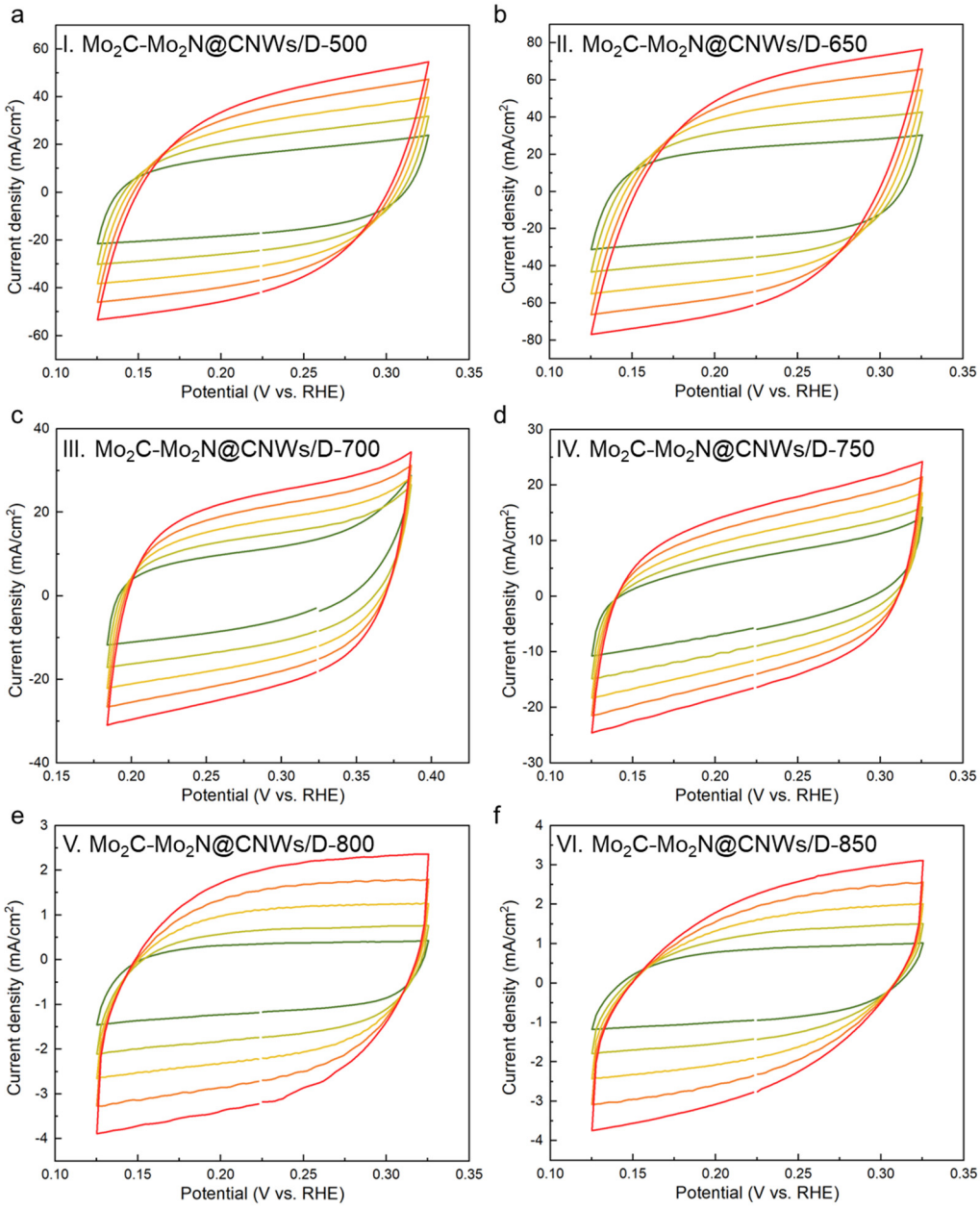

Figure S7. CV curves of (a) Mo_2C-Mo_2N@CNWs/D-500, (b) Mo_2C-Mo_2N@CNWs/D-650, (c) Mo_2C-Mo_2N@CNWs/D-700, (d) Mo_2C-Mo_2N@CNWs/D-750, (e) Mo_2C-Mo_2N@CNWs/D-800, and (f) Mo_2C-Mo_2N@CNWs/D-850 at various scan rates ranging from 0.04 to 0.12 V/s.

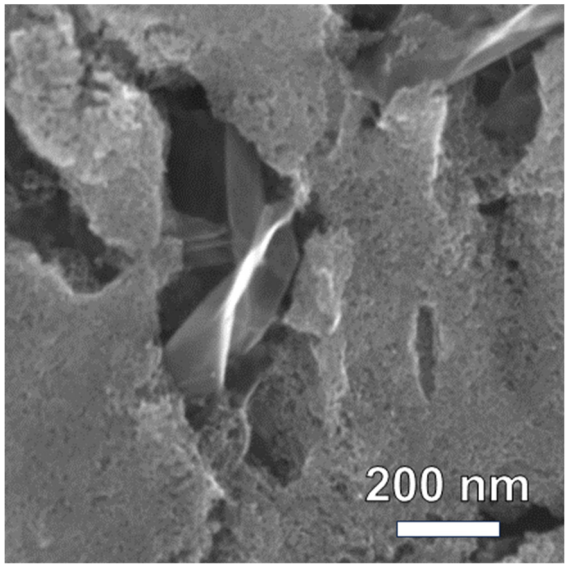

Figure S8. SEM image of Mo_2C-Mo_2N@CNWs/D-650 after a 24 h HER test at a high current density of 500 mA/cm^2.

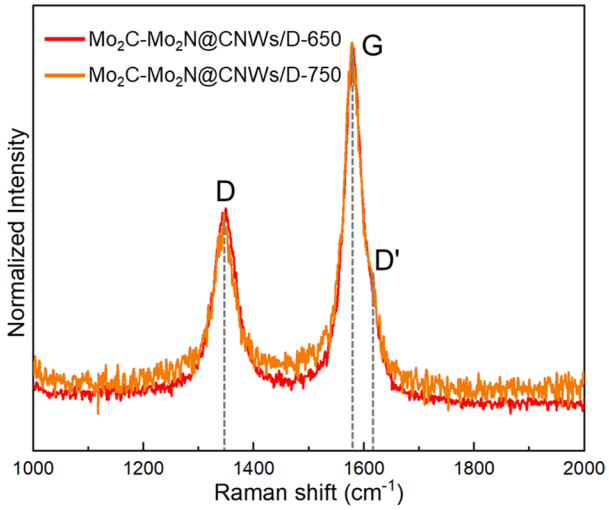

Figure S9. Raman spectra of Mo_2C-Mo_2N@CNWs/D prepared at 650 and 750 ºC.

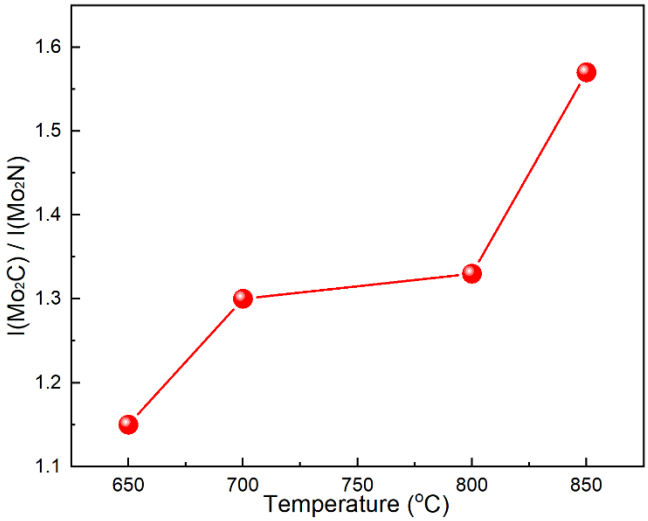

Figure S10. The intensity ratio of the Mo_2C (101) peak to the Mo_2N (111) peak in XRD patterns as a function of the temperature.

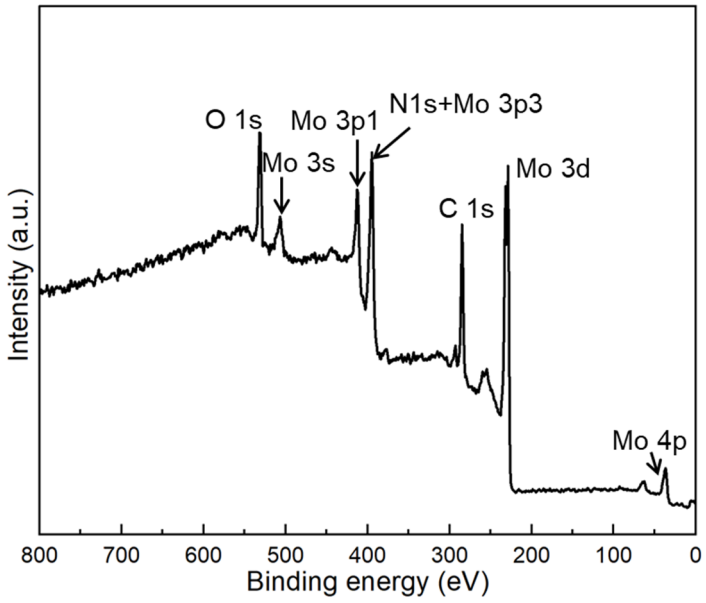

Figure S11. XPS survey spectrum of Mo_2C-Mo_2N@CNWs/D-650.

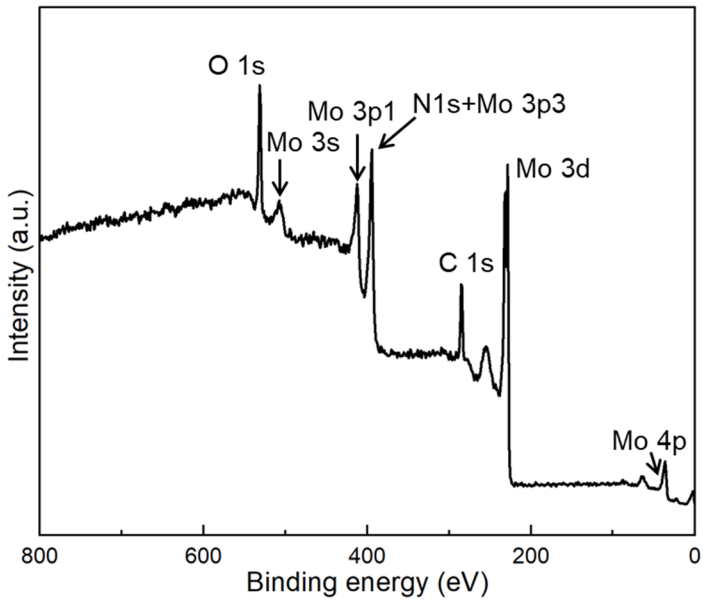

Figure S12. XPS survey spectrum of Mo_2C-Mo_2N@CNWs/D-650 after HER test.

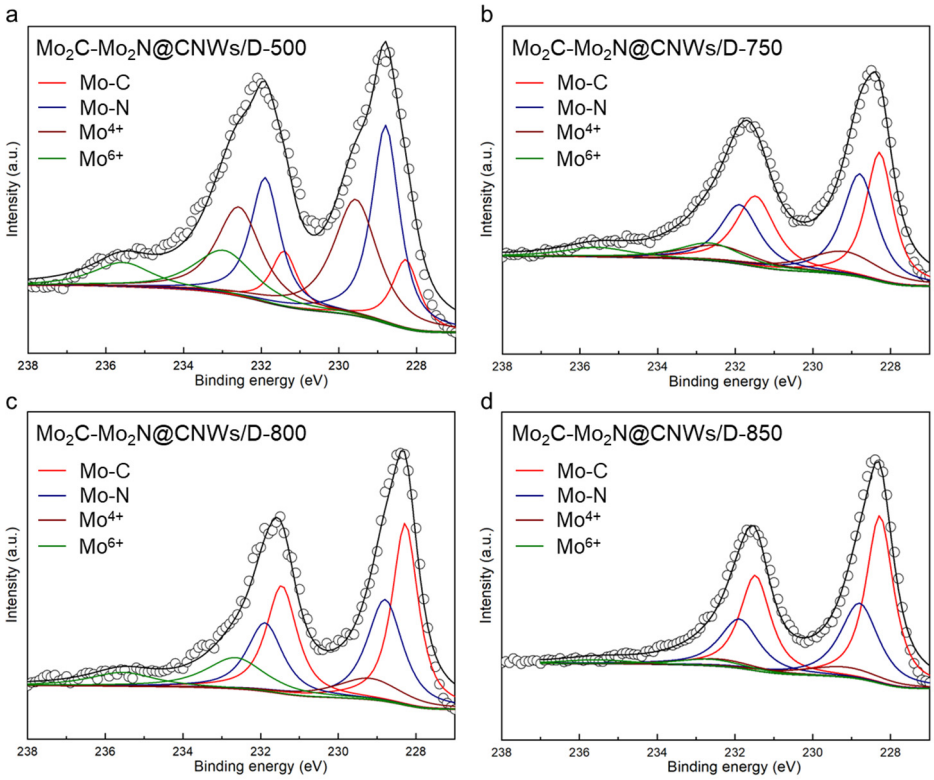

Figure S13. High-resolution Mo 3d XPS spectra of (a) Mo_2C-Mo_2N@CNWs/D-500, (b) Mo_2C-Mo_2N@CNWs/D-750, (c) Mo_2C-Mo_2N@CNWs/D-800, and (d) Mo_2C-

Mo_2N@CNWs/D-850.

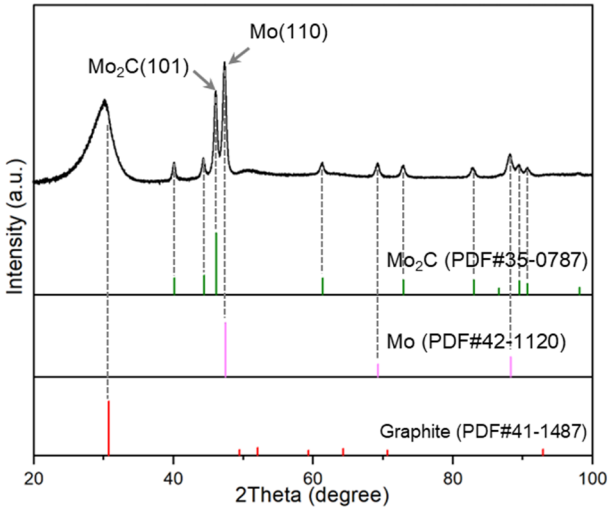

Figure S14. XRD pattern of Mo_2C@CNWs/D-650 prepared on a CC substrate.

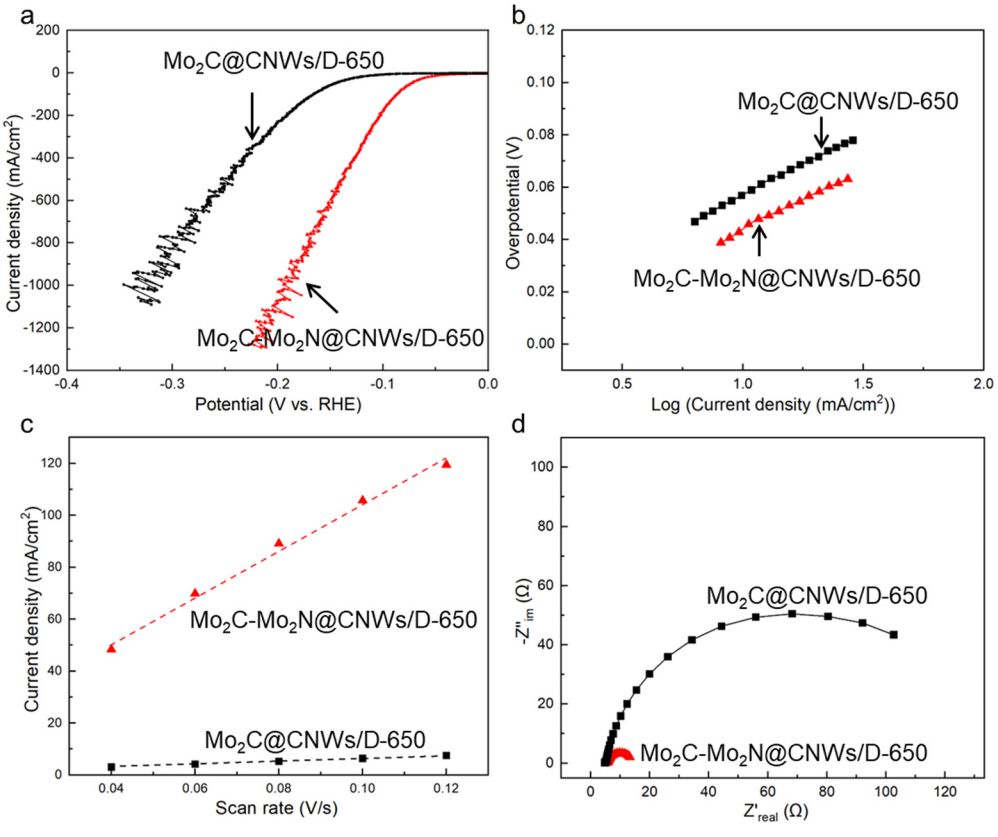

Figure S15. Electrocatalytic HER performance of Mo_2C@CNWs/D-650 in 1 M KOH. (a) Polarization curves and corresponding (b) Tafel plots. (c) Capacitive current

variation as a function of scan rate from 0.04 to 0.12 V/s. (d) Nyquist plots. The curves of Mo_2C-Mo_2N@CNWs/D-650 are demonstrated as control.

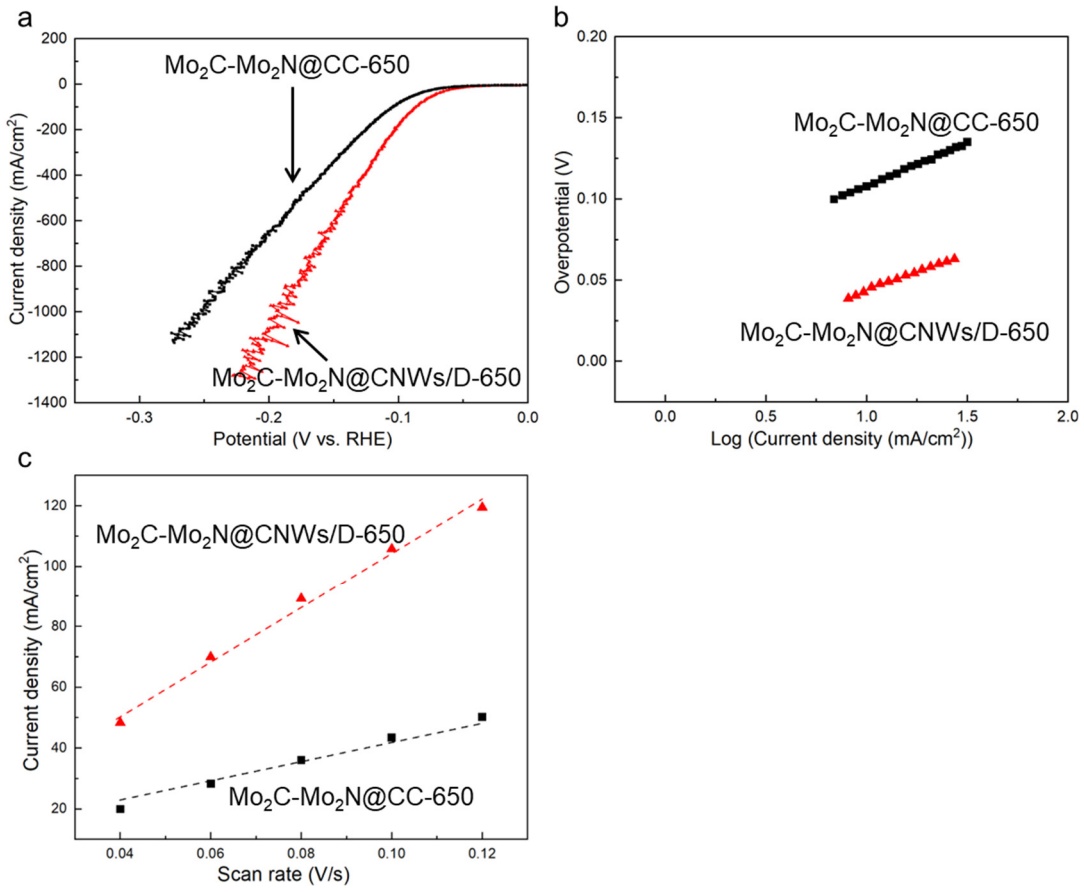

Figure S16. Electrocatalytic HER performance of Mo_2C-Mo_2N@CC-650 in 1 M KOH. (a) Polarization curves and corresponding (b) Tafel plots. (c) Capacitive current variation as a function of scan rate from 0.04 to 0.12 V/s. The curves of Mo_2C-Mo_2N@CNWs/D-650 are demonstrated as control.

Table S1. The adsorption energy change of H^* species (ΔE_{H*}) and the free energy change of adsorbed H^* species (ΔG_{H*}) on different sites of Mo_2C (101), Mo_2N (111), and Mo_2C (101)-Mo_2N (111) heterostructure.

Species	ΔE_{H*} **(eV)**	ΔG_{H*} **(eV)**
H^* on Mo site of Mo_2C	-0.4544	-0.3178
H^* on Mo site of Mo_2N	-0.9586	-0.5889
H^* on Mo site of Mo_2C-Mo_2N	-0.2915	-0.1673
H^* on N site of Mo_2C-Mo_2N	-0.1826	0.0913
H^* on C site of Mo_2C-Mo_2N	-0.9137	-0.6604

Table S2. Electrocatalytic HER characteristics of Mo_2C@CNWs/D-650 prepared without melamine, Mo_2C-Mo_2N@CC-650 prepared on CC, and Mo_2C-Mo_2N@CNWs/D-650.

Samples	η_{10} **(mV)**	η_{500} **(mV)**	η_{1000} **(mV)**	**Tafel slope (mV/dec)**	R_{ct} **(Ω)**	**Capacitance (mF/cm²)**
Mo_2C@CNWs/D-650	107.9	253.8	316.6	52.9	129.42	55
Mo_2C-Mo_2N@CC-650	56.9	176.3	251.7	47.3	13.94	379
Mo_2C-Mo_2N@CNWs/D-650	42.8	137.8	194.4	45.6	8.59	891