Fan *et al. Chem Synth* 2024;4:36
DOI: 10.20517/cs.2023.72

Chemical Synthesis

Supplementary Materials

Microwave-pulse assisted synthesis of tunable ternary-doped 2D molybdenum carbide for efficient hydrogen evolution

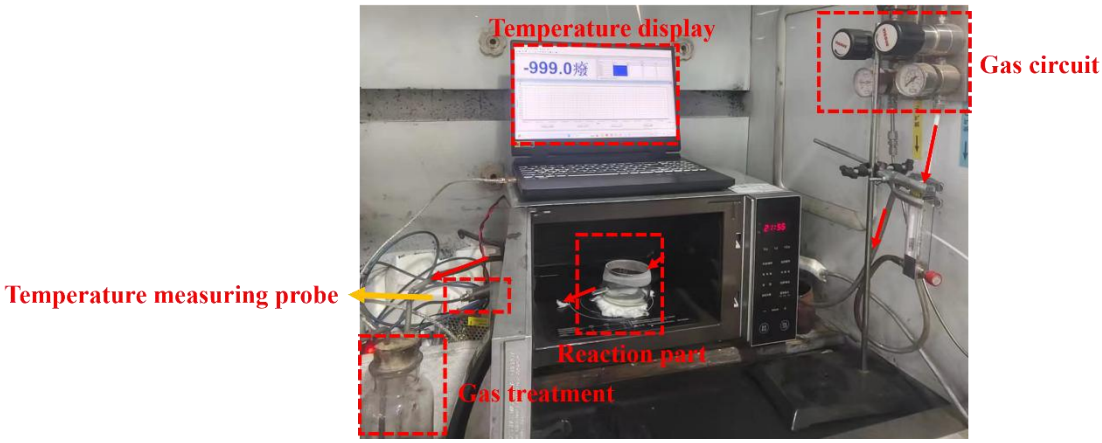
Miao Fan[#], Jiayue Guo[#], Guangyu Fang[#], Haoran Tian, Yongfei You, Zhenhui Huang, Jingru Huang, Huiyu Jiang, Weilin Xu, Jun Wan[*]

State Key Laboratory of New Textile Materials and Advanced Processing Technologies, Hubei Key Laboratory of Biomass Fibers and Eco-Dyeing & Finishing, Wuhan Textile University, Wuhan 430200, Hubei, China.
[#]Authors contributed equally.

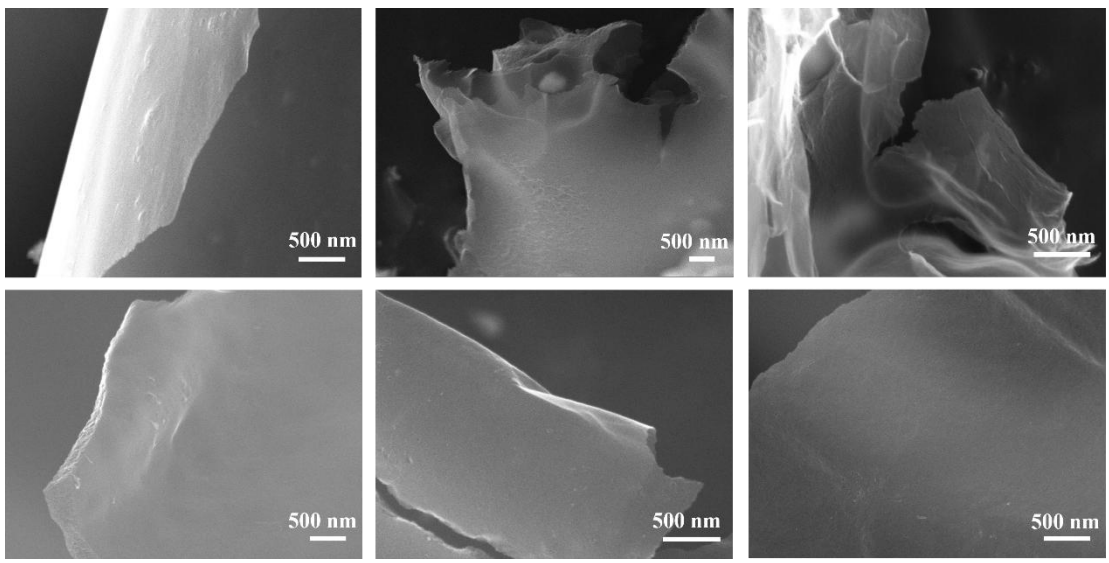
[*]**Correspondence to:** Prof. Jun Wan, State Key Laboratory of New Textile Materials and Advanced Processing Technologies, Hubei Key Laboratory of Biomass Fibers and Eco-Dyeing & Finishing, Wuhan Textile University, 1 Sunny Avenue, Wuhan 430200, Hubei, China. E-mail: wanj@wtu.edu.cn

1. **Supplementary Figures 1-17**
2. **Supplementary Tables 1-3**
3. **References**

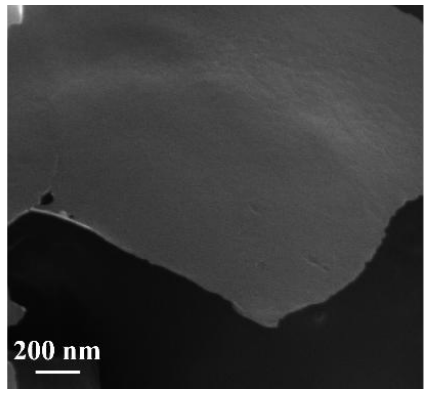
1. Supplementary Figures 1-17



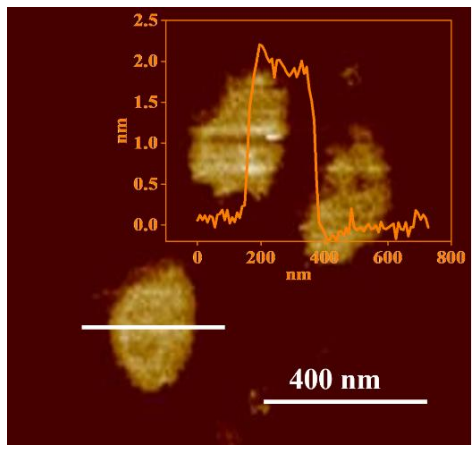
Supplementary Figure 1. Detailed optical picture of microwave pulse reaction equipment.



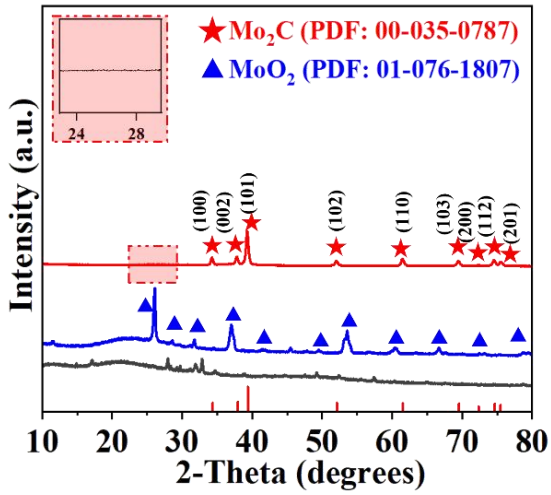
Supplementary Figure 2. (A-F) SEM images of 2D P-Mo_2C, 2D N-Mo_2C, 2D S-Mo_2C, 2D P,N-Mo_2C, 2D P,S-Mo_2C, 2D N,S-Mo_2C, respectively.



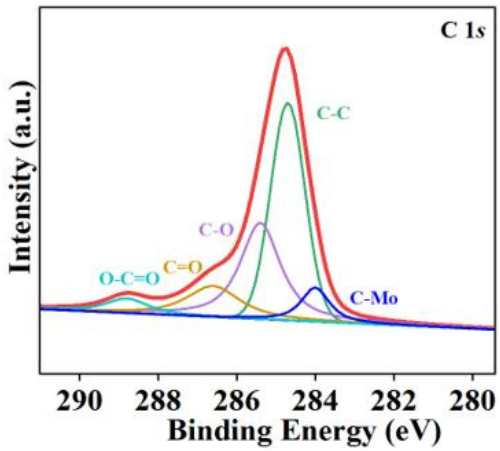
Supplementary Figure 3. SEM images of 2D Mo_2C.



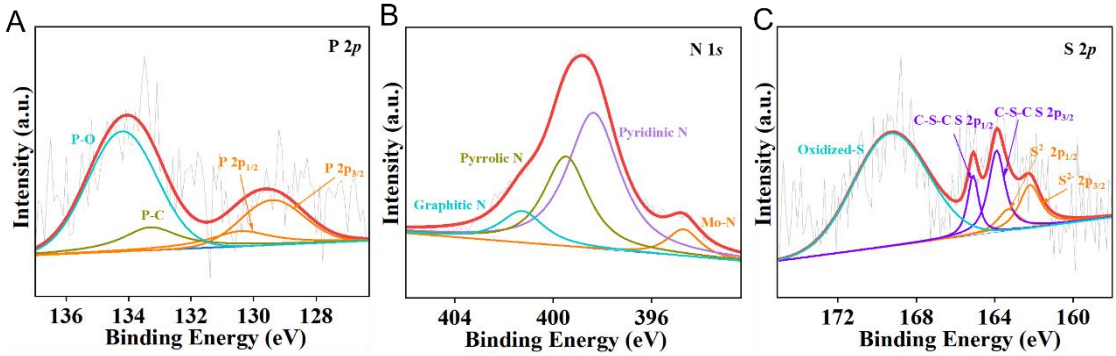
Supplementary Figure 4. AFM images of 2D P,N,S-Mo_2C.



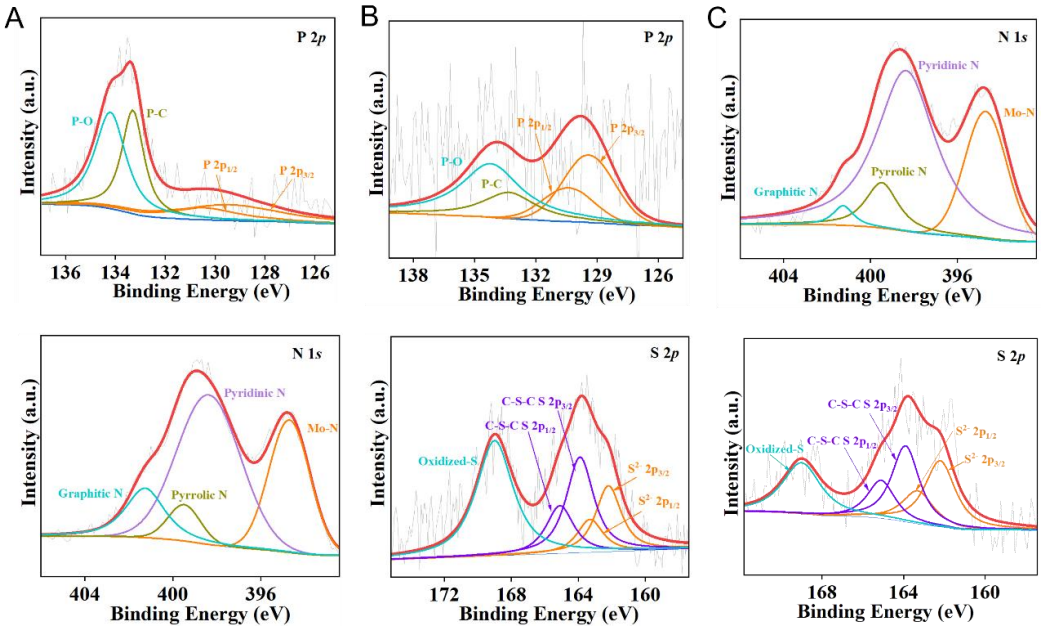
Supplementary Figure 5. XRD patterns of T_1, T_2 and T_3, respectively.



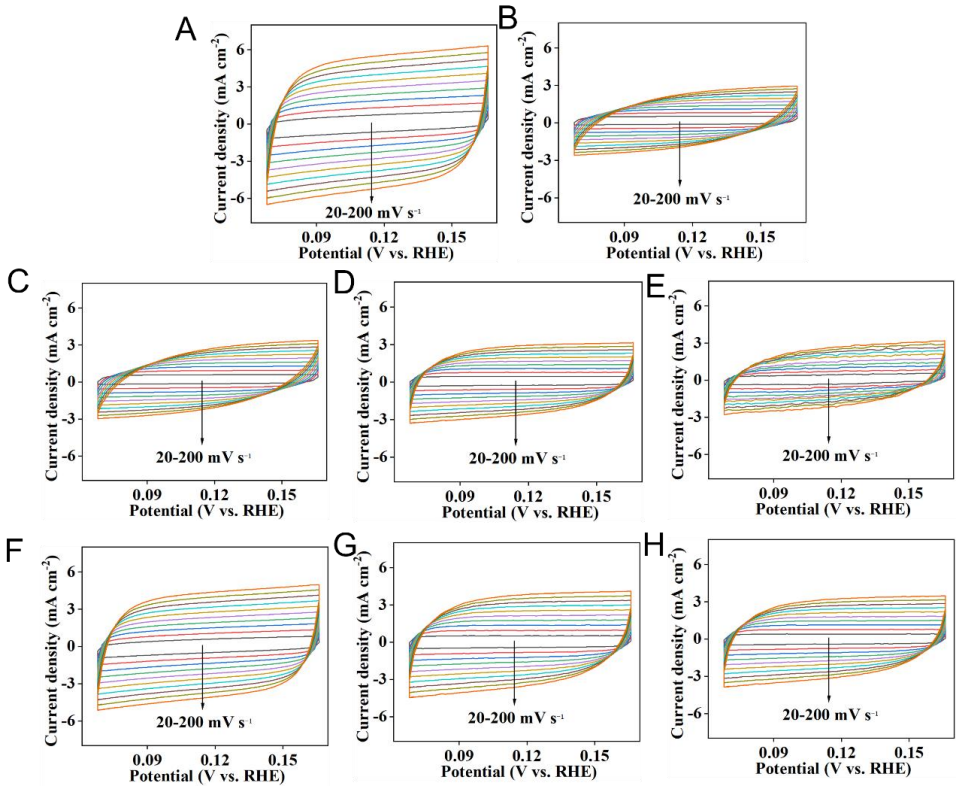
Supplementary Figure 6. C 1*s* spectrum of 2D P,N,S-Mo_2C.



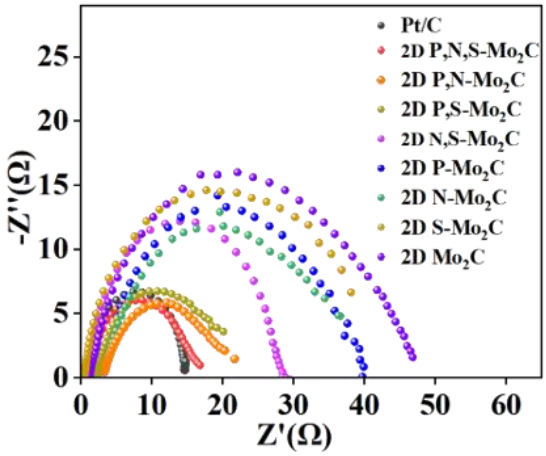
Supplementary Figure 7. (A) High-resolution XPS spectra of P 2*p* for 2D P-Mo_2C. (B) High-resolution XPS spectra of N 1*s* for 2D N-Mo_2C. (C) High-resolution XPS spectra of S 2*p* for 2D S-Mo_2C.



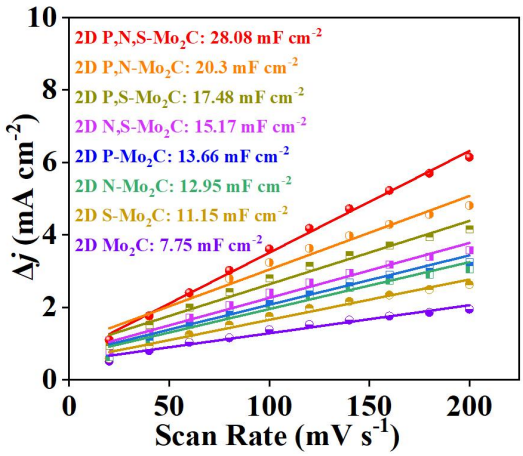
Supplementary Figure 8. (A) High-resolution XPS spectra of N 1*s* and P 2*p* for 2D P,N-Mo_2C. (B) High-resolution XPS spectra of P 2*p* and S 2*p* for 2D P,S-Mo_2C. (C) High-resolution XPS spectra of N 1*s* and S 2*p* for 2D N,S-Mo_2C.



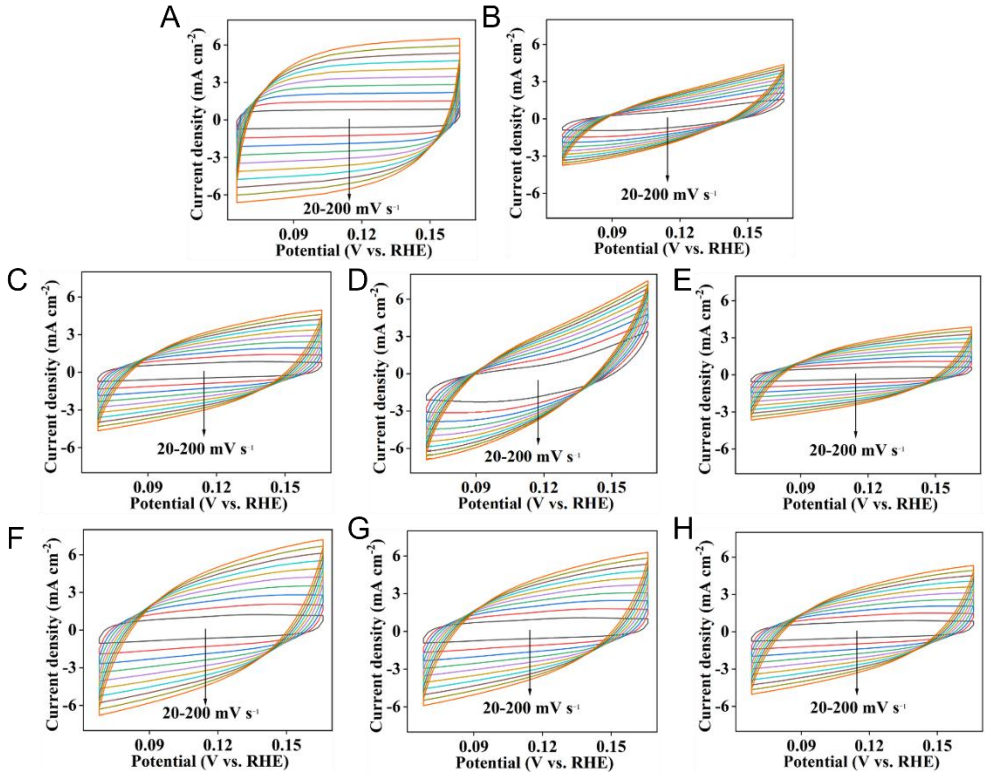
Supplementary Figure 9. Cyclic voltammograms of different electrodes in 0.5 M H_2SO_4. (A-H) The Cyclic voltammograms of 2D P,N,S-Mo_2C, 2D Mo_2C, 2D P-Mo_2C, 2D N-Mo_2C, 2D S-Mo_2C, 2D P,N-Mo_2C, 2D P,S-Mo_2C, 2D N,S-Mo_2C, respectively.



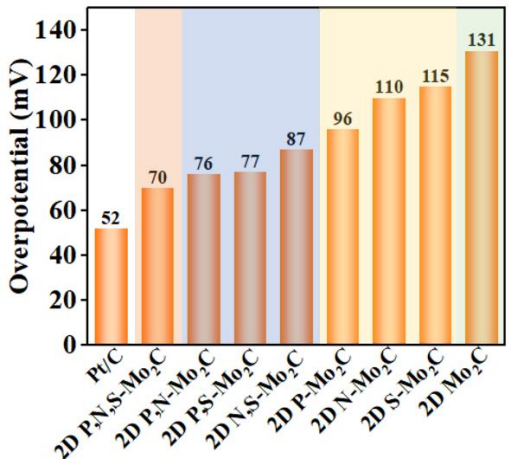
Supplementary Figure 10. Nyquist plots of different samples.



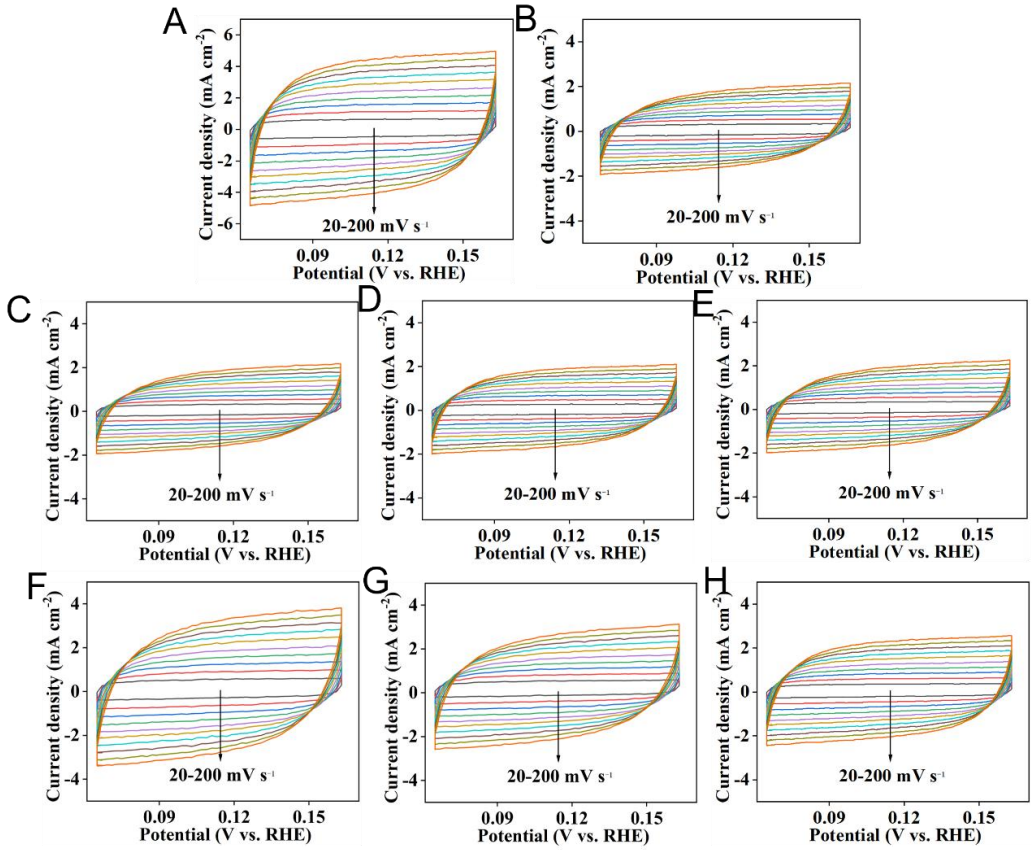
Supplementary Figure 11. C_{dl} after long-term stability test in 0.5 M H_2SO_4.



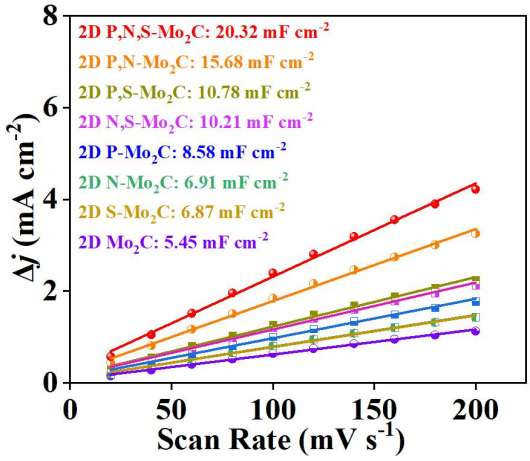
Supplementary Figure 12. Cyclic voltammograms of different electrodes in 0.5 M H_2SO_4. (A-H) The cyclic voltammograms of 2D P,N,S-Mo_2C, 2D Mo_2C, 2D P- Mo_2C, 2D N- Mo_2C, 2D S- Mo_2C, 2D P,N- Mo_2C, 2D P,S- Mo_2C, 2D N,S- Mo_2C, respectively.



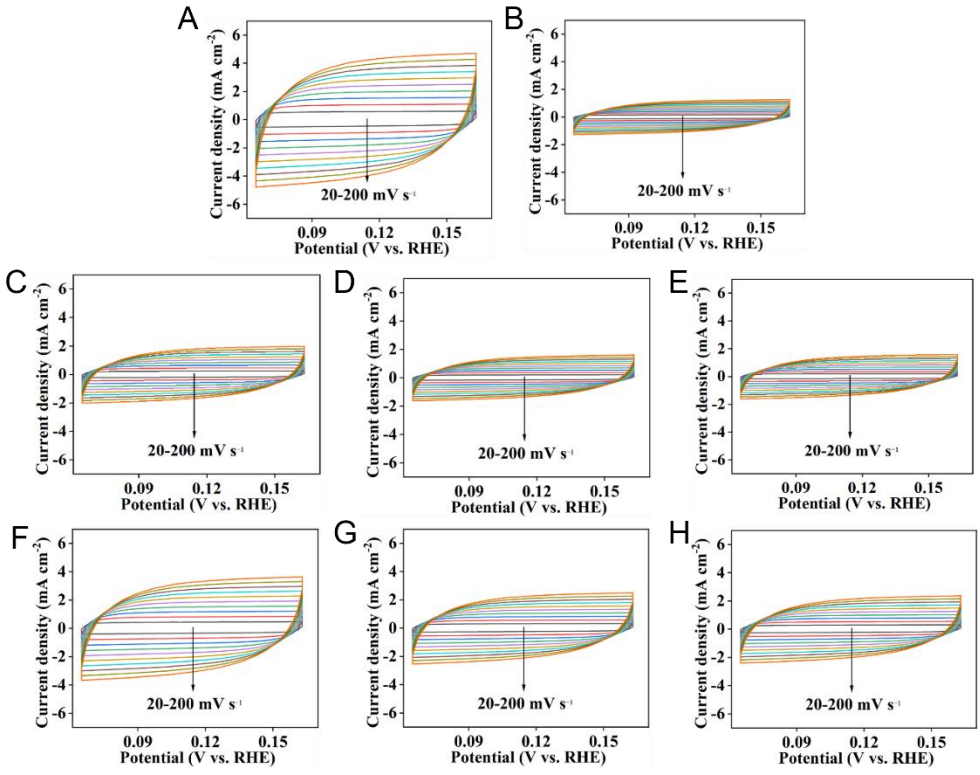
Supplementary Figure 13. Overpotentials at 10 mA·cm^{-2}.



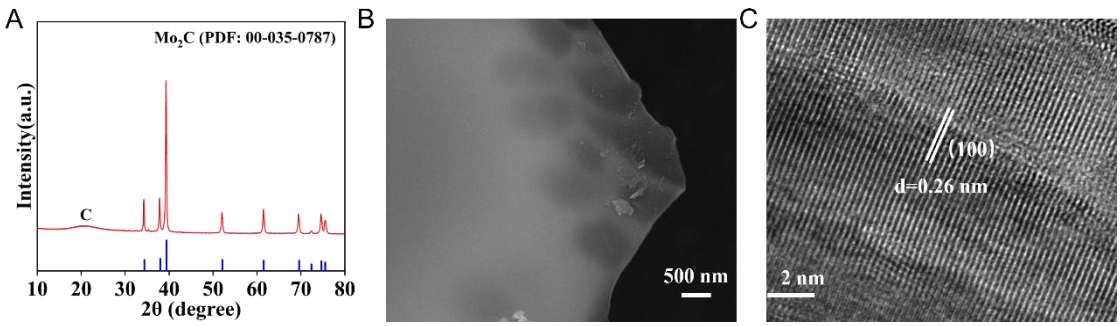
Supplementary Figure 14. Cyclic voltammograms of different electrodes in 1 M KOH. (A-H) The Cyclic voltammograms of 2D P,N,S-Mo_2C, 2D Mo_2C, 2D P-Mo_2C, 2D N-Mo_2C, 2D S-Mo_2C, 2D P,N-Mo_2C, 2D P,S-Mo_2C, 2D N,S-Mo_2C, respectively.



Supplementary Figure 15. C_{dl} after long-term stability test in 1 M KOH.



Supplementary Figure 16. Cyclic voltammograms of different electrodes in 1 M KOH. (A-H) The cyclic voltammograms of 2D P,N,S- Mo_2C, 2D Mo_2C, 2D P- Mo_2C, 2D N- Mo_2C, 2D S- Mo_2C, 2D P,N- Mo_2C, 2D P,S- Mo_2C, 2D N,S- Mo_2C, respectively.



Supplementary Figure 17. (A) The XRD spectrum of 2D P,N,S-Mo_2C after accelerated durability tests. (B) SEM image of 2D P,N,S-Mo_2C after accelerated durability tests. (C) TEM image of 2D P,N,S-Mo_2C after accelerated durability tests.

Supplementary Tables 1-3

Supplementary Table 1. Parameters of the 2D P,N,S-Mo_2C from Rietveld refinement. The space group, lattice constants and fitting index of the corresponding from Rietveld refinement.

			2D P,N,S-Mo_2C
Space group			P63/mmc
Lattice (Å)	Parameters	a	3.015030
		b	3.015030
		c	4.747621
		α(°)	90.000
		β(°)	90.000
		γ(°)	120.000
		V (Å^3)	37.376

Supplementary Table 2. Comparison of HER properties of different catalysts in 0.5 M H_2SO_4

Authors	**Mateial**	**Electrolyte**	**Overpotential (mV *vs.* RHE)**	**Tafel slop ($mV \cdot dec^{-1}$)**
This work	2D N,P,S-Mo_2C	0.5 M H_2SO_4	58	48
Wang *et al.*[1]	Mo_2C&MoS_2@NSC$_3$	0.5 M H_2SO_4	209	85.5
Zhang *et al.*[2]	Co-Mo_2C-CN_x-2	0.5 M H_2SO_4	116	105
Li et al.[3]	PC@Ni-Mo_2C	0.5 M H_2SO_4	156	65
Wang *et al.*[4]	NP-Mo_2C	0.5 M H_2SO_4	210	64
Li *et al.*[5]	Zn, N co-doped Mo_2C	0.5 M H_2SO_4	169.5	62.2
Chi *et al.*[6]	Rich N-doped Mo_2C	0.5 M H_2SO_4	150	61
Shi *et al.*[7]	P-Mo_2C@C-2.9	0.5 M H_2SO_4	89	42
Lu *et al.*[8]	Mo_2C@2D-NPC	0.5 M H_2SO_4	86	62

Supplementary Table 3. Comparison of HER properties of different catalysts in 1 M KOH.

Authors	Mateial	Electrolyte	Overpotential (mV *vs.* RHE)	Tafel slop ($mV \cdot dec^{-1}$)
This work	2D N,P,S-Mo_2C	1 K KOH	70	54
Ouyang *et al.*[9]	Mo_2C@N-CNTs	1 K KOH	170	92
Yang *et al.*[10]	3D Mo_2C (1:1)	1 K KOH	110	73.9
Lu *et al.*[11]	MoC-Mo_2C/PNCDs	1 K KOH	121	60
Jing *et al.*[12]	N-Mo_2C@NC-1-120-700	1 K KOH	136	58
Wang *et al.*[13]	NSMB-1.25	1 K KOH	118	74
Yuan *et al.*[14]	Ni/Mo_2C/NC-60	1 K KOH	180	63
Gong *et al.*[15]	MS-Mo_2C@NCNS	1 K KOH	98	99
Luo *et al.*[16]	Co_9S_8-NSC@Mo_2C	1 K KOH	89	86.7

REFERENCES

1. Wang Q, Yu R, Shen D, et al. One-pot synthesis of Mo_2C&MoS_2 loaded on N/S co-doped carbon materials as the electrocatalyts for hydrogen evolution reaction. *Fuel* 2022;318.123615. DOI

2. Zhang P, Liu Y, Liang T, et al. Nitrogen-doped carbon wrapped Co-Mo_2C dual Mott–Schottky nanosheets with large porosity for efficient water electrolysis. *Appl Catal B Environ* 2021;284:119738. DOI

3. Li Z, Fang W, Wu Y, et al. Efficient electrocatalyst for hydrogen evolution reaction: Ni-doped Mo_2C nanoparticles embedded in porous carbon. *Mater Lett* 2020;280:128611. DOI

4. Wang D, Liu T, Wang J, et al. N, P (S) Co-doped Mo_2C/C hybrid electrocatalysts for improved hydrogen generation. *Carbon* 2018;139:845-852. DOI

5. Li P, Zheng D, Gao M, et al. Bimetallic MOF-templated fabrication of porous Zn, N Co-doped Mo_2C for an efficient hydrogen evolution reaction. *ACS Appl Energy Maters* 2021;4:8875-82. DOI

6. Chi J Q, Yan K L, Gao W K, et al. Solvothermal access to rich nitrogen-doped molybdenum carbide nanowires as efficient electrocatalyst for hydrogen evolution reaction. *J Alloy Compd* 2017;714:26-34. DOI

7. Shi Z, Nie K, Shao Z J, et al. Phosphorus-Mo_2C@carbon nanowires toward efficient electrochemical hydrogen evolution: composition, structural and electronic regulation. *Energy Environ Sci* 2017;10:1262-71. DOI

8. Lu C, Tranca D, Zhang J, et al. Molybdenum carbide-embedded nitrogen-doped porous carbon nanosheets as electrocatalysts for water splitting in alkaline media. *ACS Nano* 2017;11:3933-42. DOI

9. Ouyang T, Ye Y Q, Wu C Y, et al. Heterostructures Composed of N-Doped Carbon Nanotubes Encapsulating Cobalt and β-Mo2C Nanoparticles as Bifunctional Electrodes for Water Splitting. *Angew Chem Int Ed* 2019;58:4923-28. DOI

10. Yang X, Cheng J, Yang X, et al. Facet-tunable coral-like Mo_2C catalyst for electrocatalytic hydrogen evolution reaction. *Chem Eng J* 2023;451:138977. DOI

11. Lu X F, Yu L, Zhang J, et al. Ultrafine dual-phased carbide nanocrystals confined in porous nitrogen-doped carbon dodecahedrons for efficient hydrogen Evolution reaction. *Adv Mater* 2019;31:e1900699. DOI

12. Jing Q, Zhu J, Wei X, et al. An acid-base molecular assembly strategy toward N-doped Mo_2C@C nanowires with mesoporous Mo_2C cores and ultrathin carbon shells for efficient hydrogen evolution. *J Colloid Interf Sci* 2021;602:520-533. DOI

13. Wang, X., Xia L, Guo C, et al. Interfacial engineering of N, S-doped Mo_2C-Mo/C heterogeneous nanorods for enhanced alkaline hydrogen evolution. *Appl Surf Sci* 2023;614:156276. DOI

14. Yuan Q, Chen W, Hu R, et al. Metal-polydopamine derived N-doped carbon nanorod wrapping Ni and Mo_2C nanoparticles for efficient hydrogen evolution reaction. *Mater Lett* 2022;307:130989. DOI

15. Gong T, Liu Y, Cui K, et al. Binary molten salt in situ synthesis of sandwich-structure hybrids of hollow β-Mo_2C nanotubes and N-doped carbon nanosheets for hydrogen evolution reaction. *Carbon Energy* 2023;e349. DOI

16. Luo X, Zhou Q, Du S, et al. Porous Co_9S_8/Nitrogen, Sulfur-Doped Carbon@Mo_2C Dual Catalyst for Efficient Water Splitting. *ACS Appl Mater Inter* 2018;10:22291-302. DOI