

Supporting Information

Hollow Sandwiched Structure of Ni-Modified MoS₂ Wrapped into Symmetrical N-Doped Carbon toward a Superior Hydrogen Evolution Electrocatalyst

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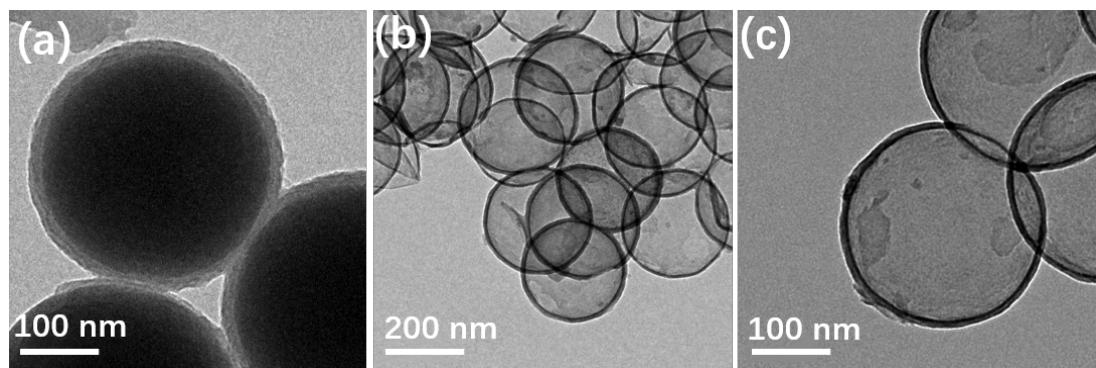


Figure S1 TEM images of (a) $\text{SiO}_2@\text{NC}$ NSs and (b, c) NC HNSs.

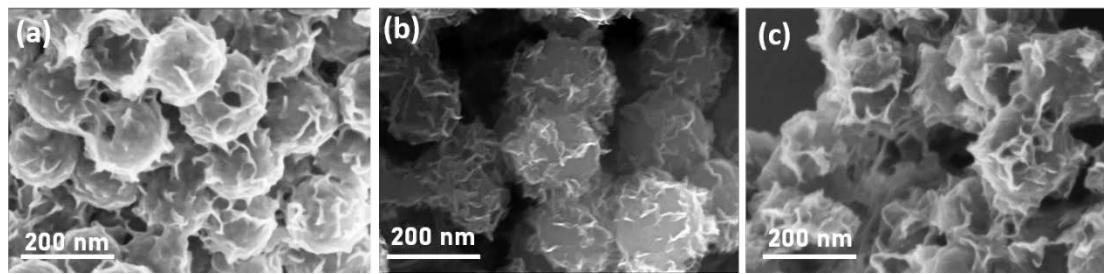


Figure S2 SEM images of NC@MoS₂/Ni-NC HNSs prepared by (a) 8 mg, (b) 15 mg and (c) 25 mg nickel acetate.

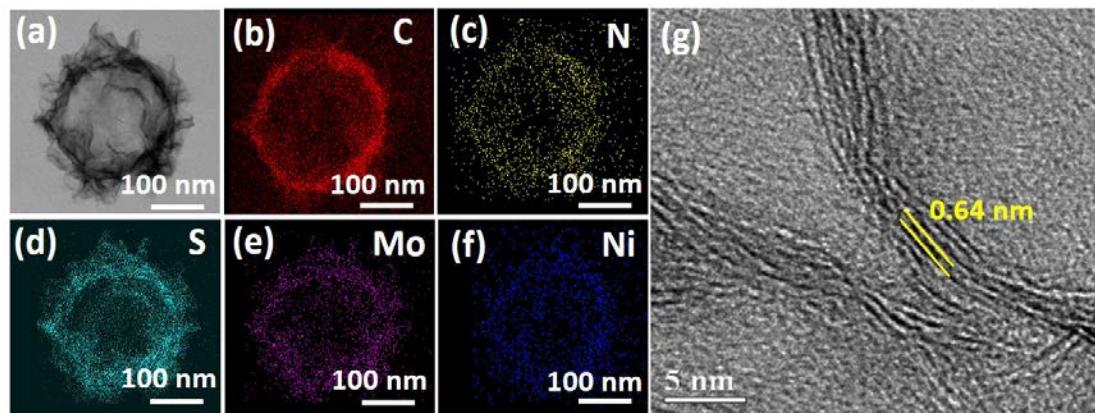


Figure S3. (a-f) EDS mapping of the elemental distributions and (g) HRTEM images of NC@MoS₂/Ni HNSs.

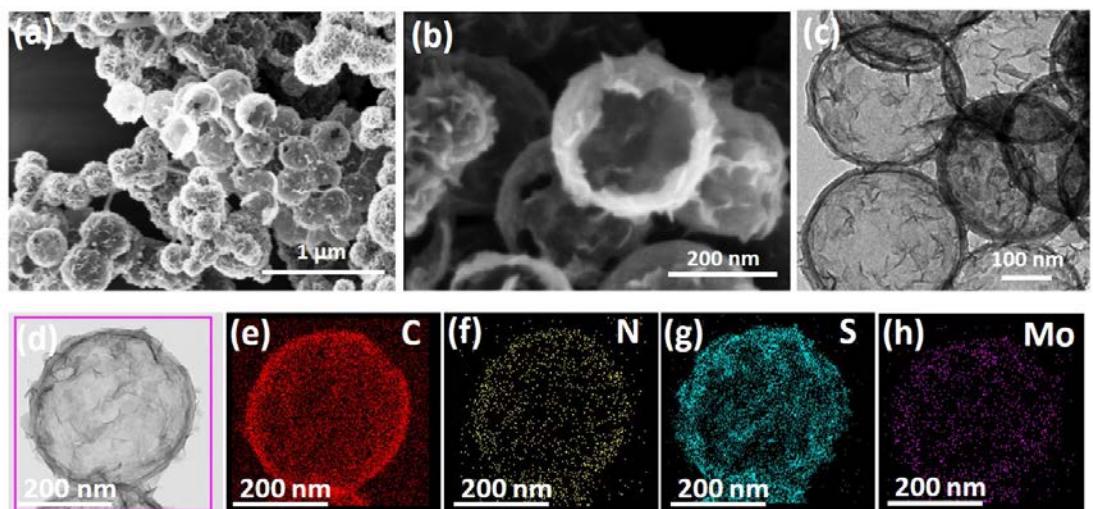


Figure S4. Microstructure of NC@MoS₂ HNSs: (a, b) SEM, (c) TEM image, (d-h) EDS mapping of the elemental distributions.

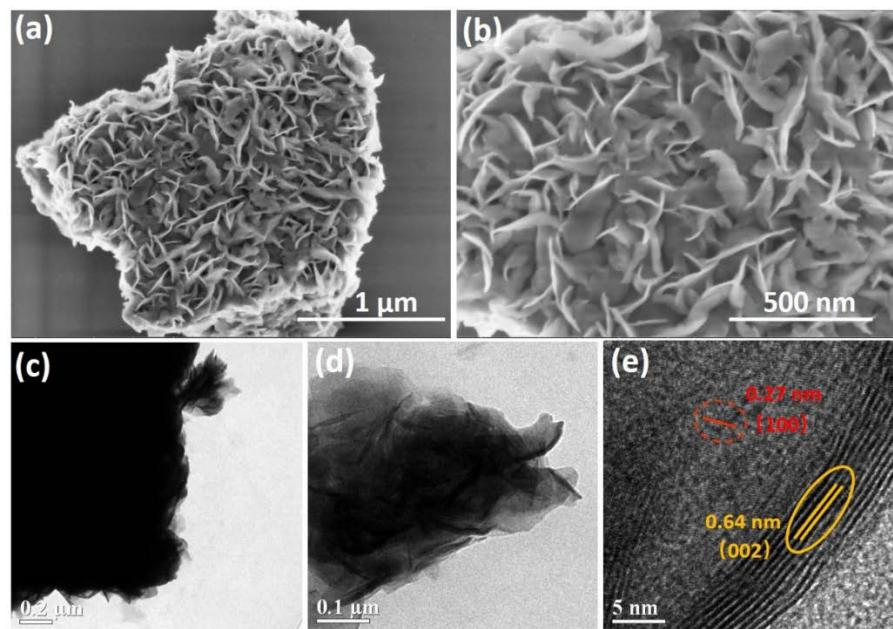


Figure S5. (a, b) SEM, (c, d) TEM and (e) HRTEM images of bulk MoS₂.

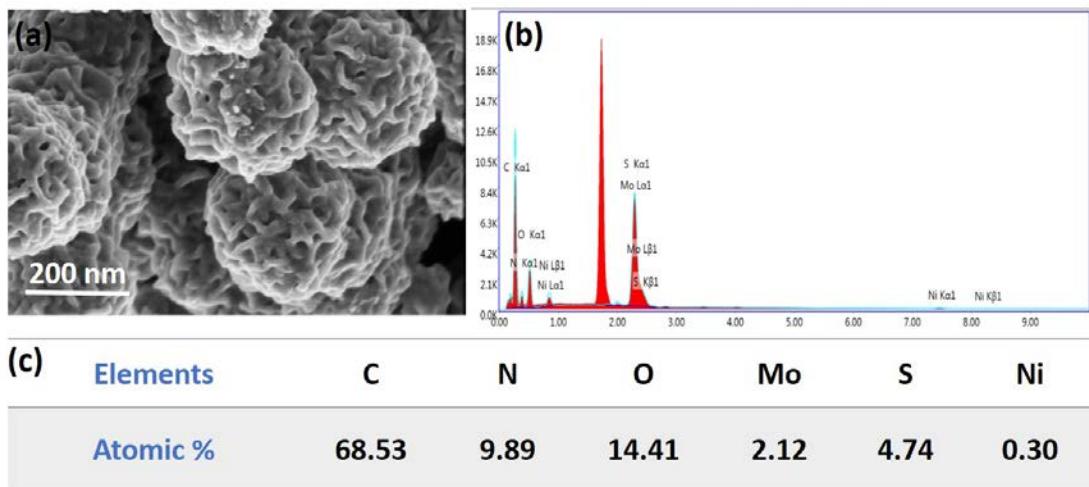


Figure S6. (a) SEM, (b) EDS spectrum and (c) Element content distribution of NC@MoS₂/Ni-NC HNSs.

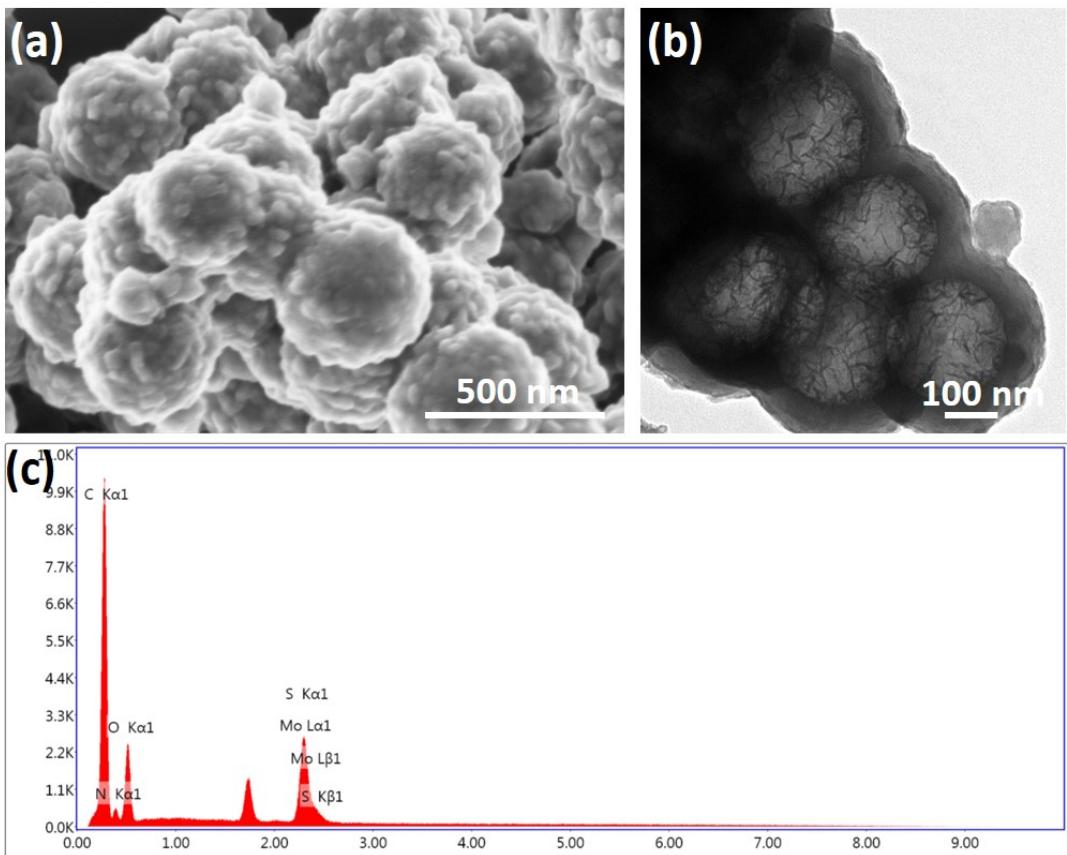


Figure S7. (a) SEM, (b) TEM image and (c) EDS spectrum of NC@MoS₂-NC HNSs.

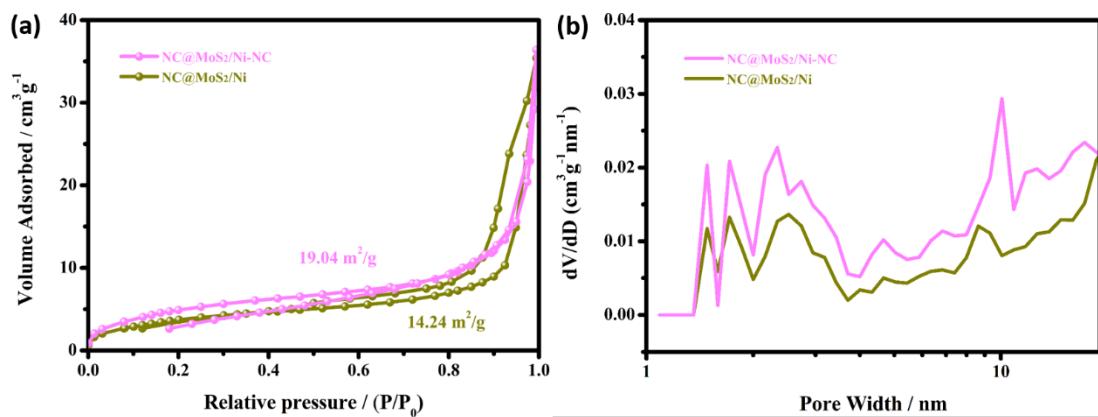


Figure S8. (a) N₂ adsorption-desorption isotherm, and (b) Pore-size distribution of NC@MoS₂/Ni-NC HNSs and NC@MoS₂/Ni HNSs.

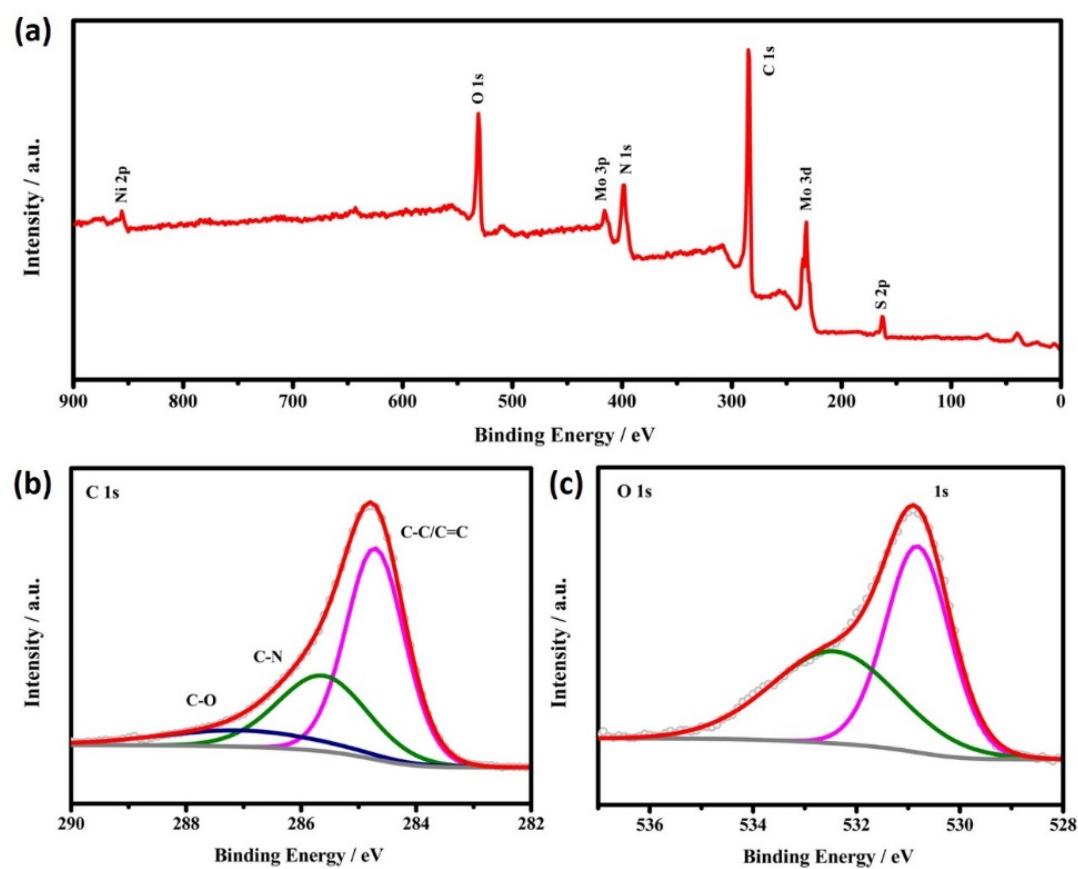


Figure S9. (a) Survey XPS spectrum, (b) C 1s, (c) O 1s of NC@MoS₂/Ni-NC HNSs.

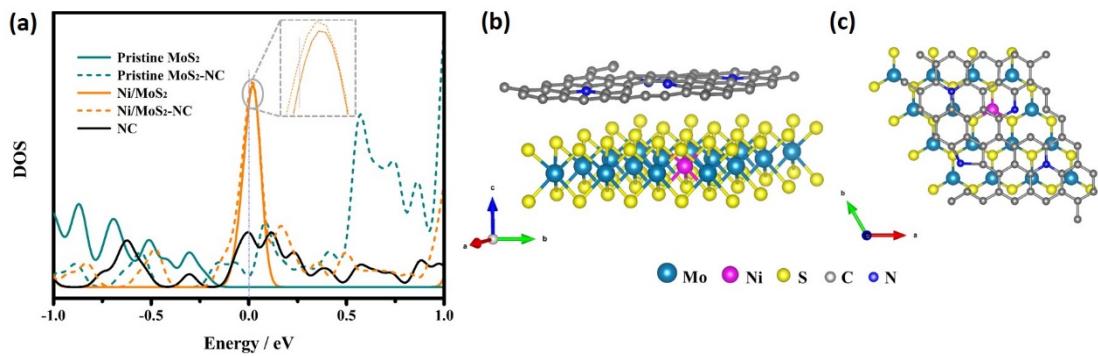


Figure S10. (a) Density of states (DOS) plots of pristine MoS₂, Ni/MoS₂, NC, MoS₂-NC and Ni/MoS₂-NC, (b, c) the models structure of Ni/MoS₂-NC system.

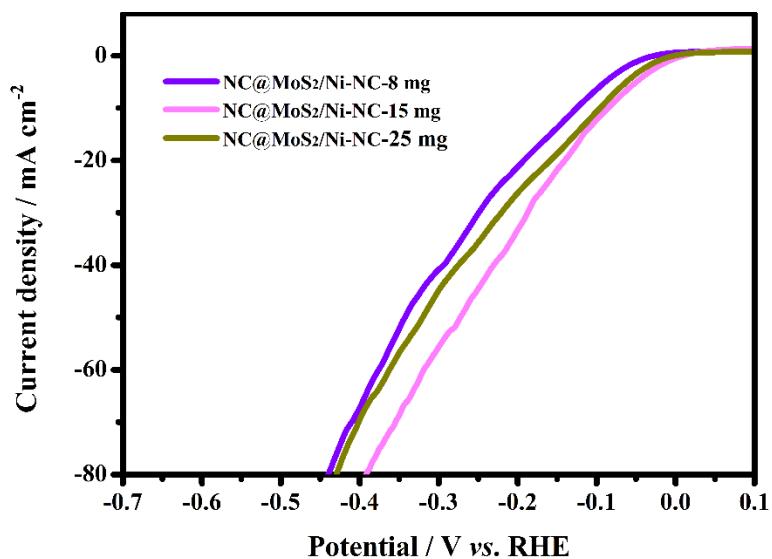


Figure S11 Polarization curves of NC@MoS₂/Ni-NC HNSs prepared by 8 mg, 15 mg and 25 mg nickel acetate.

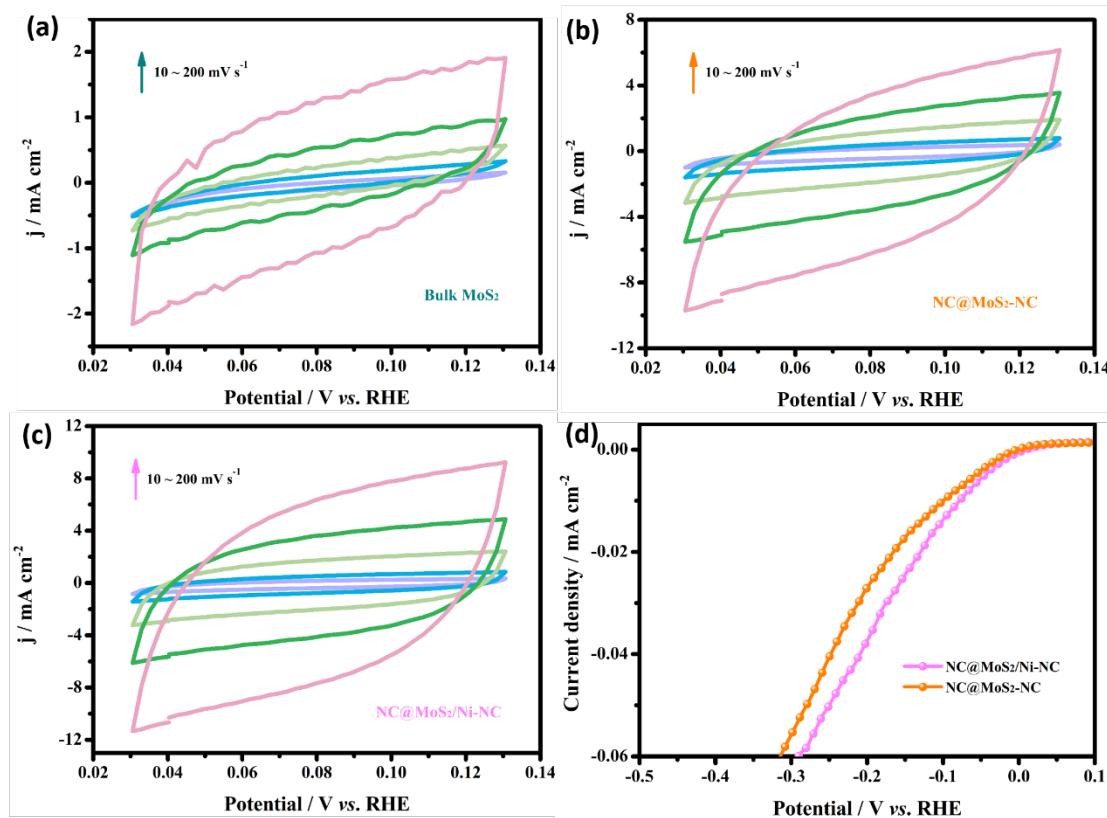


Figure S12. The electrochemical double-layer capacitance (C_{dl}) measurements with different scanning rates of 10, 20, 50, 100 and 200 mV s^{-1} for (a) Bulk MoS₂, (b) NC@MoS₂-NC HNSs, (c) NC@MoS₂/Ni-NC HNSs, (d) HER polarization curves of NC@MoS₂/Ni-NC HNSs and NC@MoS₂-NC HNSs catalysts normalized by ECSA.

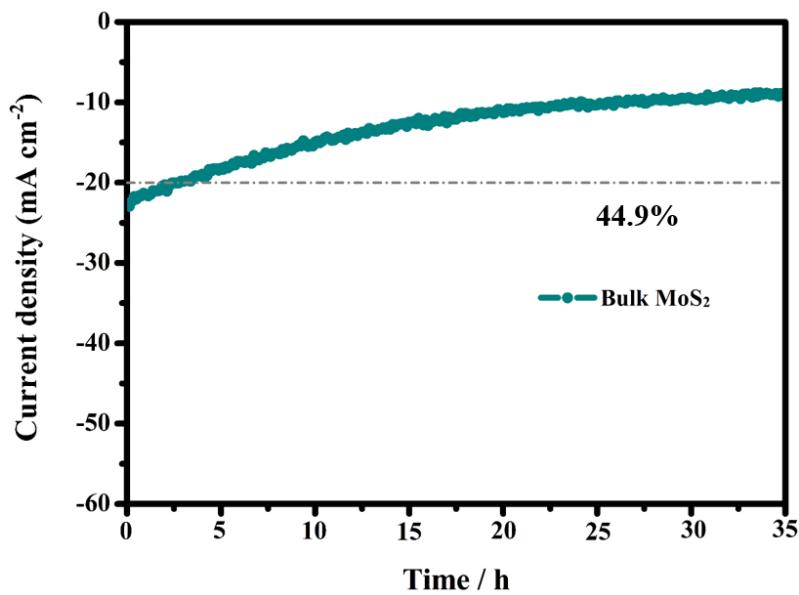


Figure S13. Time-dependence of the current density curve of bulk MoS₂ at 20 mA cm⁻².

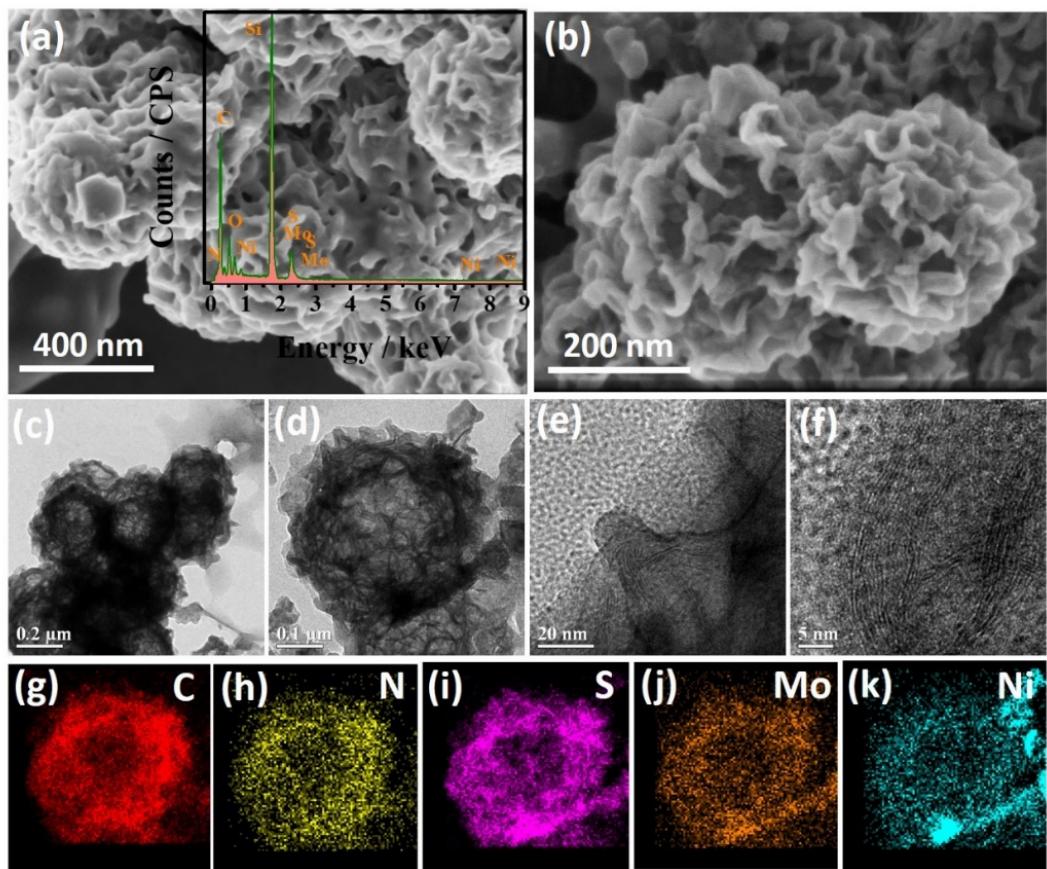


Figure S14. (a, b) SEM and EDS spectrum (inset in a), (c, d) TEM, (e, f) HRTEM and (g-k) EDX mapping images of NC@MoS₂/Ni-NC HNSs after HER durability tests.

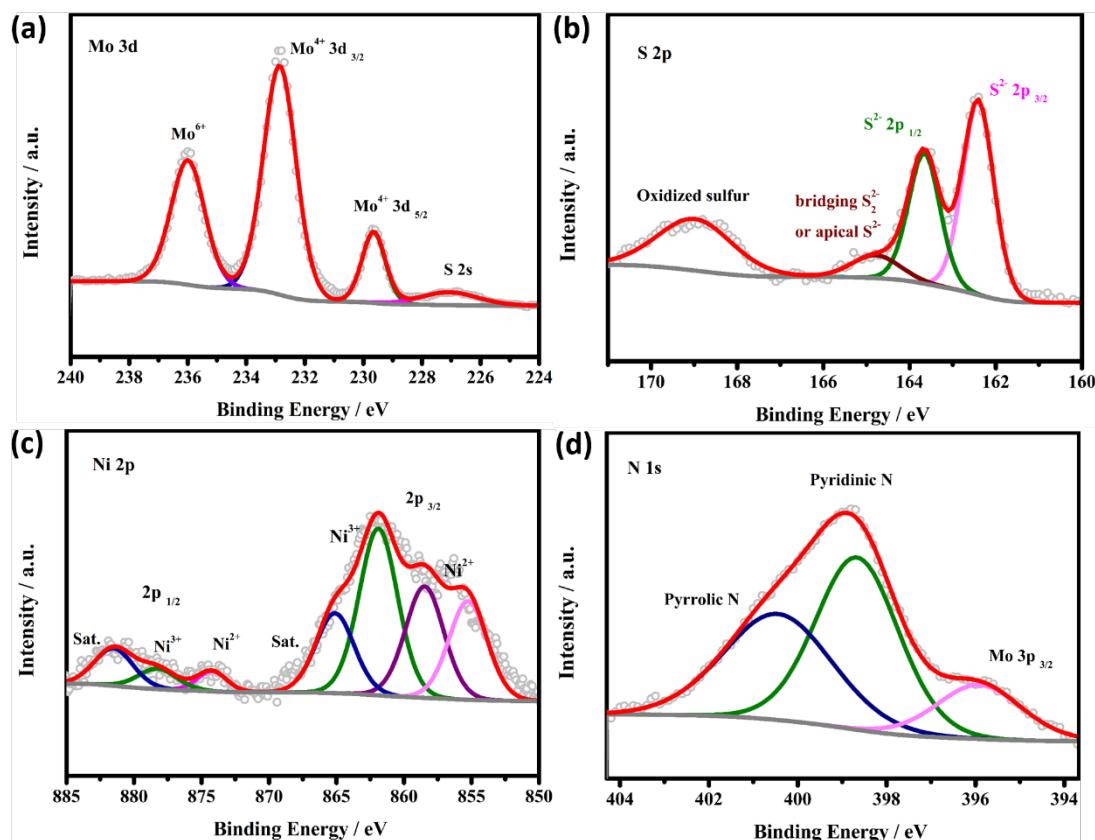


Figure S15. XPS spectra of (a) Mo 3d, (b) S 2p, (c) Ni 2p and (d) N 1s of NC@MoS₂/Ni-NC HNSs

after the HER durability test.

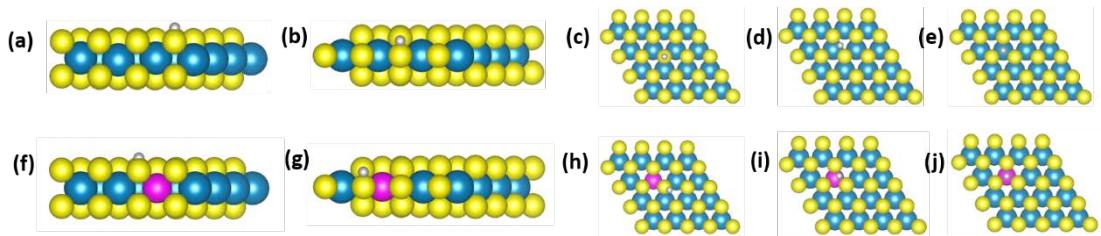


Figure S16 Structure models with H^* adsorption on catalytic sites in pristine MoS_2 and Ni doped MoS_2 , respectively. (a, f) S-edge, (b, g) Mo-edge, and basal plane (c, h) at S-top; (d, i) at S bridge, and (e, j) at Mo or Ni top.

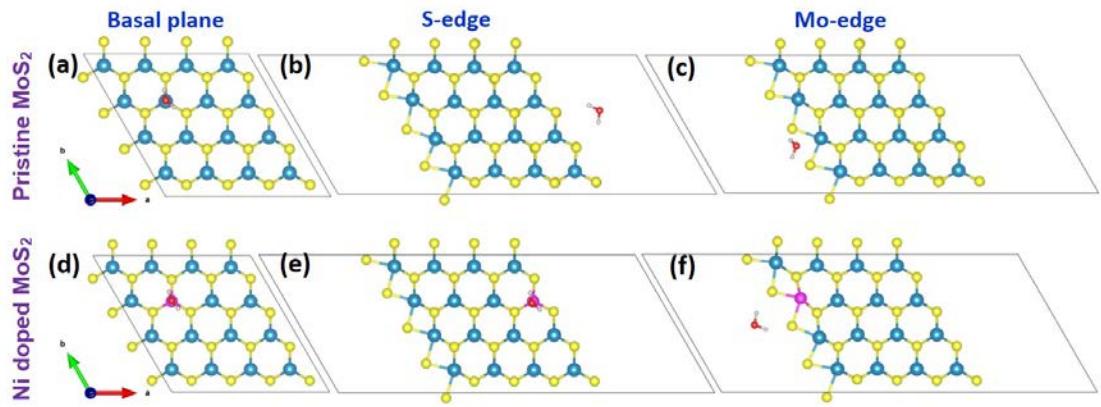
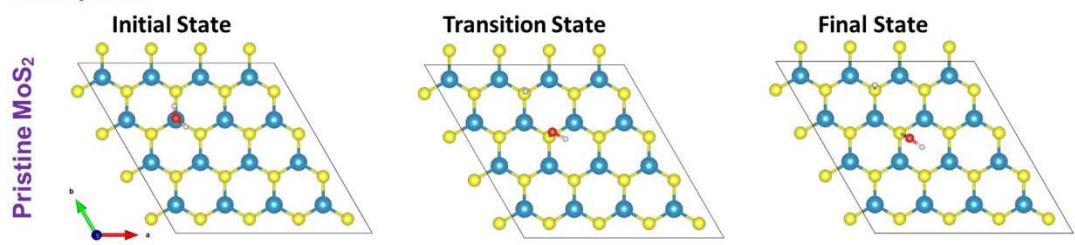
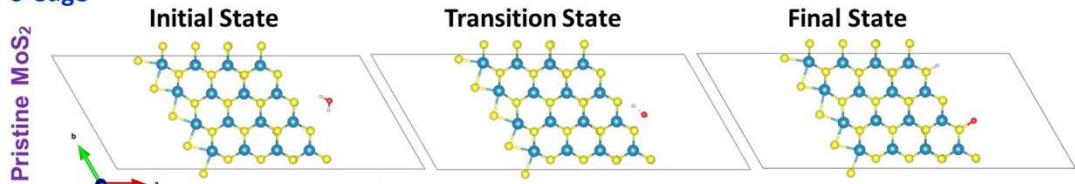


Figure S17. The models of water molecules adsorbed on pristine MoS₂ and Ni doped MoS₂ at (a, d) basal plane, (b, e) S-edge and (c, f) Mo-edge, respectively.

Basal plane



S-edge



Mo-edge

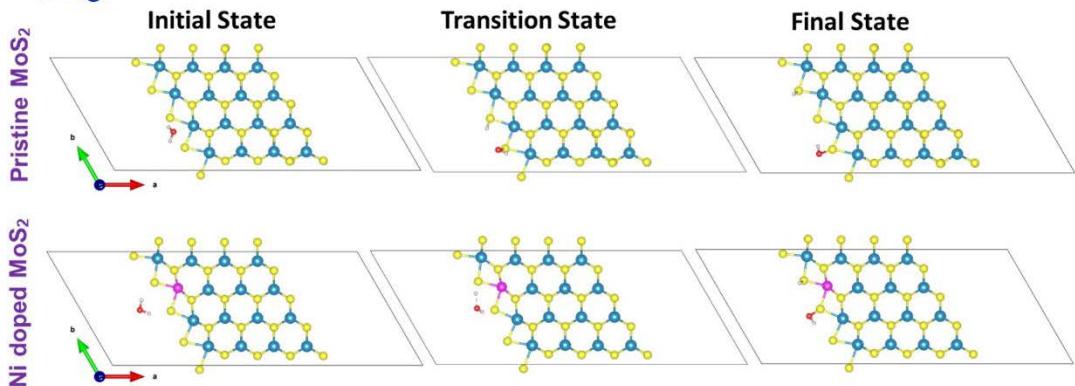


Figure S18. The initial, transition and final states of water dissociation of pristine MoS_2 and Ni doped MoS_2 on basal plane, S-edge and Mo-edge, respectively.

Table S1. Adsorption free energy of H* on different catalytic sites for pristine MoS₂ and Ni doped MoS₂, respectively.

Systems	Sites	Energy (eV)			
		E _{surface}	E _{H+surface}	ΔE _{H*}	ΔG _{H*}
Pristine MoS ₂	S-edge	-363.5447	-367.6975	-0.7827	-0.54
	Mo-edge	-363.5457	-366.9910	-0.0603	0.18
	Basal plane-S top		-360.6904	0.9924	1.23
	Basal plane-Mo top	-358.2979	-359.9786	1.7042	1.94
	Basal plane- S-bridge		-360.4110	1.2718	1.51
Ni doped MoS ₂	S-edge	-353.5673	-357.5132	-0.5610	-0.32
	Mo-edge	-355.9764	-359.2202	0.1412	0.38
	Basal plane-S top		-351.0931	-0.4019	-0.16
	Basal plane-Ni top	-347.3062	-350.0555	0.6356	0.88
	Basal plane- S-bridge		-350.2720	0.4191	0.66

Table S2. Comparison of HER activity at 10 mA cm⁻² and stability of various MoS₂-based catalysts.

Catalyst	η_{10}/mV	Stability	Electrolyte	Reference
NC@MoS ₂ /Ni-NC HNSs	82.1	35 h	1M KOH	This work
Mo ₂ C@MoS ₂ NS	121	48 h	1M KOH	R1
Fe-MoS ₂	173	25 h	1M KOH	R2
Ni-Mo-S	79	1 h	1M KOH	R3
Fe-MoS ₂ /Ni ₃ S ₂ /NF	130.6	2000 CV cycles	1M KOH	R4
SrTiO ₃ @MoS ₂	165	3000 CV cycles	1 M KOH	R5
Co ₃ O ₄ /MoS ₂	205	14 h	1 M KOH	R6
(Ni, Fe)S ₂ @MoS ₂	130	44 h	1 M KOH	R7
Cu-Pd-MoS ₂	93	50 h	0.5 M H ₂ SO ₄	R8
Lamellar MoS ₂	217	10 h	0.5 M H ₂ SO ₄	R9
MoS ₂ /Ti ₃ C ₂	280	36 h	0.5 M H ₂ SO ₄	R10
w-Au@MoS ₂	120	10 h	0.5 M H ₂ SO ₄	R11
hollow MoS ₂	85	16 h	0.5 M H ₂ SO ₄	R12
MoS ₂ /VS ₂	199.6	12 h	0.5 M H ₂ SO ₄	R13
Porous hollow MoS ₂	90	3 h	0.5 M H ₂ SO ₄	R14
Ni@NC@MoS ₂	82	8 h	0.5 M H ₂ SO ₄	R15
Co-doped MoS ₂ /G	194	10 h	0.5 M H ₂ SO ₄	R16
NPNi-MoS ₂ /RGO	205	30000 s	0.5 M H ₂ SO ₄	R17
Zn@MoS ₂	194	2000 CV cycles	0.5 M H ₂ SO ₄	R18
1%Pd-MoS ₂	89	5000 CV cycles	0.5 M H ₂ SO ₄	R19
L-Co/MoS ₂	156	2000 CV cycles	0.5 M H ₂ SO ₄	R20
P-MoS ₂	219	1000 CV cycles	0.5 M H ₂ SO ₄	R21
MoS ₂ /RGO	81	1000 CV cycles	0.5 M H ₂ SO ₄	R22

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