Supporting Information

Coral-like Fe-doped MoO_2/C heterostructure with rich oxygen vacancies for efficient electrocatalytic N_2 reduction

Zhifeng He[a], Xin Cui[a], Guangping Lei[b], Zeyi Liu[a], Xiaoyang Yang[a], Yifu Liu[a], Jiafeng Wan[a], Fangwei Ma[a] *

[a] Key Laboratory of Chemical Engineering Processes&Technology for High-efficiency Conversion (College of Heilongjiang Province), School of Chemistry and Material Science. Heilongjiang University, Harbin, 150080, China.
[b] School of Energy and Power Engineering North University of China, Taiyuan, 030051, China.

*Email: fangwei_ma@hotmail.com.

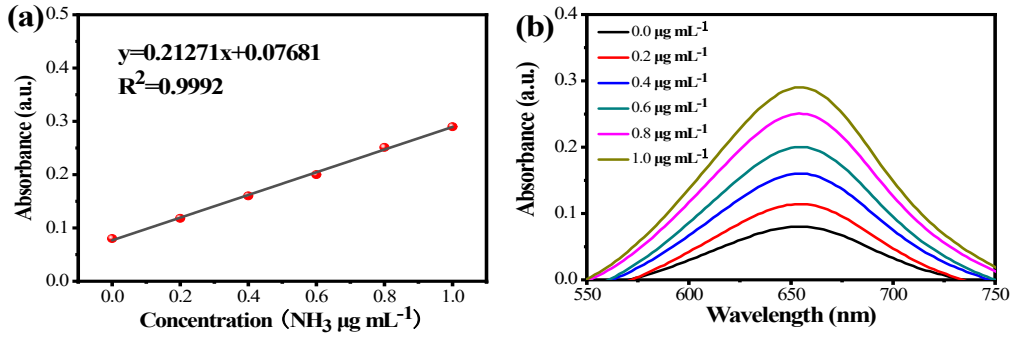

Fig. S1 (a) Calibration curve used for calculation of NH_4^+ concentrations. (b) UV-Vis absorption spectra of various NH_4^+ concentrations using the method of indophenol blue method after incubation for 2 hours at room temperature.

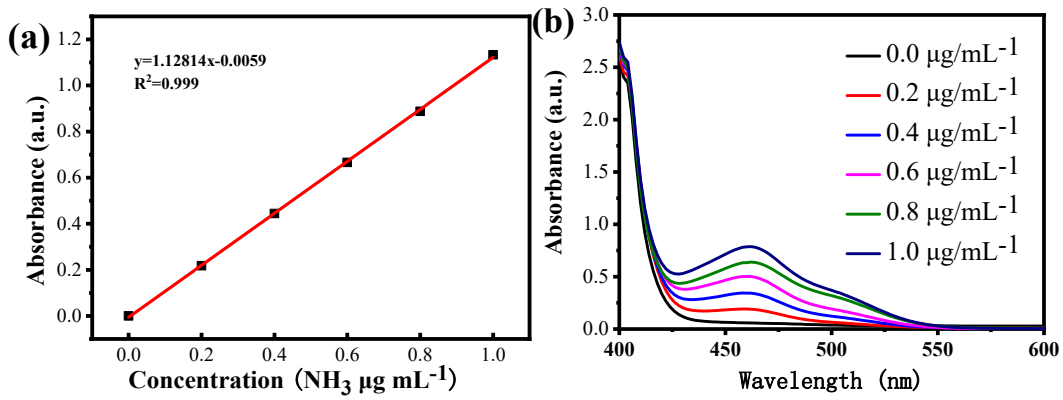

Fig. S2 (a) Calibration curve used for calculation of N_2H_4 concentrations. (b) UV-Vis absorption spectra of various N_2H_4 concentrations using the method of Watt and Chrisp after incubation for 20 min at room temperature.

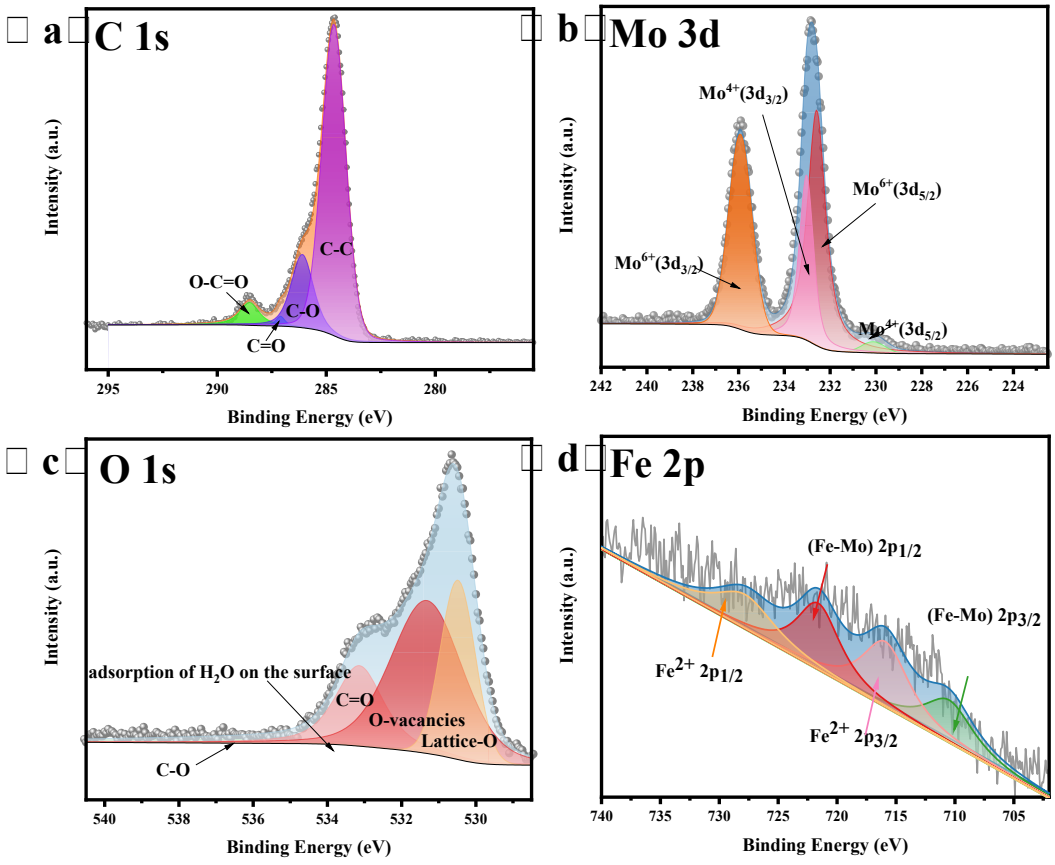

Fig. S3 (a-d) XPS spectrum of Fe-MoO_2/C (1:100): (a) C 1s; (b) Mo 3d; (c) O 1s; (d) Fe 2p.

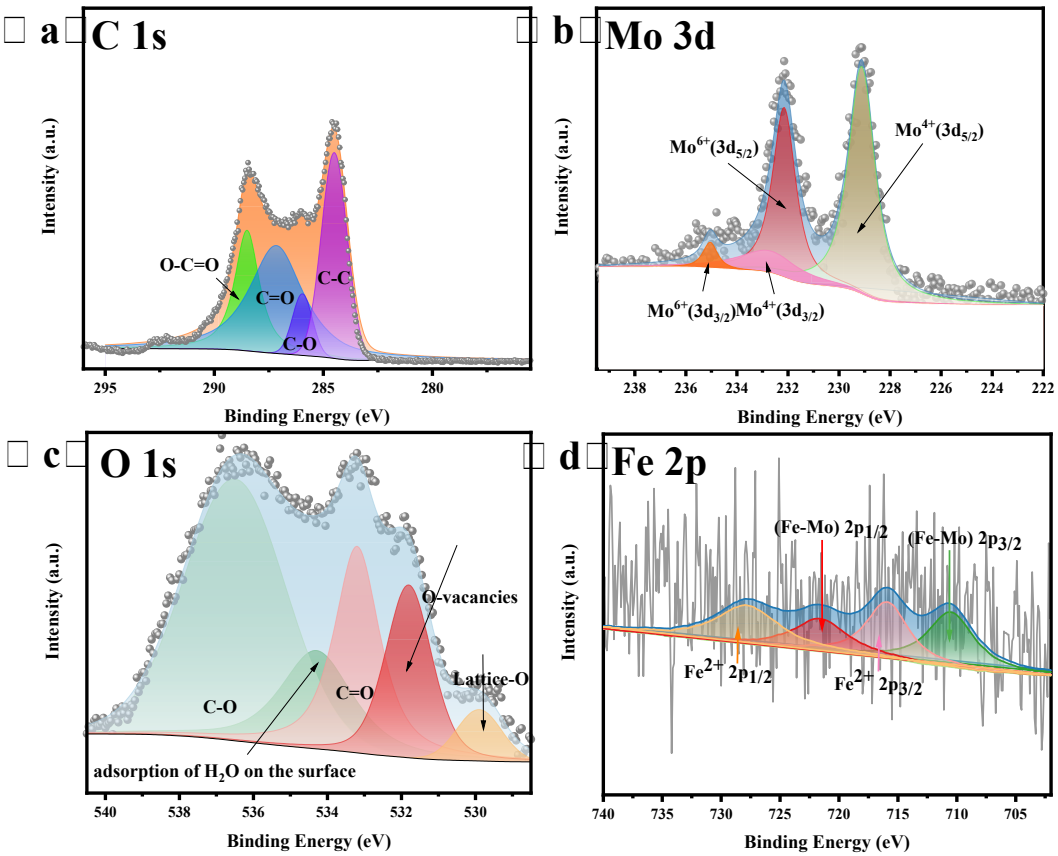

Fig. S4 (a-d) XPS spectrum of Fe-MoO_2/C (1:50): (a) C 1s; (b) Mo 3d; (c) O 1s; (d) Fe 2p.

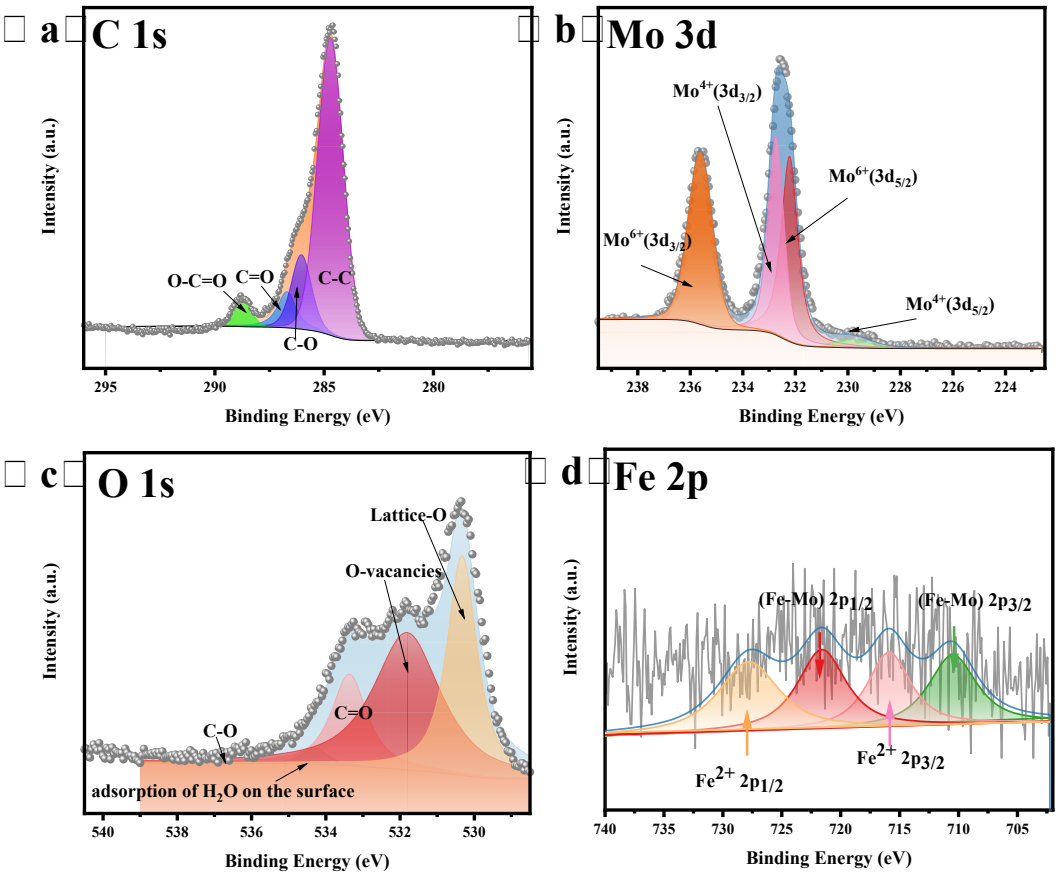

Fig. S5 (a-d) XPS spectrum of Fe-MoO_2/C (1:25): (a) C 1s; (b) Mo 3d; (c) O 1s; (d) Fe 2p.

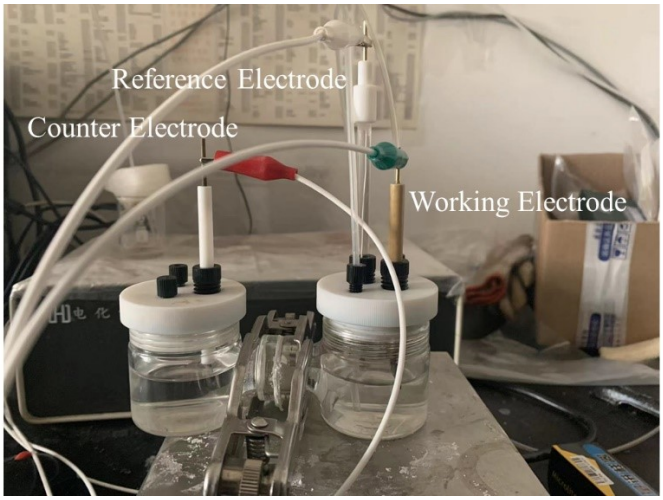

Fig. S6 Photograph of the reactor.

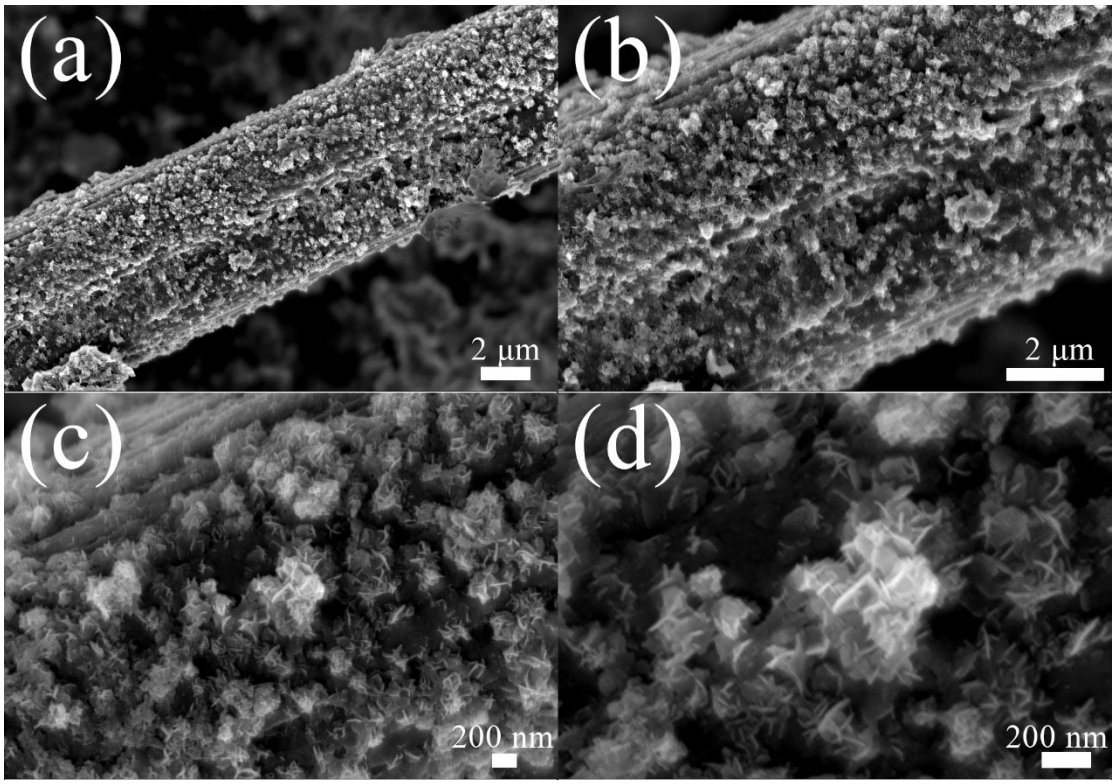

Fig. S7 High and low magnification SEM images of Vo-Fe-MoO_2/C (1:50) through e-NRR (a-d).

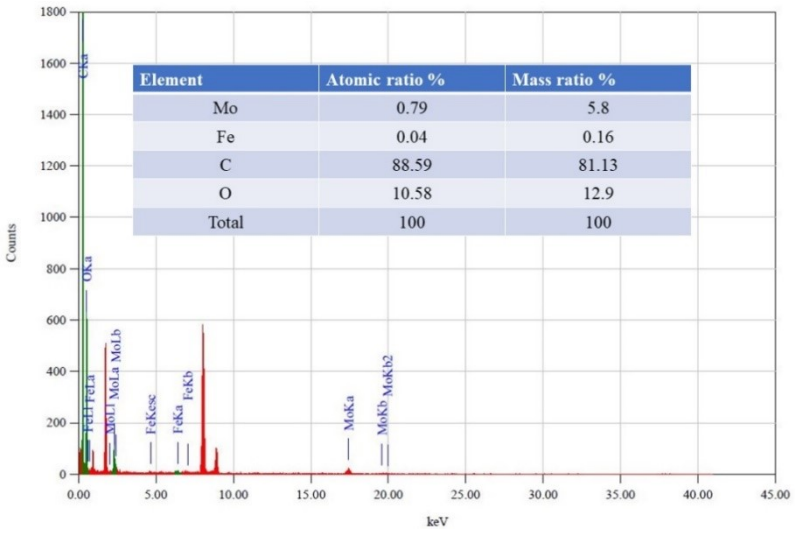

Fig. S8 EDX spectra of Vo-Fe-MoO_2/C (1:50)

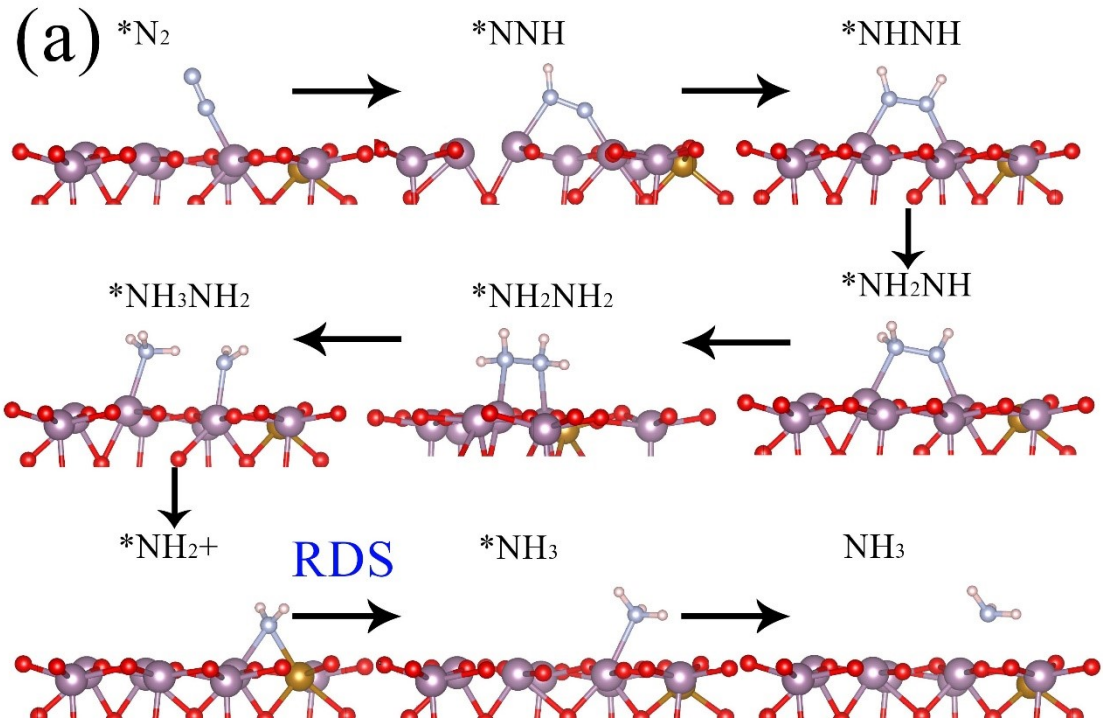

Fig. S9 Schematic illustrations showing the alternating for N_2 electroreduction over Fe-MoO_2/C (1:50) structure.

Table S1 The elemental ratio of sample from ICP

Catalyst	**Element**	**ICP Element content (W%)**
Fe-MoO_2/C (1:50)	Mo	60.5776%
	Fe	1.5336%
Vs-Fe-MoO_2/C (1:50)	Mo	46.4845%
	Fe	1.6986%

Table S2 Comparison of the electrocatalytic N_2 reduction performance for Vo-Fe-MoO_2/C (1:50) with other aqueous-based NRR electrocatalysts.

Catalyst	Potential (V *vs* RHE)	Electrolyte	NH_3 yield rate ($\mu g\ h^{-1}\ mg^{-1}$)	Faradaic efficiency (%)	Ref.

Vo-Fe-MoO_2/C(1:50)	-0.5	0.1 M Na_2SO_4	15.87± 0.3	13.4	This work
Vo-MoO_2@C	-0.5	0.1 M Na_2SO_4	9.75	3.24	1
Fe−S−C	-0.1	0.1 M KOH	8.8± 1.3	6.1± 0.9	2
Ru–SnO_2/CC	-0.2	0.1 M Na_2SO_4	4.83	17.01	3
$Ce_{1/3}NbO_3$	-0.8	0.1 M Na_2SO_4	10.34	6.87	4
Cu/OV-TiO_2	-0.5	0.1 M Na_2SO_4	13.6	17.9	5
Mo_2C-MoO_2	-0.15	0.1 M Na_2SO_4	13.94 ± 0.39	12.72± 0.58	6

References

1. Y. Du, Z. He, F. Ma, Y. Jiang, J. Wan, G. Wu and Y. Liu, *Inorg. Chem.*, 2021, **60**, 4116-4123.
2. M. I. Ahmed, L. J. Arachchige, Z. Su, D. B. Hibbert, C. Sun and C. Zhao, *ACS Catal.*, 2022, **12**, 1443-1451.
3. Y. Sun, Q. Wu, H. Li, S. Jiang, J. Wang, W. Zhang, X. Song, B. Jia, J. Qiu and T. Ma, *Carbon*, 2022, **195**, 199-206.
4. X. Hu, Y. Sun, S. Guo, J. Sun, Y. Fu, S. Chen, S. Zhang and J. Zhu, *Appl. Catal. B*, 2021, **280**, 119419.
5. W. P. Utomo, H. Wu and Y. H. Ng, *Small*, 2022, **18**, 2200996.
6. Y. Wan, Z. Wang, J. Li and R. Lv, *ACS Nano*, 2022, **16**, 643-654.