

Supplementary information

N-doped Mo₂C Particles as Cathode Catalyst of Asymmetric Neutral-alkaline Microbial Electrolysis Cells for Hydrogen Production

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Fig.S1. Pictures of Microbial Electrolysis Cells.

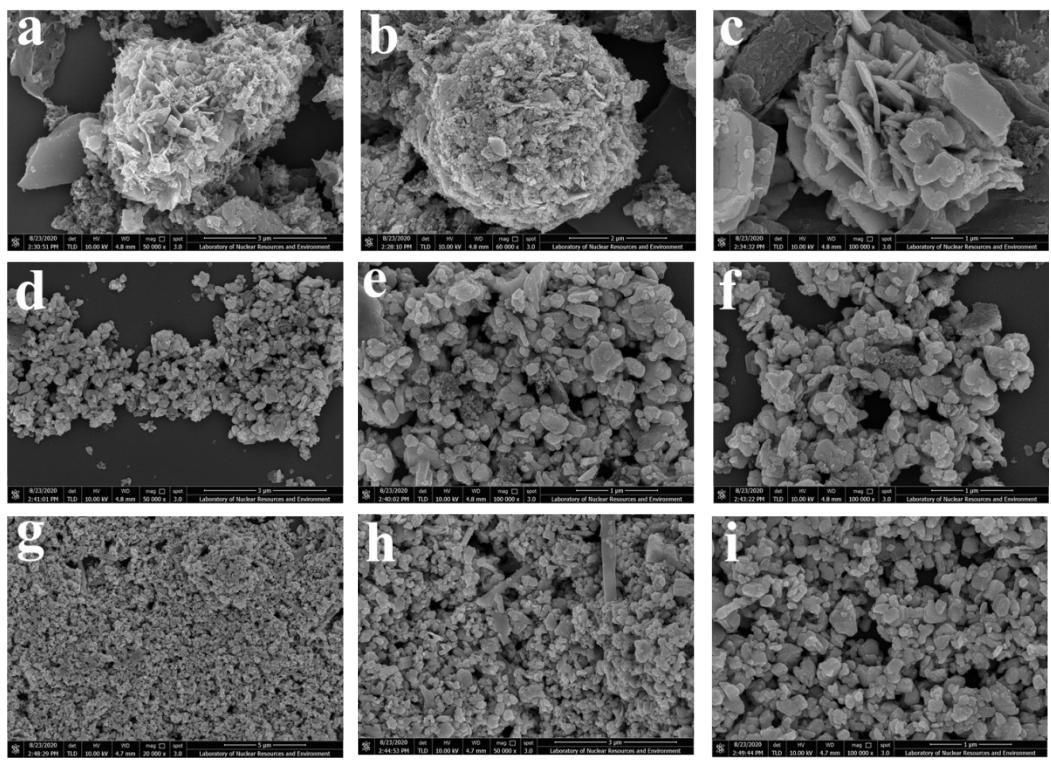


Fig.S2. SEM diagrams of Mo₂C-800 (a-c), Mo₂C-900 (d-f) and Mo₂C-1000 (g-i).

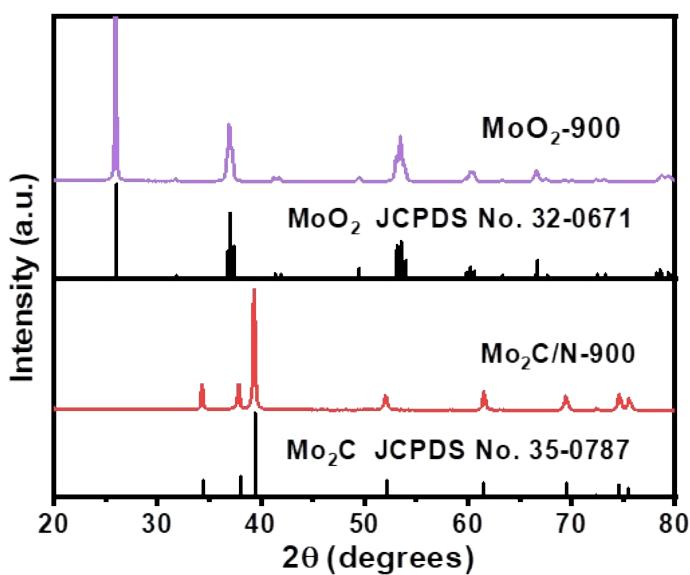


Fig.S3. XRD patterns of MoO_2 .

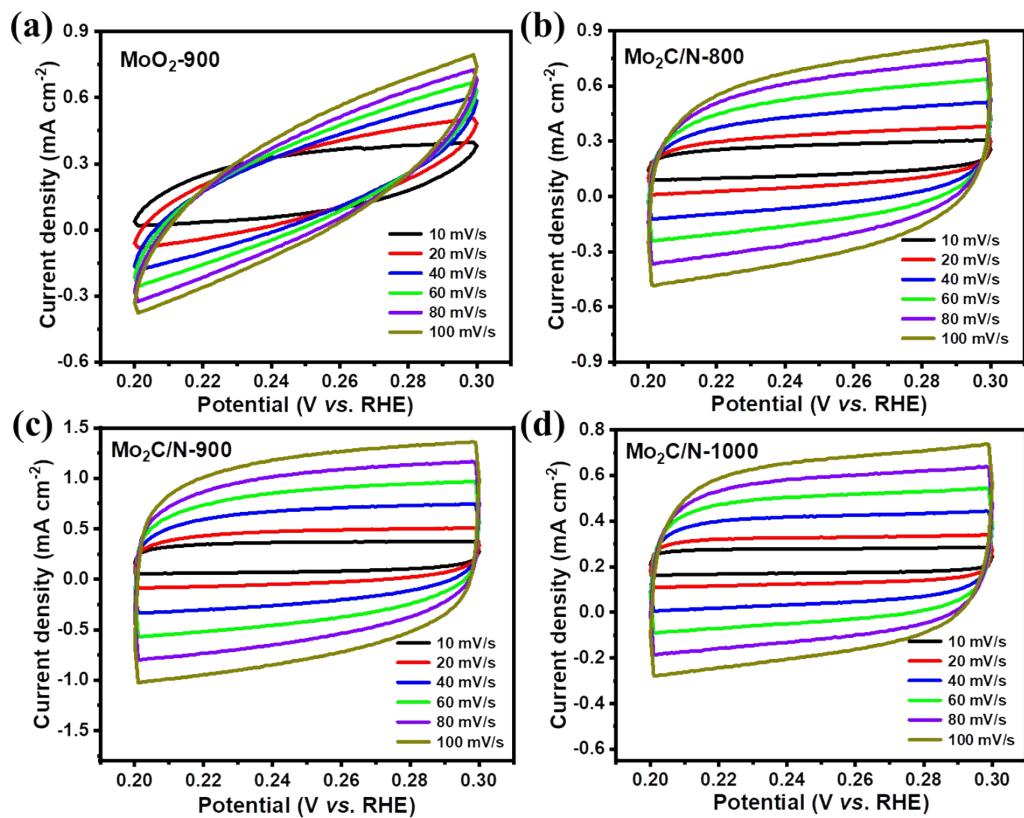


Fig.S4. (a-e) CV images of different sweep speeds of MoO_2 , $\text{Mo}_2\text{C/N-800}$, $\text{Mo}_2\text{C/N-900}$ and $\text{Mo}_2\text{C/N-1000}$, all tests were performed in 1 M KOH.

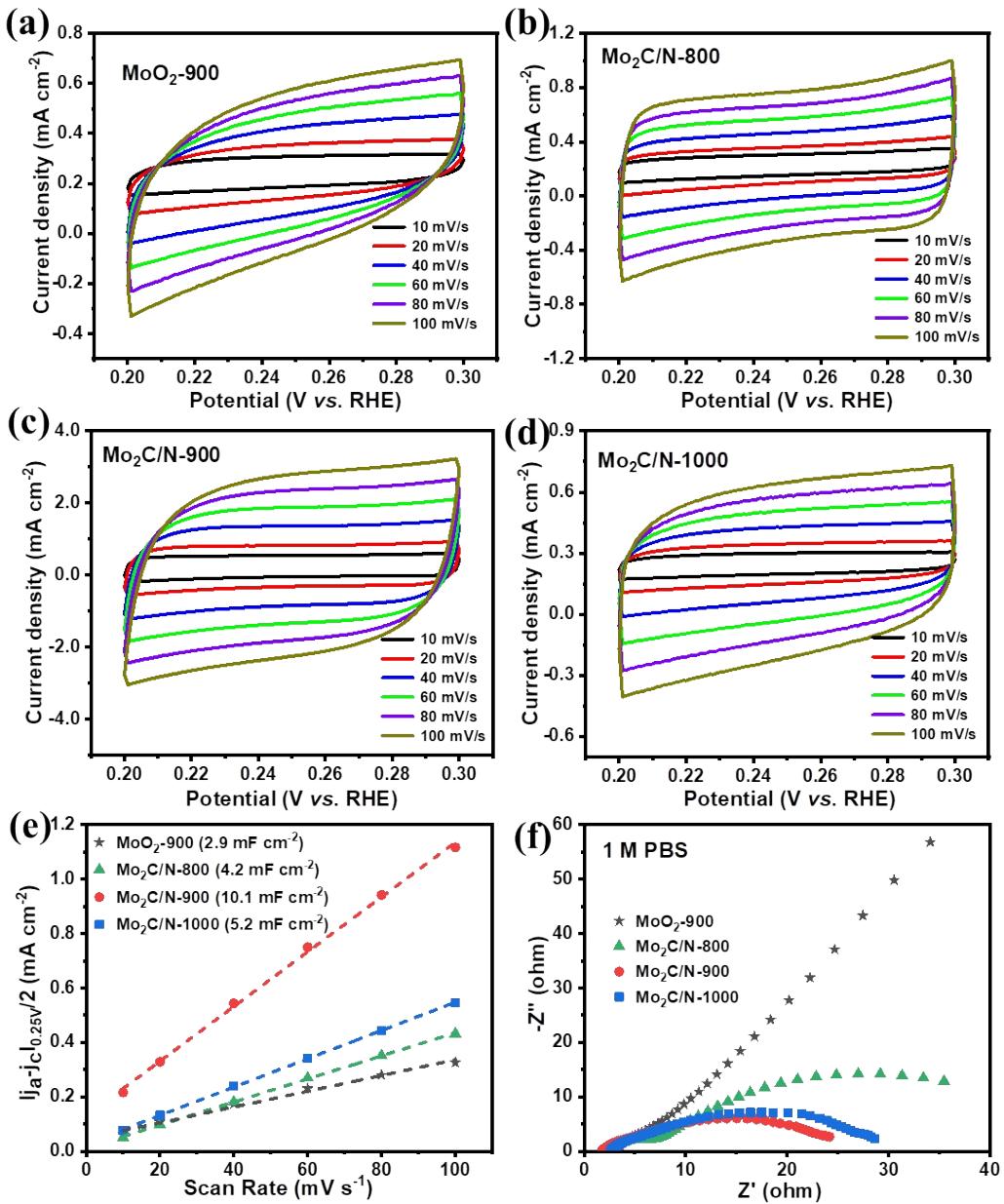


Fig.S5. (a-d) CV images of different sweep speeds, (e) the C_{dl} images of all materials and (f) Nyquist plots of different electrode, all tests were performed in 1 M PBS.

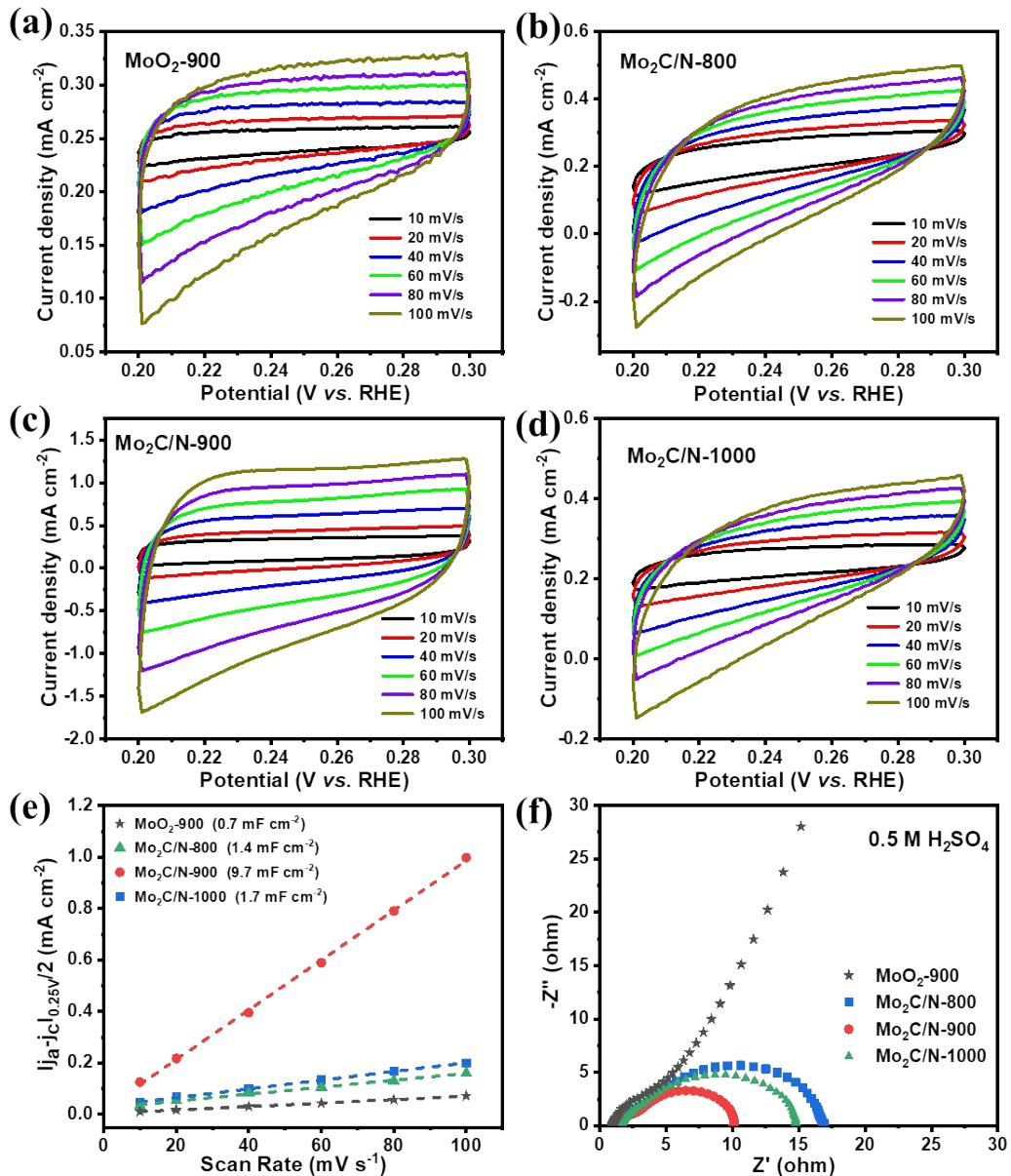


Fig.S6. CV images of different sweep speeds, (e) the C_{dl} images of all materials and (f) Nyquist plots of different electrode, all tests were performed in $0.5 \text{ M H}_2\text{SO}_4$.

Table S1 Hydrogen production efficiency of different catalyst MECs in 0.1 M KOH catholyte

Cathode materials	^a E _{ap} [V]	^b C _{total} [C]	^c CE [%]	^d R _{cat} [%]	^e R _{H2} [%]	^f Q _{H2} [L m ⁻² d ⁻¹]
CC	0.8	272.4	44.5	5.5	2.5	9.5
Pt _{20%} /C	0.8	583.1	95.3	86.9	82.9	138.5
Mo ₂ C/N-800	0.8	464.5	75.9	60.1	45.6	61.0
Mo ₂ C/N-900	0.8	524.9	85.8	71.5	61.4	103.0
Mo ₂ C/N-1000	0.8	476.3	77.9	62.4	48.6	75.5

a: applied voltage; *b*: total coulombic amount; *c*: coulombic efficiency; *d*: cathode hydrogen recovery rate; *e*: total hydrogen recovery rate; *f*: hydrogen production rate.

Table S2 Hydrogen production efficiency of different catalyst MECs in 0.1 M PBS catholyte

阴极材料	^a E _{ap} [V]	^b C _{total} [C]	^c CE [%]	^d R _{cat} [%]	^e R _{H2} [%]	^f Q _{H2} [L m ⁻² d ⁻¹]
CC	0.8	208.6	34.1	6.1	2.1	2.5
Pt _{20%} /C	0.8	552.7	90.4	85.6	75.5	105.0
Mo ₂ C/N-800	0.8	324.6	53.1	38.1	20.2	17.5
Mo ₂ C/N-900	0.8	542.6	88.7	48.6	43.1	41.0
Mo ₂ C/N-1000	0.8	419.1	68.5	35.6	24.4	27.2

References

1. M. Lyu, C. Zhang, X. Bao, J. Song and Z. Liu, *Advances in Mechanical Engineering*, 2017, **9**, 1687814017747158.
2. K. Kaygusuz, *Renewable and Sustainable Energy Reviews*, 2012, **16**, 1116-1126.
3. T. Ahmad and D. Zhang, *Energy Reports*, 2020, **6**, 1973-1991.
4. J. D. Holladay, J. Hu, D. L. King and Y. Wang, *Catalysis Today*, 2009, **139**, 244-260.
5. B. E. Logan, D. Call, S. Cheng, H. V. M. Hamelers, T. H. J. A. Sleutels, A. W. Jeremiassie and R. A. Rozendal, *Environmental Science & Technology*, 2008, **42**, 8630-8640.
6. H. Yuan and Z. He, *The Chemical Record*, 2017, **17**, 641-652.
7. H. Li, S. Chen, Y. Zhang, Q. Zhang, X. Jia, Q. Zhang, L. Gu, X. Sun, L. Song and X. Wang, *Nature Communications*, 2018, **9**, 2452.
8. C. Zhang, Y. Shi, Y. Yu, Y. Du and B. Zhang, *ACS Catalysis*, 2018, **8**, 8077-8083.
9. L. Zhang, J. Lu, S. Yin, L. Luo, S. Jing, A. Brouzgou, J. Chen, P. K. Shen and P. Tsakaras, *Applied Catalysis B: Environmental*, 2018, **230**, 58-64.
10. H. Yuan, S. Wang, X. Gu, B. Tang, J. Li and X. Wang, *Journal of Materials Chemistry A*, 2019, **7**, 19554-19564.
11. W.-F. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T. Muckerman, Y. Zhu and R. R. Adzic, *Angewandte Chemie International Edition*, 2012, **51**, 6131-6135.
12. H. Yan, Y. Xie, Y. Jiao, A. Wu, C. Tian, X. Zhang, L. Wang and H. Fu, *Advanced Materials*, 2018, **30**, 1704156.
13. Y. Li, Z. Dong and L. Jiao, *Advanced Energy Materials*, 2020, **10**, 1902104.
14. Q. Gao, W. Zhang, Z. Shi, L. Yang and Y. Tang, *Advanced Materials*, 2019, **31**, 1802880.
15. Y. Yang, W. Zhang, Y. Xiao, Z. Shi, X. Cao, Y. Tang and Q. Gao, *Applied Catalysis B: Environmental*, 2019, **242**, 132-139.
16. S. Lu, B. Lu, G. Tan, W. Moe, W. Xu, Y. Wang, D. Xing and X. Zhu, *Biosensors and Bioelectronics*, 2020, **167**, 112491.
17. K.-Y. Kim, S. E. Habas, J. A. Schaidle and B. E. Logan, *Bioresource Technology*, 2019, **293**, 122067.
18. Y. Huang, Q. Gong, X. Song, K. Feng, K. Nie, F. Zhao, Y. Wang, M. Zeng, J. Zhong and Y. Li, *ACS Nano*, 2016, **10**, 11337-11343.
19. K.-Y. Kim, W. Yang and B. E. Logan, *Environmental Science & Technology*, 2018, **52**, 7131-7137.
20. A. Miller, L. Singh, L. Wang and H. Liu, *Environment International*, 2019, **126**, 611-618.
21. L. Dai, C. Jia, B. Liu, Z. Wen, K. Li and S. Ci, *Sustainable Energy & Fuels*, 2022, **6**, 4982-4990.
22. C. Rao, Z. Zhao, Z. Wen, Q. Xu, K. Chen, T. Zhang and S. Ci, *Electrochimica Acta*, 2022, **431**, 141142.
23. L. Rago, J. A. Baeza and A. Guisasola, *Bioelectrochemistry*, 2016, **109**, 57-62.
24. F. Yang, Y. Chen, G. Cheng, S. Chen and W. Luo, *ACS Catalysis*, 2017, **7**, 3824-3831.
25. Y. Li, H. Zhang, M. Jiang, Y. Kuang, X. Sun and X. Duan, *Nano Research*, 2016, **9**, 2251-2259.
26. X. Liu and M. Antonietti, *Carbon*, 2014, **69**, 460-466.
27. J. Li, L. Tian, F. Liang, J. Wang, L. Han, J. Zhang, S. Ge, L. Dong, H. Zhang and S. Zhang, *Carbon*, 2019, **141**, 739-747.
28. Y. Zhao, D.-B. Ji, P. Wang, Y.-D. Yan, Y. Xue, H.-B. Xu, Y. Liang, H.-J. Luo, M.-L. Zhang and W. Han, *Chemical Engineering Journal*, 2018, **349**, 613-621.
29. W. Liu, X. Wang, F. Wang, K. Du, Z. Zhang, Y. Guo, H. Yin and D. Wang, *Nature*

- Communications, 2021, 12, 6776.
- 30. J. Qiu, Z. Yang and Y. Li, Journal of Materials Chemistry A, 2015, 3, 24245-24253.
 - 31. R. Ma, Y. Zhou, Y. Chen, P. Li, Q. Liu and J. Wang, Angewandte Chemie International Edition, 2015, 54, 14723-14727.
 - 32. X. Wang, Y. Fei, W. Wang, W. Yuan and C. M. Li, ACS Applied Energy Materials, 2019, 2, 8851-8861.
 - 33. S. Wu, M. Chen, W. Wang, J. Zhou, X. Tang, D. Zhou and C. Liu, Carbon, 2021, 171, 385-394.
 - 34. X. Wang, Y. Fei, J. Chen, Y. Pan, W. Yuan, L. Y. Zhang, C. X. Guo and C. M. Li, Small, 2022, 18, 2103866.
 - 35. X. Fan, X. Wang, W. Yuan and C. M. Li, Sustainable Energy & Fuels, 2017, 1, 2172-2180.
 - 36. Y. Ding, P. Cai and Z. Wen, Chemical Society Reviews, 2021, 50, 1495-1511.
 - 37. R. A. Rozendal, H. V. M. Hamelers, G. J. W. Euverink, S. J. Metz and C. J. N. Buisman, International Journal of Hydrogen Energy, 2006, 31, 1632-1640.