

Supporting information

CuO/Mn₂O₃ heterojunction catalyst for efficient electrocatalytic nitrate reduction to ammonia

Xuetao Cheng, Huilin Zhao, Chao Fan, Yun Duan and Yan-Qin Wang*

Inner Mongolia Key Laboratory of Chemistry and Physics of Rare Earth Materials,
College of Chemistry and Chemical Engineering, Inner Mongolia University, 24
Zhaojun Road, Hohhot 010021, P. R. China
E-mail: yqwang_chem@imu.edu.cn

1. Experimental

Materials:

Carbon cloth (CC) was purchased from Shanghai Xianren Instrument and Meter Co., Ltd, CuSO_4 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, urea, potassium nitrate, potassium hydroxide, Potassium nitrate- ^{15}N were purchased from Shanghai Maclin Biochemical Technology Co., Ltd. All chemicals were not proceeded for further purification and treatment.

2. Experimental Section

Synthesis of $\text{CuO}/\text{Mn}_2\text{O}_3$: Carbon cloth (CC) was pretreated before use. The specific steps were as follows: first, CC was cut into 2 cm * 2 cm and soaked in concentrated nitric acid, and heated in an oil bath at 80°C for 8 hours. Then, CC was rinsed several times with deionized water and alcohol. 0.264 g (1.65 mmol) CuSO_4 , 0.262 g (1.65 mmol) $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 0.198 g (3.3 mmol) urea were added into 15 mL of deionized water and sonicated for 5 minutes to completely dissolve, which was added into a 20 mL Teflon autoclave with a piece of above pretreated CC. The autoclave was sealed and heated in an oven at 135°C for 12 hours, which the obtained product was then annealed at 500°C in a muffle furnace for two hours, and the finally obtained product was named as $\text{CuO}/\text{Mn}_2\text{O}_3$.

Synthesis of CuO and Mn_2O_3 : The preparation of CuO and Mn_2O_3 was similar to that of $\text{CuO}/\text{Mn}_2\text{O}_3$, except that the reactant was replaced by only CuSO_4 or $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ during the synthesis process, and the corresponding obtained product was named as CuO or Mn_2O_3 .

3. Material characterization

X-ray diffraction (XRD) measurements were performed by a PANalytical Empyrean diffractometer at a scanning rate of 0.013° in the Bragg angle ranging from 5° to 80° with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were performed by a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers. All spectra were calibrated with the C-C peak of $\text{C}1s$ orbitals as 284.8 eV. Scanning electron

micrographs were measured by a QUANTA430 field emission scanning electron microscope (FE-SEM). Transmission electron microscopy and scanning transmission electron microscopy characterizations were performed on an FEL-Tecnai G220 field-emission transmission electron microscope (FE-TEM). Ultraviolet-visible (UV-Vis) spectroscopy data were measured by using a UV-Vis-NIR spectrometer (Cary 5000) with an integrating sphere unit and automation of reflectance measurement unit, and the measurements were corrected by baseline/blank correction with dark correction. ^1H NMR spectra were recorded at a Bruker NMR instrument (600 MHz), chemical shifts were reported in ppm using tetramethylsilane as an internal standard in d -DMSO solvent.

Electrochemical measurements of nitrate reduction reaction (NO_3RR)

The electrochemical measurements were carried out using a CHI 660E electrochemical workstation in a H-type electrolytic cell separated by a Nafion 211 membrane. $\text{CuO}/\text{Mn}_2\text{O}_3$ catalysts, Hg/HgO and platinum foil were used as the working electrode, reference electrode and counter electrode, respectively. 40 mL of 0.1 M KOH and 0.1 M KNO_3 solution were added into the cathode and anode chambers for NO_3^- reduction. Before the ENO_3RR experiment, high purity Argon gas (99.99%) was fed into the electrolyte for 15 minutes. Then the LSV (linear scanning voltammetry) measurements were proceeded at a rate of 5 mV s^{-1} ($-0.2 \sim -1.2 \text{ V vs. RHE}$). Furthermore, the i - t (one-hour chronoamperometry) test was applied to investigate ammonia yield and Faraday efficiency (FE) at five different potentials. All potentials were referenced to the reversible hydrogen electrode (RHE) based on the Nernst equation ($E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \times \text{pH} + 0.098$).

Determination of ion concentration

The ultraviolet-visible (UV-Vis) spectrophotometer was used to detect the ion concentration of pre- and post-tested electrolytes after diluting to appropriate concentration to match the range of calibration curves. The specific test methods are as follows:

Determination of ammonia

Ammonia-N was determined using salicylic acid-potassium sodium citrate

chromogenic reagent as the color reagent. First, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to 2 mL to the detection concentration range. Next, 2 mL salicylic acid-potassium sodium citrate chromogenic reagent was added into the diluted electrolyte, and mixed thoroughly. Then, 1 mL sodium hypochlorite and 0.2 mL sodium nitroprusside solution were put into the above solution. Then, the above-mentioned mixed solution was tested with a UV-Vis spectrophotometer in the wavelength range of 800 ~ 500 nm, and the absorbance values at 655 nm was recorded. The concentration-absorbance curve was calibrated using a series of standard ammonium chloride solutions.

Determination of NO_3^-

Firstly, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to 5 mL. Then, 0.6 mL 1 M HCl and 0.01 mL 0.8 wt% sulfamic acid solution were added into the aforementioned solution. The absorption spectrum was measured using a UV-Vis spectrophotometer and the absorption intensity at wavelengths of 220 and 275 nm were recorded. The final absorbance was calculated using the following formula: $A = A_{220\text{nm}} - 2A_{275\text{nm}}$. The concentration-absorbance curve was calibrated using a series of standard potassium nitrate solutions.

Determination of NO_2^-

Color reagent was a mixture of p-aminobenzenesulfonamide (0.1 g), N-(1-naphthyl) ethylenediamine dihydrochloride (0.01 g), deionized water (5 mL) and phosphoric acid (0.294 mL, $\rho = 1.685 \text{ g mL}^{-1}$). First, the electrolyte was diluted to the detection concentration range. Subsequently, 1 mL color reagent was added into the diluted electrolyte in a colorimetric cuvette. After shaking and standing for 10 minutes, the absorbance was measured at 540 nm using UV-Vis spectrophotometer, and then the concentration of NO_2^- was calculated from the calibration curve. Calibration curves were obtained using a series of standard concentration NaNO_2 solutions.

Determination of N_2H_4

First, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to 2 mL to the detection concentration range. Subsequently, 1 mL color reagent was added into the diluted electrolyte in a colorimetric cuvette. Color reagent

was a mixture of anhydrous ethanol (50 mL), HCl (5 mL) and p-C₉H₁₁NO (1 g). The absorption intensity at a wavelength of 455 nm using UV-Vis spectrophotometer was recorded after standing for 20 min.

Isotope Labeling Experiments

K¹⁵NO₃ was used as the feeding N-source to perform the isotopic labeling nitrate reduction experiments to verify the source of ammonia. 0.1 M KOH was used as the electrolyte, and K¹⁵NO₃ with a concentration of 0.1 M ¹⁵NO₃⁻ was added into the cathode compartment as the reactant. After electroreduction, electrolyte with obtained ¹⁵NH₄⁺ was taken out and the pH value was adjusted to be weak acidic with 1 M HCl for qualitative analysis by ¹H NMR (600 MHz) with external standards of maleic acid.

4. Supporting Figures and Table

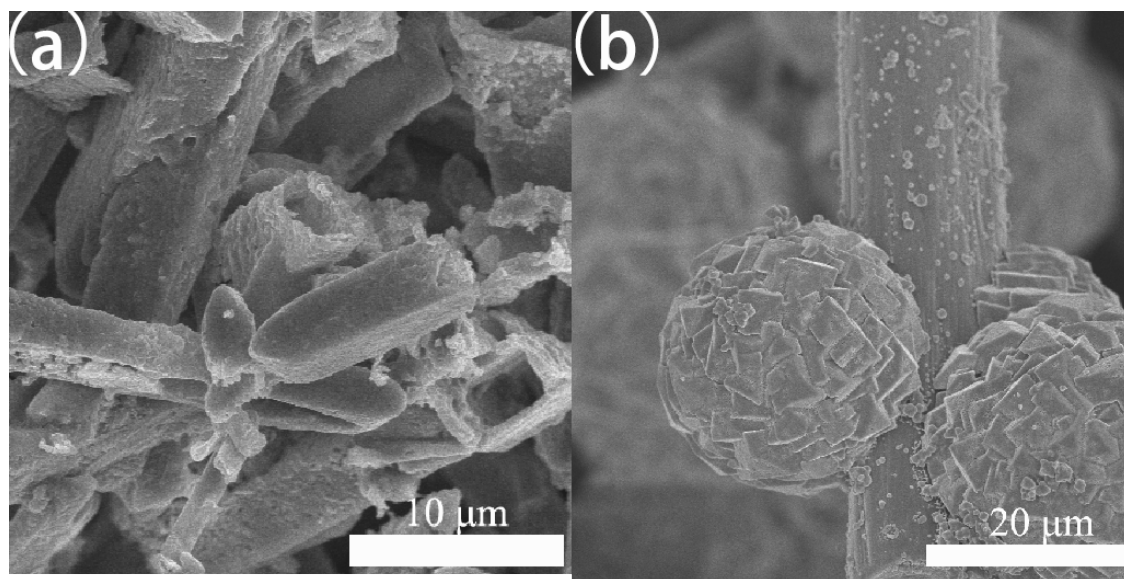


Fig. S1. SEM images of (a) CuO, (b) Mn₂O₃.

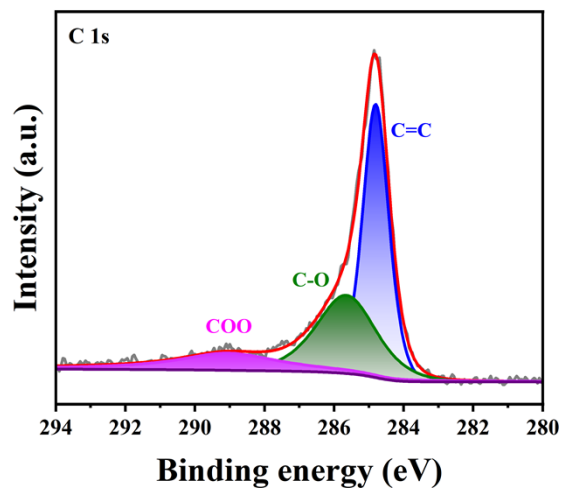


Fig. S2. The high-resolution XPS spectra of C1s

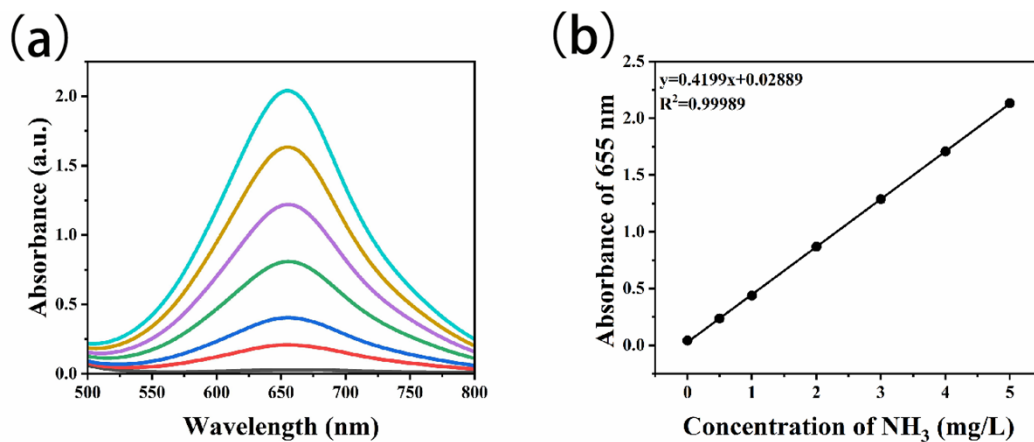


Fig. S3. (a) UV-Vis absorption spectra for various concentrations of NH_4^+ ions. (b) Calibration curve used to estimate the concentration of NH_4^+ ions.

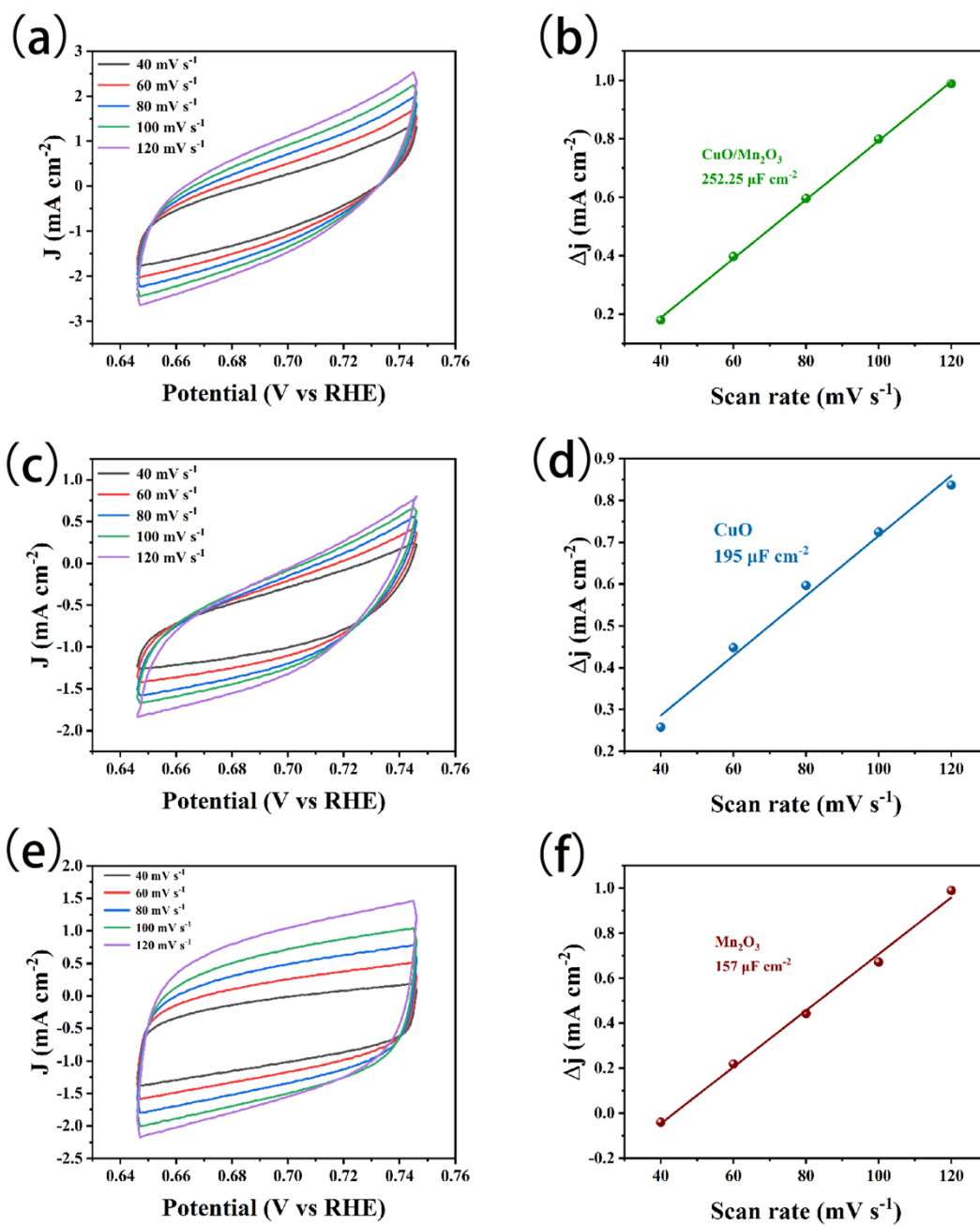


Fig. S4. (a) The CV curves and (b) the determination of double layer capacitance of $\text{Cu/Mn}_2\text{O}_3$ at different scan rates. (c) The CV curves and (d) the determination of double layer capacitance of CuO at different scan rates. (e) The CV curves and (f) the determination of double layer capacitance of Mn_2O_3 at different scan rates.

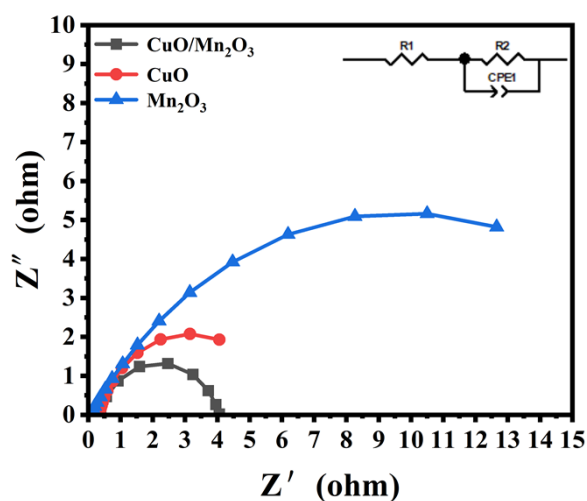


Fig. S5. Nyquist plots of CuO/Mn₂O₃, CuO and Mn₂O₃ at -0.7 V (vs. RHE) in 0.1 M KOH solution.

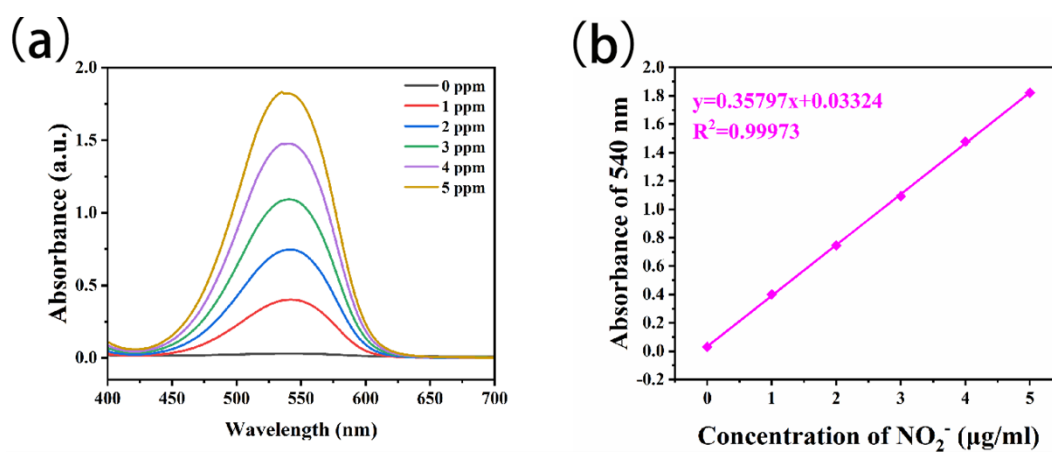


Fig. S6. (a) UV-Vis absorption spectroscopies for various concentrations of NO₂⁻ ions. (b) Calibration curve used to estimate the concentration of NO₂⁻ ions.

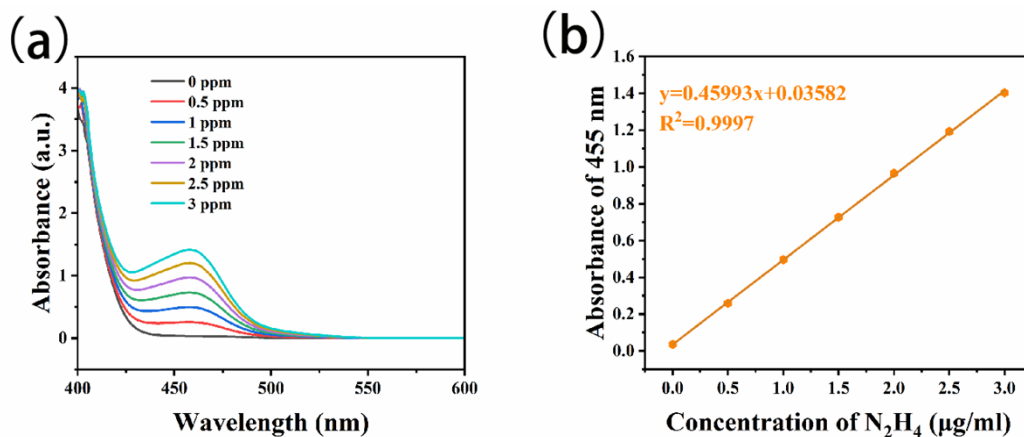


Fig. S7. (a) UV-Vis absorption spectroscopies for various concentrations of N_2H_4 . (b) Calibration curve used to estimate the concentration of N_2H_4 .

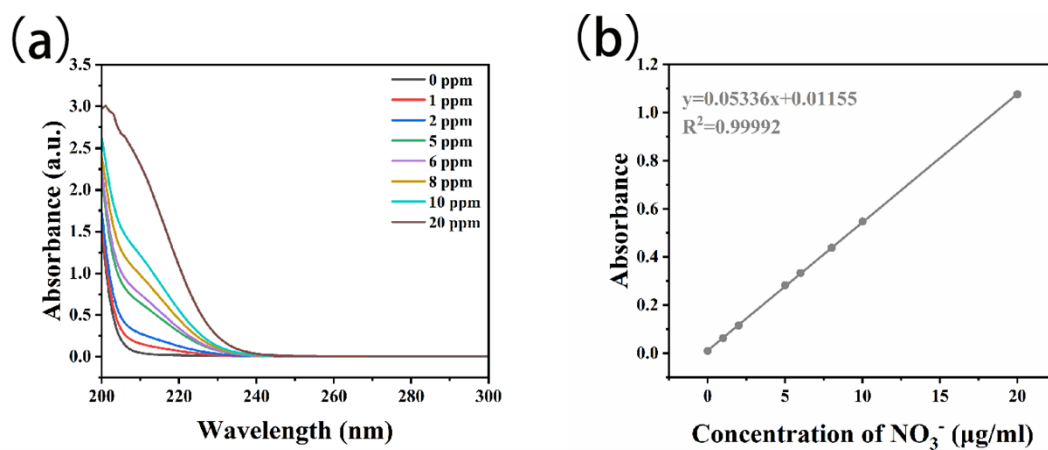


Fig. S8. (a) UV-Vis absorption spectroscopies for various concentrations of NO_3^- ions. (b) Calibration curve used to estimate the concentration of NO_3^- ions.

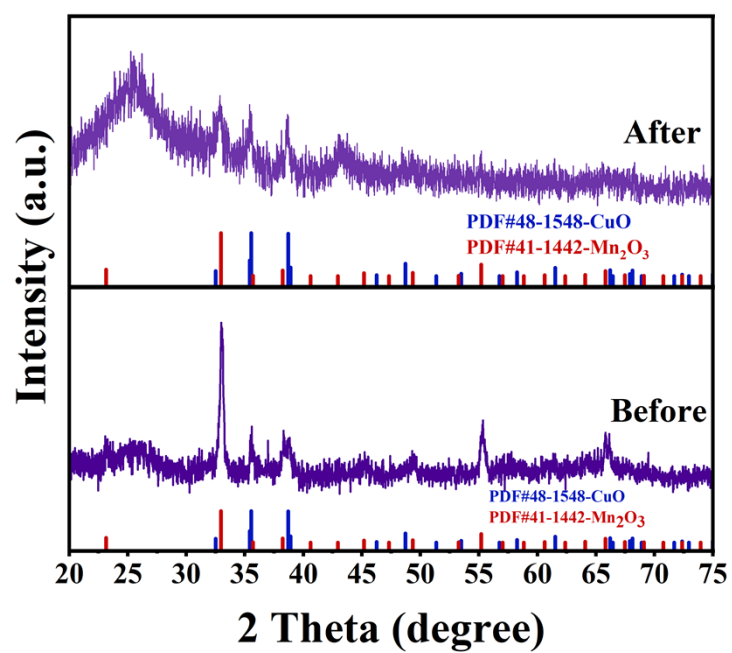


Fig. S9. XRD patterns of CuO/Mn₂O₃ before and after NO₃RR testing.

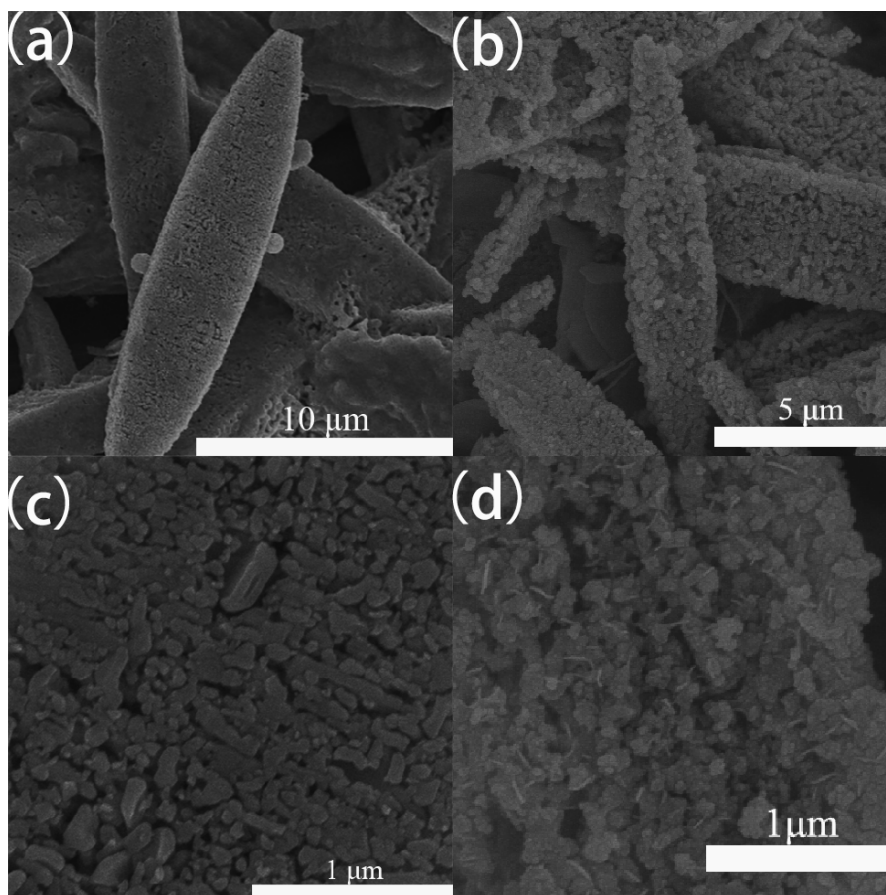


Fig. S10. SEM images of CuO/Mn₂O₃ before (a), (c) and after (b), (d) NO₃RR tests.

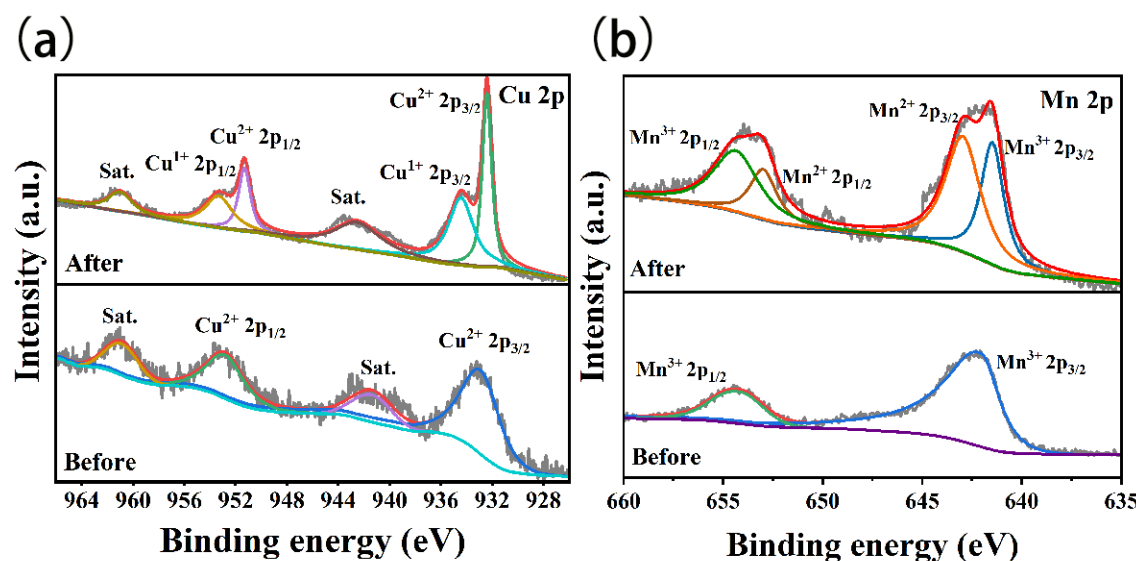


Fig. S11. The high-resolution XPS spectra of CuO/Mn₂O₃ before (a), and after cycle tests (b).

Fig. S1. A comparison of the NO₃RR performance of CuO/Mn₂O₃ with the electrocatalysts recently reported in literature in alkaline medium.

Catalyst	Electrolyte	NH ₃ yield (mg h ⁻¹ cm ⁻²)	FE _{NH3}	Potential (vs. RHE)	Ref
CuO/Mn ₂ O ₃	1 M KOH (0.1 M KNO ₃)	12.99	98.44%	-0.7 V	This work
Fe-V ₂ O ₅	1.0 M KOH (0.1 M KNO ₃)	12.5	97.1%	-0.7 V	[1]
CoP/CC	1 M NaOH (2 mM NaNO ₃)	0.32	65%	-0.4 V	[2]
CoO@NCN	0.1 M NaOH (0.1 M NaNO ₃)	9.04	93.8%	-0.6 V	[3]
30Cu-Co ₃ O ₄	0.1 M KOH (0.1 M NaNO ₃)	9.9	92.4%	-0.4 V	[4]

	M KNO ₃)						
Cu@Ni ₂ P-	1 M KOH	6.36	94.63%	-0.2 V	[5]		
NF	(20 mM KNO ₃)						
Cu@B-	0.1 M KOH	(0.1 9.35	94.6%	-0.77 V	[6]		
SnS _{2-x}	M KNO ₃)						
Ru-	0.1 M KOH	(0.1 2.18	48.3%	-0.7 V	[7]		
Cu/Cu ₂ O@T	M KNO ₃)						
i ₃ C ₂							
Cu@ZnO	0.1 M KOH	(0.05 6.03	89.14%	-0.6 V	[8]		
NWA	M KNO ₃)						
MWCNTs	0.1 M KOH	(0.1 4.03	84.72%	-0.16 V	[9]		
	M KNO ₃)						
CoS ₂ /MoS ₂	0.1 M KOH	7.5	97.07%	-0.25 V	[10]		
	(600ppm KNO ₃)						
GDY-MnO _x	0.1 M KOH	(0.1 6.5	95.4%	-0.9 V	[11]		
	M KNO ₃)						
i-	1 M KOH	(0.1 M 4.3	94.3%	-0.25 V	[12]		
Ag/Co ₃ O ₄ N	KNO ₃)						
Ws							

References

- [1] N. N. Zhang, G. K. Zhang, P. Shen, H. Zhang, D. W. Ma, K. Chu, *Adv. Funct. Mater.*, 2023, **33**, 2211537
- [2] H. Zhang, G. Q. Wang, C. J. Wang, Y. L. Liu, Y. Yang, C. X. Wang, W. M. Jiang, L. M. Fu, J. Xu, *J. Electroanal. Chem.*, 2022, **910**, 116171.
- [3] Q. R. Chen, J. Liang, L. C. Yue, Y. S. Luo, Q. Liu, N. Li, A. A. Alshehri, T. S. Li, H. R. Guo, X. P. Sun, *Chem. Commun.*, 2022, **58**, 5901 – 5904.
- [4] M. He, R. Chen, Y. Zhong, H. Li, S. Chen, C. Zhang, S. Deng, F. Gao, *Colloid Surfaces.*, 2024, **681**, 132746.

- [5] M. Li, L. P. Sun, L. H. Huo and H. Zhao , *Appl. Catal. A.* , 2024, **676**, 119650.
- [6] H. Li, Y. Z. Wang, S. H. Chen, F. Peng and F. M. Gao, *Small*, . 2024, 2308182.
- [7] F. Zhao, G. X. Li, Q. Q. Hua, J. H. Cao, J. l. Song, L. G. Gao, T. l. Ma, X. F. Ren and A. M. Liu, *Catal. Sci. Technol.*, 2023, **13**, 5543 – 5548.
- [8] A. l. Feng, Y. D. Hu, X. X. Yang, H. J. Lin, Q. Wang, J. Xu, A. M. Liu, G. Wu and Q. Y. Li, *ACS Catal.* , 2024, **14**, **8**, 5911 – 5923.
- [9] M. H. Ye, X. l. Jiang, Y. G. Zhang, Y. Liu, Y. X. Liu and L. Zhao, *Nanomaterials*, . 2024, **14**, 102.
- [10] Z. X. Tan, F. Du, M. q. Tong, J. d. Hu, N. Zhang, S. y. Huang and C. X. Guo, *Energy Fuels.* , 2023, **37**, **23**, 18085 – 18092.
- [11] X. Y. Luan, L. Qi, Z. Q. Zheng, S. Y. Zhao, Y. Q. Gao, Y. R. Xue and Y. l. Li, *Chem. Commun.* , 2023, **59**, 7611.
- [12] S. l. Wu, Y. Y. Jiang, W. J. Luo, P. Xu, L. L. Huang, Y. W. Du, H. Wang, X. M. Zhou, Y. J. Ge, J. J. Qian, H. G. Nie and Z. Yang, *Adv. Sci.* , 2023,**10**, 2303789.