The following supplements is included as supporting materials for this paper:

Table S1 EIS parameters for bare NF, Co_3O_4/NF and Cu-Co_3O_4/NF

cathode	R_s (Ω cm^2)	R_{ct} (Ω cm^2)
NF	4.143	24.69
Co_3O_4/NF	4.579	7.562
Cu-Co_3O_4/NF	4.093	6.059

Table S2 Energy consumption of different cathodes

Cathode	Applied current (A)	Voltage (V)	Energy consumption (K Wh/g NO_3^--N)
NF	0.2	6.83	5.4099
Co_3O_4/NF	0.2	5.82	0.2836
Cu-Co_3O_4/NF	0.2	3.52	0.1164

Table S3 Comparison of eNO_3RR with other cathodes

Electro-catalysts	Preparation method	Electrolyte	Reaction time	NO_3^--N conversion	NH_4^+-N selectivity	Ref.
Cu(I/II)@NF	hydrothermal	50 mg L^{-1} NO_3^- + 0.05 M Na_2SO_4	24 h	95.4%	/	[1]
Porous Cu	coprecipitation + calcination	0.01 M NO_3^- + 0.1 M $HClO_4$	8 h	98%	94%	[2]
Cu_2O/CuO/CF	solvent oxidation + electrocatalytic reduction	5 mM NO_3^- + 0.1 M KOH	60 h	100%	99.35%	[3]
Co_3O_4/NF	hydrothermal + calcination	0.1 M NO_3^- + 1.0 M NaOH	2 h	95%	85.36%	[4]
Fe-CoO/CuO@CF	hydrothermal + calcination	0.1 M NO_3^- + 3.5 M KCl	2 h	93.8%	/	[5]
Cu_2O-Cu@Ti	electrodeposition	0.01 M NO_3^- + 1 M KOH	1.5 h	90%	79%	[6]
Cu-Pt	electrodeposition	30 mg L^{-1} NO_3^--N + 12.5 mM Na_2SO_4	2 h	94%	84%	[7]
Co-P/TP	electrodeposition	200 mg L^{-1} NO_3^- + 0.2 M Na_2SO_4 +	10 h	86.9%	/	[8]
NiCoP/NF	electrodeposition	50 mg L^{-1} NO_3^- + 0.05 M Na_2SO_4	5 h	97.68%	95.44%	[9]
CoO/Cu	electrodeposition + calcination	0.04 M NO_3^- + 0.4 M Na_2SO_4	0.5 h	87.6%	97.3%	[10]
Cu-Co_3O_4	electrodeposition + calcination	50 mg L^{-1} NO_3^- + 0.01 M Na_2SO_4	2 h	96.78%	97.58%	This work

Table S4 Reaction energy consumption at different electrolyte concentrations*

Electrolyte concentration（M）	Solution conductivity（μS/cm）	Reaction voltage（V）	NO_3^--N removal rate（%）	Energy consumption（kWh/g NO_3^--N）
0.01	2720	3.52	97.77	0.1164
0.05	8940	2.21	97.58	0.0724
0.1	15530	2.03	96.75	0.0671
0.2	25800	1.87	95.91	0.0624

* data were obtained as the average value of three independent experiments.

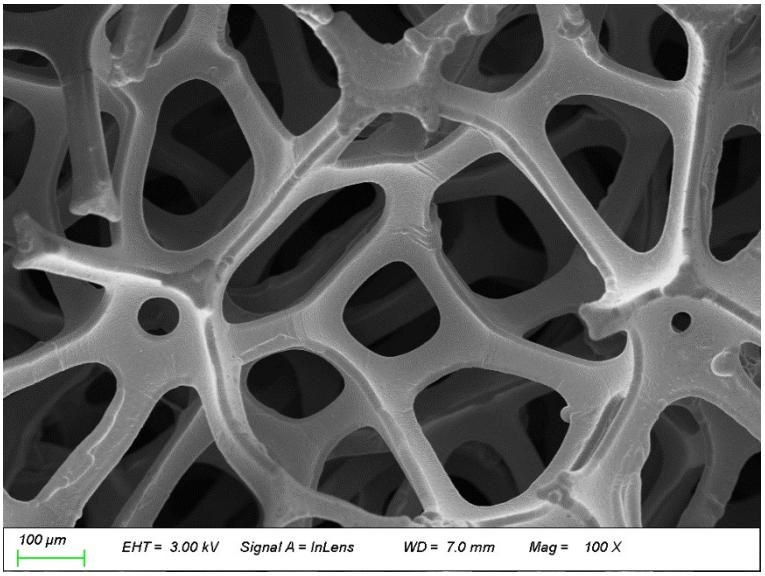

Fig. S1 SEM image of bare NF

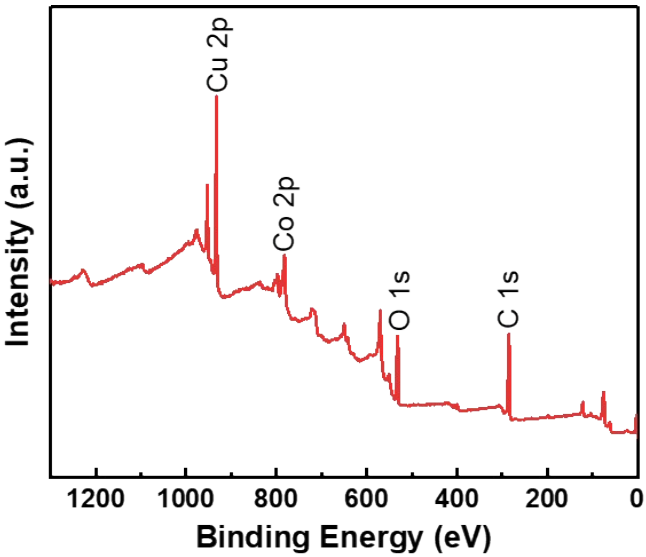

Fig. S2 XPS survey spectrum for Cu-Co_3O_4/NF

Fig. S3 Hydrogen evolution in high current reaction

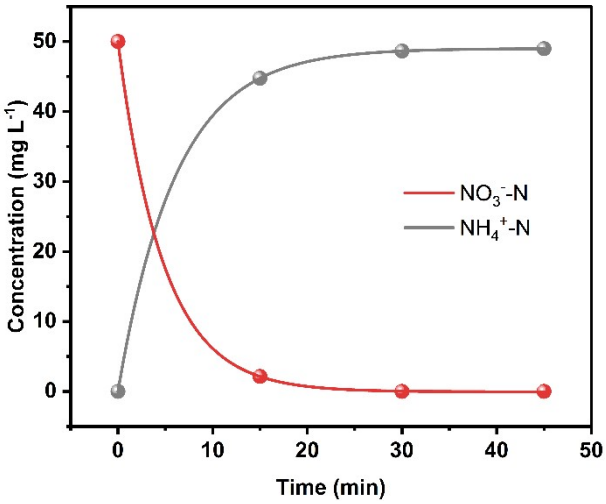

Fig. S4 Time-dependent NO_3^--N and NH_4^+-N concentrations in dual-chamber reactor (experimental conditions: 50 mg L^{-1} NO_3^--N, 0.2 M Na_2SO_4)

References:

1. W. Ding, K. Yan, Y. Li, C. Hu, H. Yi, C. Liu, C. Wang, C. Zhou and D. Ma, Electrocatalytic reduction of nitrate by Cu valence-regulated heterojunction electrode: A key role of Cu(I/II) composites and high nitrate reduction efficiency, *Journal of Environmental Chemical Engineering*, 2024, **12**, 114694.
2. J. F. Su and D. Mohanty, A porous copper catalyst for electrochemical nitrate reduction to ammonium, *Journal of Environmental Chemical Engineering*, 2025, **13**, 115596.
3. C. Fu, H. Wu, J. Sun, G. Song and M. Zhou, Paired electrocatalysis for simultaneous anodic oxidation of tetracycline and cathodic nitrate reduction to ammonia, *Journal of Hazardous Materials*, 2025, **489**, 137553.
4. D. Zhao, J. Yao, C. Ma, A. Wang, H. Xie, J. Zhao, J. Yan, K. Zhu, Y. Zhu, D. Cao and G. Wang, 3D integrated non-noble metal oxides nano arrays for enhanced nitrate electroreduction to ammonia, *Journal of Power Sources*, 2024, **592**, 233945.
5. J. Hu, C. Tang, Z. Bi, S. Zhou, Q. Kong, S. Gao, X. Liu, X. Zhao and G. Hu, Self-supported iron-doped cobalt-copper oxide heterostructures for efficient electrocatalytic denitrification, *Journal of Colloid and Interface Science*, 2024, **675**, 313-325.
6. M. E. Chavez, M. Biset-Peiró, S. Murcia-López and J. R. Morante, Cu_2O–Cu@Titanium Surface with Synergistic Performance for Nitrate-to-Ammonia Electrochemical Reduction, *ACS Sustainable Chemistry & Engineering*, 2023, **11**, 3633-3643.
7. G. A. Cerrón-Calle, A. S. Fajardo, C. M. Sánchez-Sánchez and S. Garcia-Segura, Highly reactive Cu-Pt bimetallic 3D-electrocatalyst for selective nitrate reduction to ammonia, *Applied Catalysis B: Environmental*, 2022, **302**, 120844.
8. Z. Li, G. Wen, J. Liang, T. Li, Y. Luo, Q. Kong, X. Shi, A. M. Asiri, Q. Liu and X. Sun, High-efficiency nitrate electroreduction to ammonia on electrodeposited cobalt–phosphorus alloy film, *Chemical Communications*, 2021, **57**, 9720-9723.
9. J. Wang, J. Feng, T.-O. Soyol-Erdene, Z. Wei and W. Tang, Electrodeposited NiCoP on nickel foam as a self-supported cathode for highly selective electrochemical reduction of nitrate to

ammonia, *Separation and Purification Technology*, 2023, **320**, 124155.

10. W. Fu, Y. Du, J. Jing, C. Fu and M. Zhou, Highly selective nitrate reduction to ammonia on CoO/Cu foam via constructing interfacial electric field to tune adsorption of reactants, *Applied Catalysis B: Environmental*, 2023, **324**, 122201.