

Electronic Supplementary Information

**Self-standing hollow Ni-doped Mo₂C nano tube arrays induced by
the Kirkendall effect for efficient hydrogen evolution reaction in
acidic and alkaline solutions**

Chen Li, Beirong Ye, Renhong Chen, Yongqi Li, Xin Liu, Tongwei Wu, Hongxian Liu,* Xinhui Xia, * Yongqi Zhang*

Prof. Y. Q. Zhang, Dr. T. Wu, C. Li, B. R. Ye, Y. Q. Li,

Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 611371, China

Email: yqzhang@uestc.edu.cn

R. H. Chen,

School of Electrical Engineering, University of South China, Hengyang 421001, China

Prof. X. Liu,

State Key Laboratory of New Textile Materials & Advanced Processing Technology

Wuhan Textile University Wuhan 430073, China

Hongxian Liu, liu_hongxian@163.com

School of Physics and Electronic Science, Zunyi Normal University, Zunyi 563000,

Guizhou, China

Prof. X. H. Xia,

School of Materials Science & Engineering, Zhejiang University of Technology,

Hangzhou 310014, China

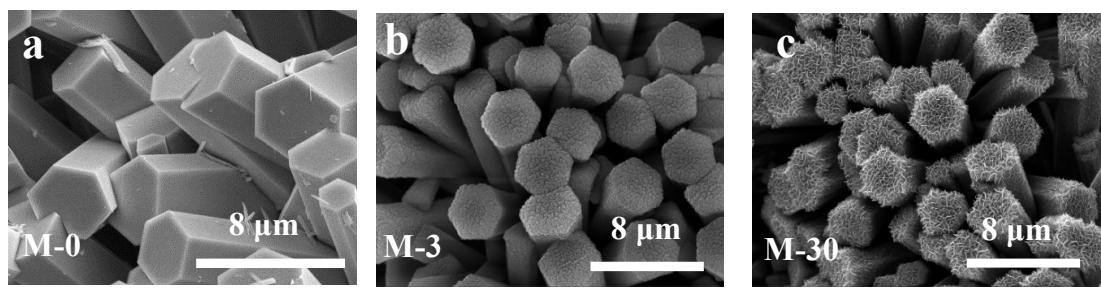


Figure S1. SEM images of M-0, M-3, and M-30

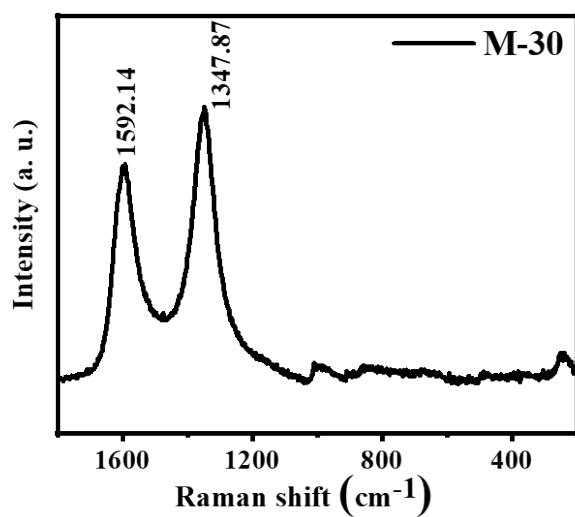


Figure S2. Raman spectra of M-30

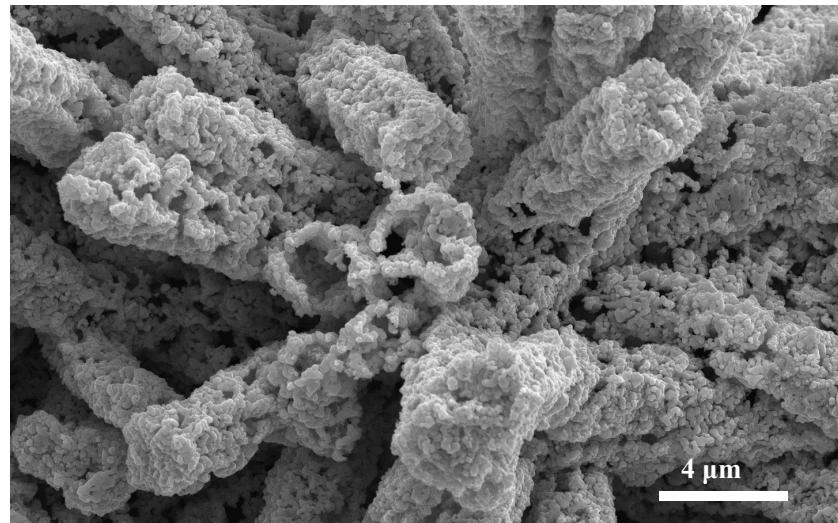


Figure S3. SEM image of M-000

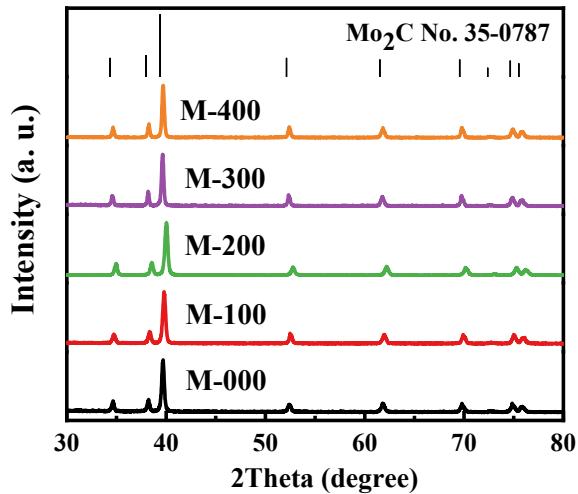


Figure S4. The XRD patterns of M-100, M-200, M-300 and M-400.

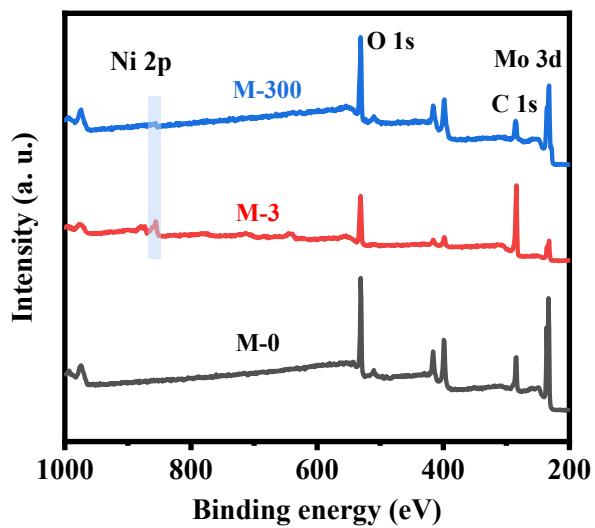


Figure S5. The XPS survey spectra of M-0, M-3, and M-300

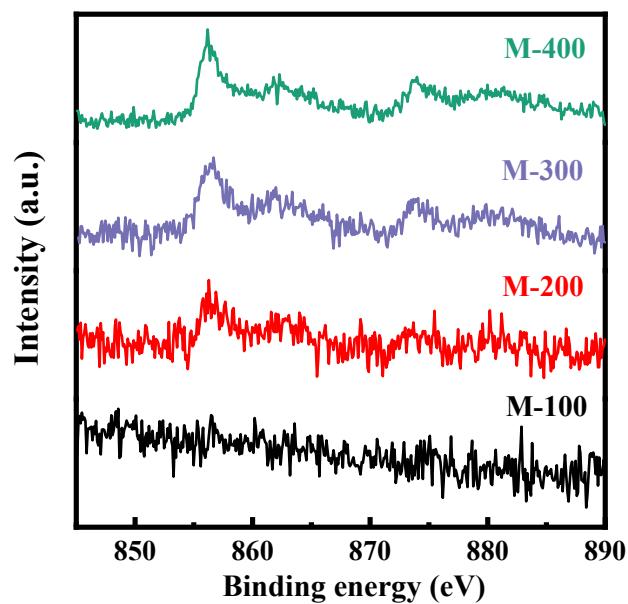


Figure S6. Ni fine spectra of M-100, M-200, M-300 and M-400

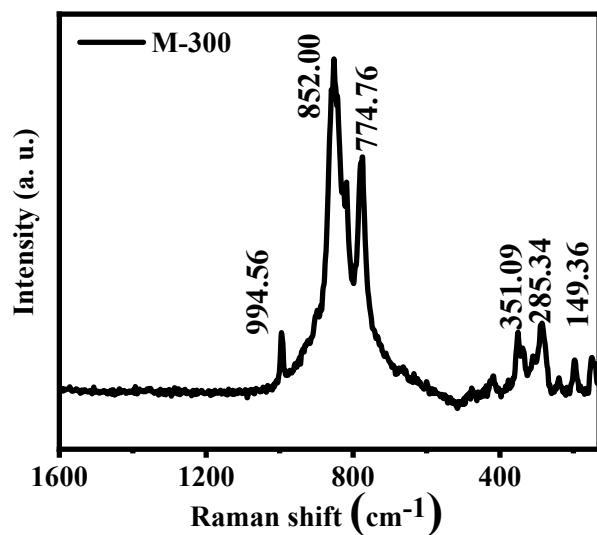


Figure S7. Raman spectrum of M-300

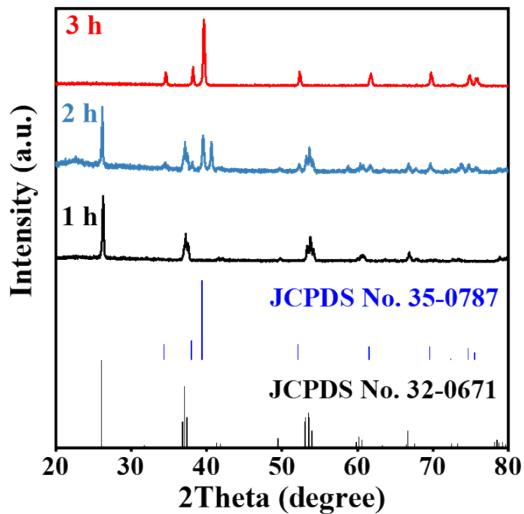


Figure S8. XRD patterns of M-30 calcined at 800°C for different time period.

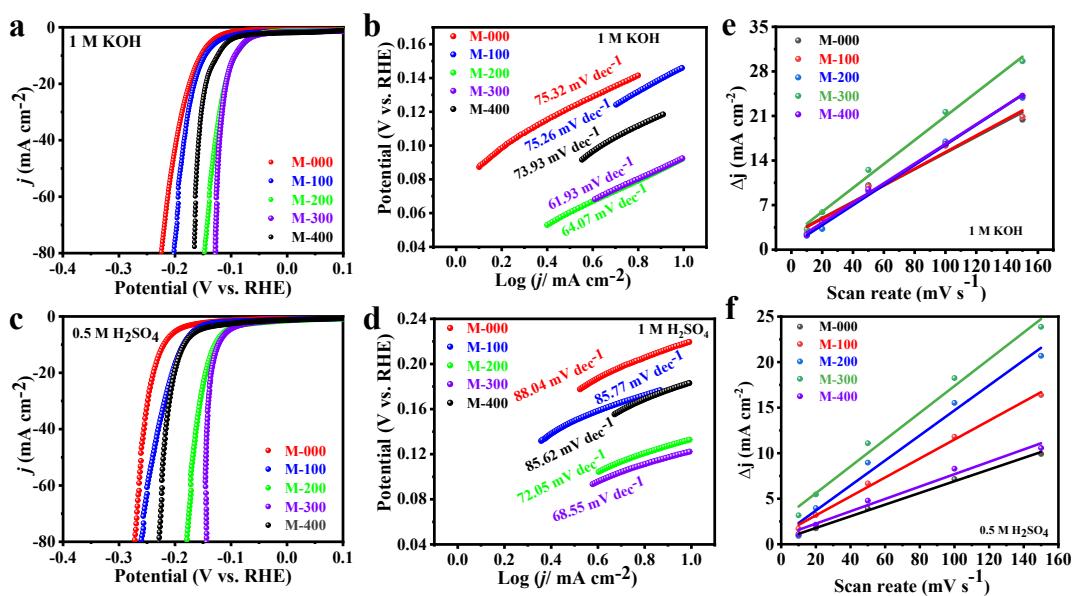


Figure S9. (a) and (c) The LSV curves, (b) and (d) the Tafel plots, (e) and (f) Current density as a function of the scan rate for M-000, M-100, M-200, M-300, and M-400 electrodes.

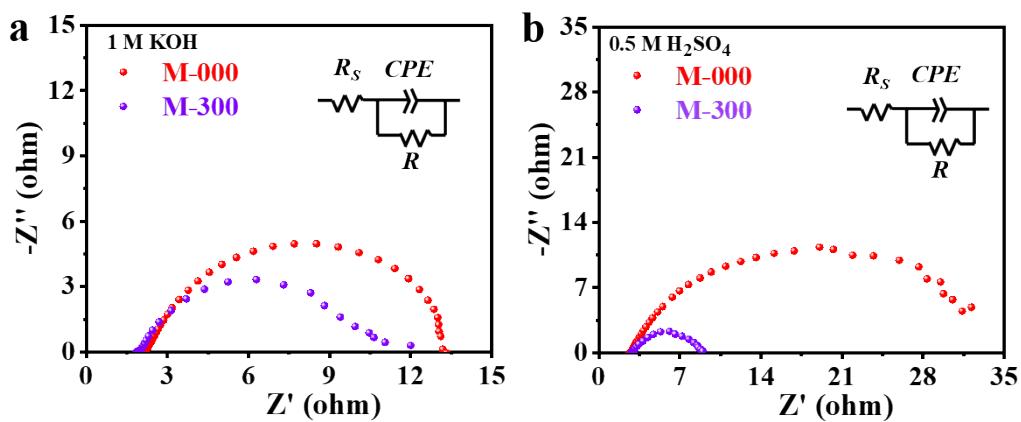


Figure S10. The Nyquist plots of M-000 and M-300.

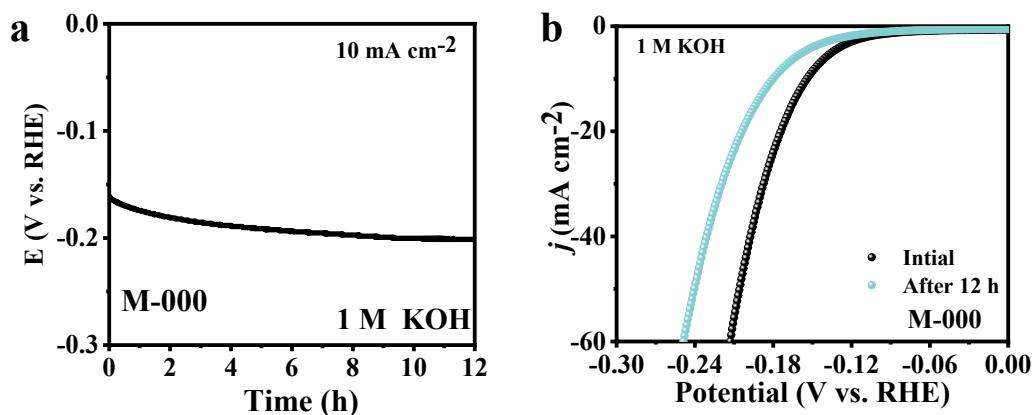


Figure S11. (a) The stability curves (voltage vs. time) and (b) LSV curves of initial and after stability tests in 1 M KOH of the M-000.

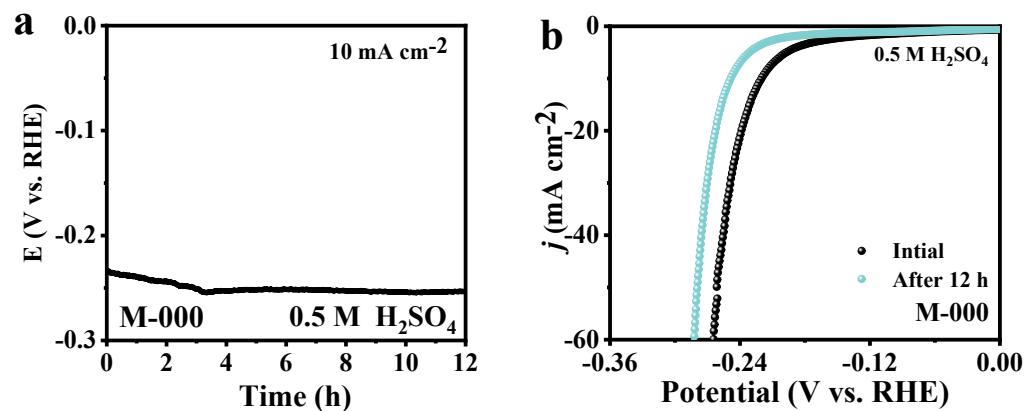


Figure S12. (a) The stability curves (voltage vs. time) and (b) LSV curves of initial and after stability tests in 0.5 M H₂SO₄ of the M-000.

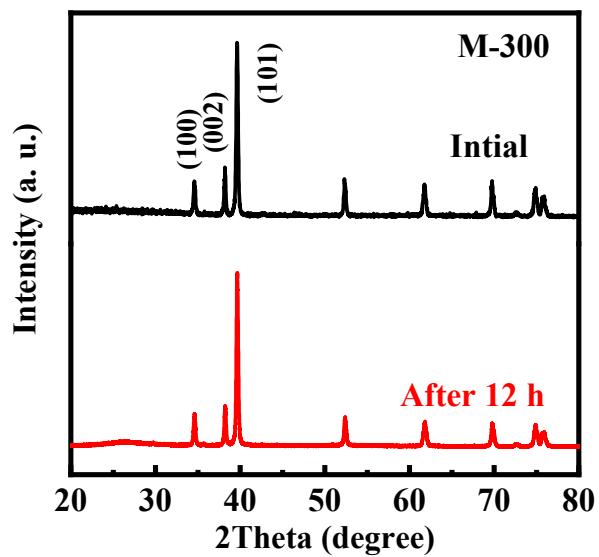


Figure S13. XRD patterns of M-300 before and after stability test in 0.5 M H_2SO_4

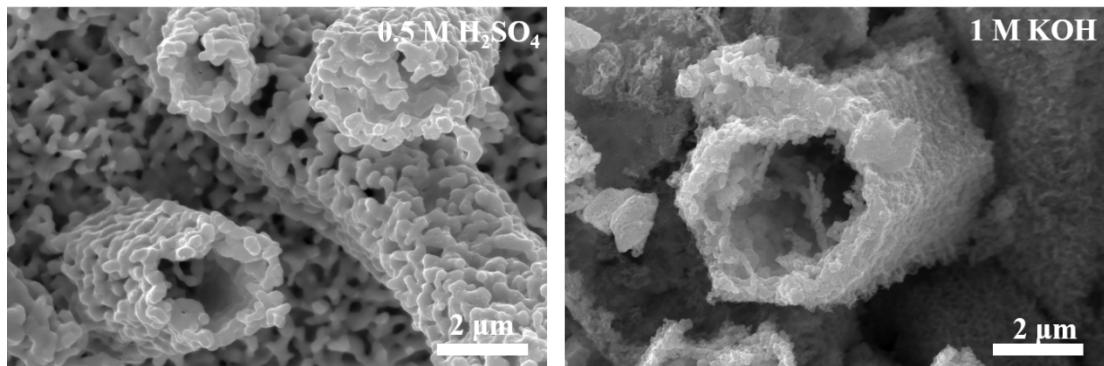


Figure S14. SEM images of M-300 after stability test

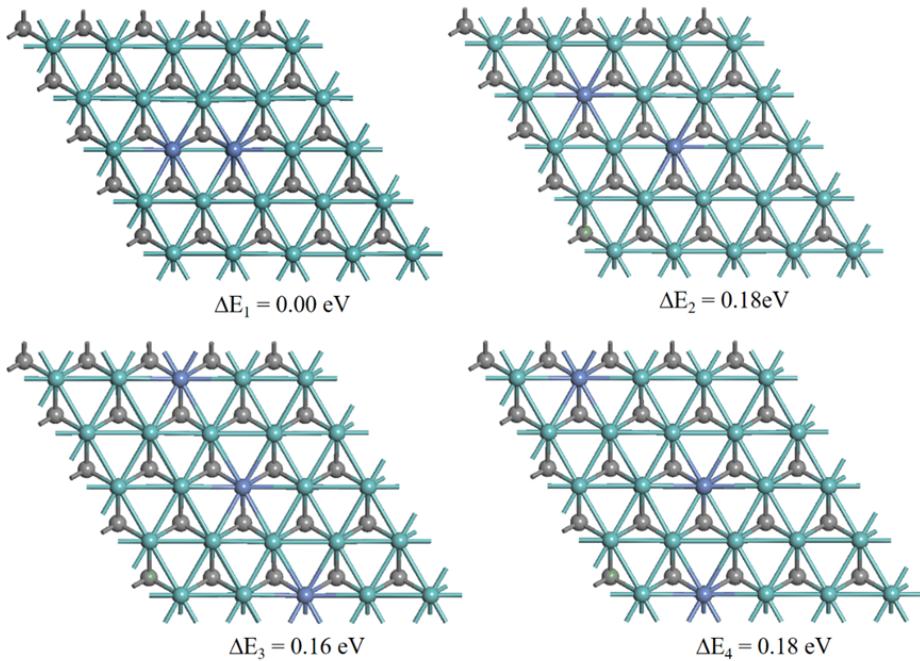


Figure S15. The optimized structures of 2Ni-doped Mo_2C .

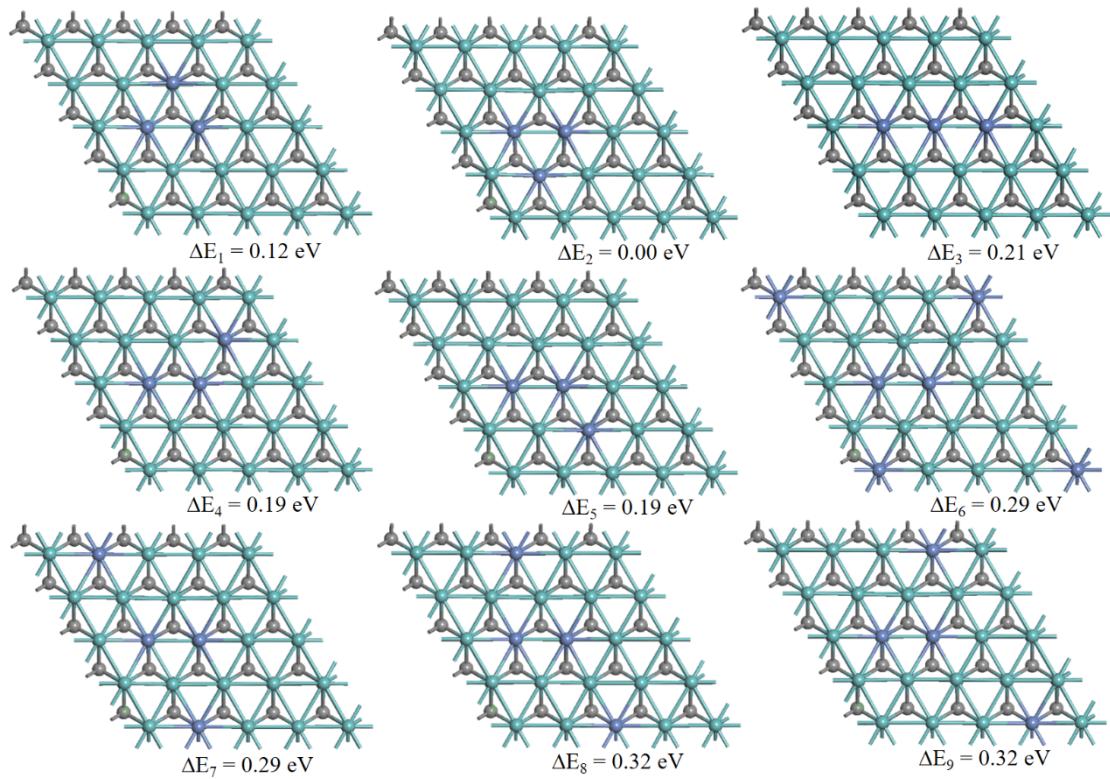


Figure S16. The optimized structures of 3Ni-doped Mo_2C .

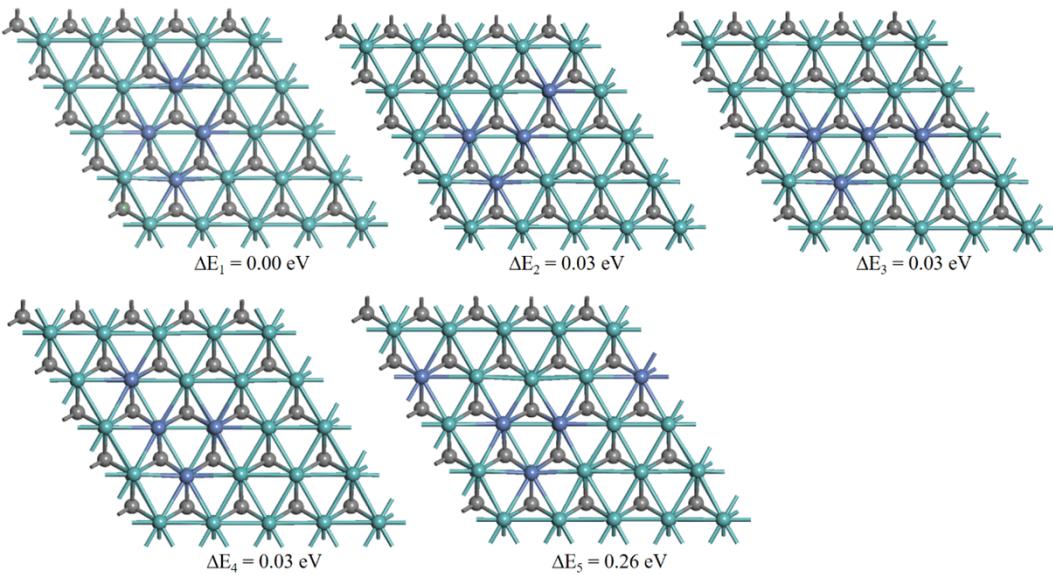


Figure S17. The optimized structures of 4Ni-dped Mo₂C.

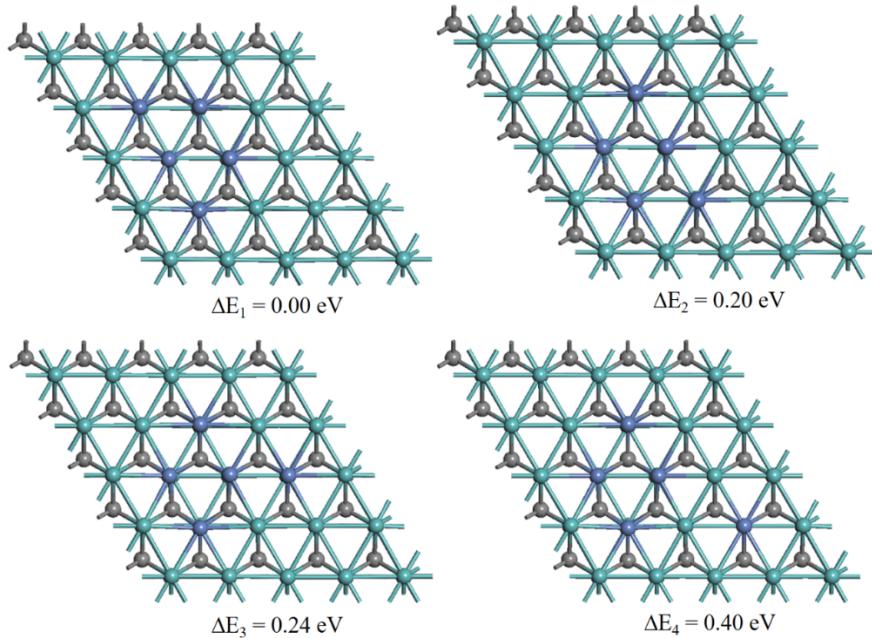


Figure S18. The optimized structures of 5Ni-dped Mo₂C.

Table S1. The content of Ni, Mo, and C was calculated from XPS fine spectra of M-100, M-200, M-300, and M-400.

	M _{Ni} (%)	M _{Mo} (%)	M _C (%)
M-100	-	38.00	61.00
M-200	3.53	80.06	16.41
M-300	8.86	75.91	15.22
M-400	10.48	72.08	17.43

Table S2. Comparison of HER electrocatalytic activity of M-300 with other recently reported high performance HER electrocatalysts.

Catalysts	Overpotential (mV) at $j=10 \text{ mA cm}^{-2}$	Electrolyte	Reference
This work (M-300)	93	1 M KOH	
Ni/Mo ₂ C(1:2)-NCNFs	143	1 M KOH	1
Co-NC@Mo ₂ C	99	1 M KOH	2
Co, Mo ₂ C-CNF	128	1 M KOH	3
Co-Mo ₂ C@C	98	1 M KOH	4
Ni/Mo ₂ C-NCSs	131	1 M KOH	5
Co-Mo ₂ C-CN _{x-2}	92	1 M KOH	6
Ni-Mo ₂ C-0.67	151.1	1 M KOH	7
This work (M-300)	122	0.5 M H₂SO₄	
Co-NC@Mo ₂ C	143	0.5 M H ₂ SO ₄	2
Mo ₂ C@NG/CNT	160	0.5 M H ₂ SO ₄	8
Mo ₂ C-GNR	152	0.5 M H ₂ SO ₄	9
Ni-Mo ₂ C-0.67	165	0.5 M H ₂ SO ₄	7
L-Mo ₂ C	170	0.5 M H ₂ SO ₄	10
Mo ₂ C/W ₂ C	140	0.5 M H ₂ SO ₄	11
VN/Mo ₂ C	140	0.5 M H ₂ SO ₄	12

Reference

1. M. Li, Y. Zhu, H. Wang, C. Wang, N. Pinna and X. Lu, *Advanced Energy Materials*, 2019, **9**, 1803185.
2. Q. Liang, H. Jin, Z. Wang, Y. Xiong, S. Yuan, X. Zeng, D. He and S. Mu, *Nano Energy*, 2019, **57**, 746-752.
3. J. Wang, R. Zhu, J. Cheng, Y. Song, M. Mao, F. Chen and Y. Cheng, *Chemical Engineering Journal*, 2020, **397**, 125481.
4. S. Yuan, M. Xia, Z. Liu, K. Wang, L. Xiang, G. Huang, J. Zhang and N. Li, *Chemical Engineering Journal*, 2022, **430**, 132697.
5. Y. Xu, J. Yang, T. Liao, R. Ge, Y. Liu, J. Zhang, Y. Li, M. Zhu, S. Li and W. Li, *Chemical Engineering Journal*, 2022, **431**, 134126.
6. P. Zhang, Y. Liu, T. Liang, E. H. Ang, X. Zhang, F. Ma and Z. Dai, *Applied Catalysis B: Environmental*, 2021, **284**, 119738.
7. W. Liu, X. Wang, J. Qu, X. Liu, Z. Zhang, Y. Guo, H. Yin and D. Wang, *Applied*

- Catalysis B: Environmental*, 2022, **307**, 121201.
- 8. C. Yang, K. Shen, R. Zhao, H. Xiang, J. Wu, W. Zhong, Q. Zhang, X. Li and N. Yang, *Advanced Functional Materials*, 2021, **32**, 2108167.
 - 9. X. Fan, Y. Liu, Z. Peng, Z. Zhang, H. Zhou, X. Zhang, B. I. Yakobson, W. A. Goddard, X. Guo, R. H. Hauge and J. M. Tour, *ACS Nano*, 2017, **11**, 384-394.
 - 10. W. Yuan, Q. Huang, X. Yang, Z. Cui, S. Zhu, Z. Li, S. Du, N. Qiu and Y. Liang, *ACS Applied Materials & Interfaces*, 2018, **10**, 40500-40508.
 - 11. Y. Ling, F. M. D. Kazim, Q. Zhang, S. Xiao, M. Li and Z. Yang, *International Journal of Hydrogen Energy*, 2021, **46**, 9699-9706.
 - 12. L. Feng, S. Li, D. He, L. Cao, G. Li, P. Guo and J. Huang, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 15202-15211.