

Supporting Information

Electrocatalysts via metal-polyphenol assembly strategy for efficient nitrate reduction

Jing Jiang ^a, Xiaoli Jiang ^a, Lin Zhao ^a, Yagang Zhang ^{a,b *}

^a School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, China

^b Energy and Information Materials Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu 611731, Sichuan, China.

* Correspondence: ygzhang@uestc.edu.cn (Y. Zhang.); Tel.: +86-18129307169

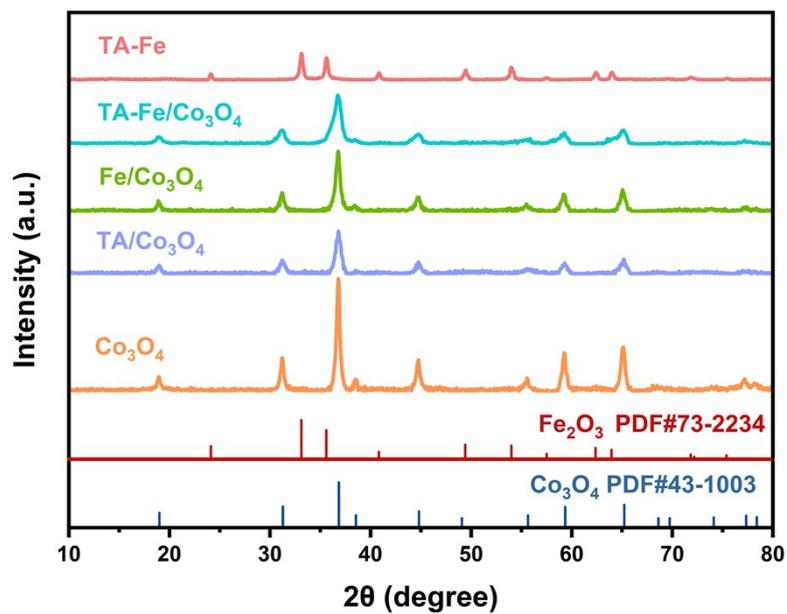


Fig. S1 Comparison of XRD patterns of Co₃O₄, TA/Co₃O₄, Fe/Co₃O₄, TA-Fe/Co₃O₄, and TA-Fe.

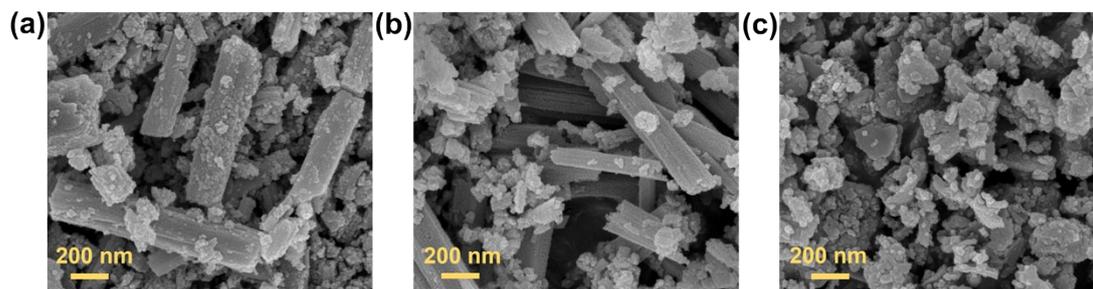


Fig. S2 SEM images of (a) TA/Co₃O₄, (b) Fe/Co₃O₄, and (c) TA-Fe.

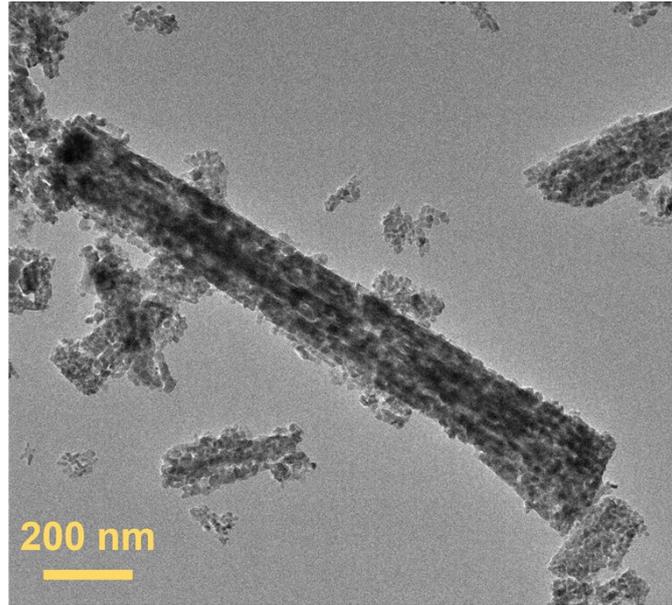


Fig. S3 TEM image of Co₃O₄.

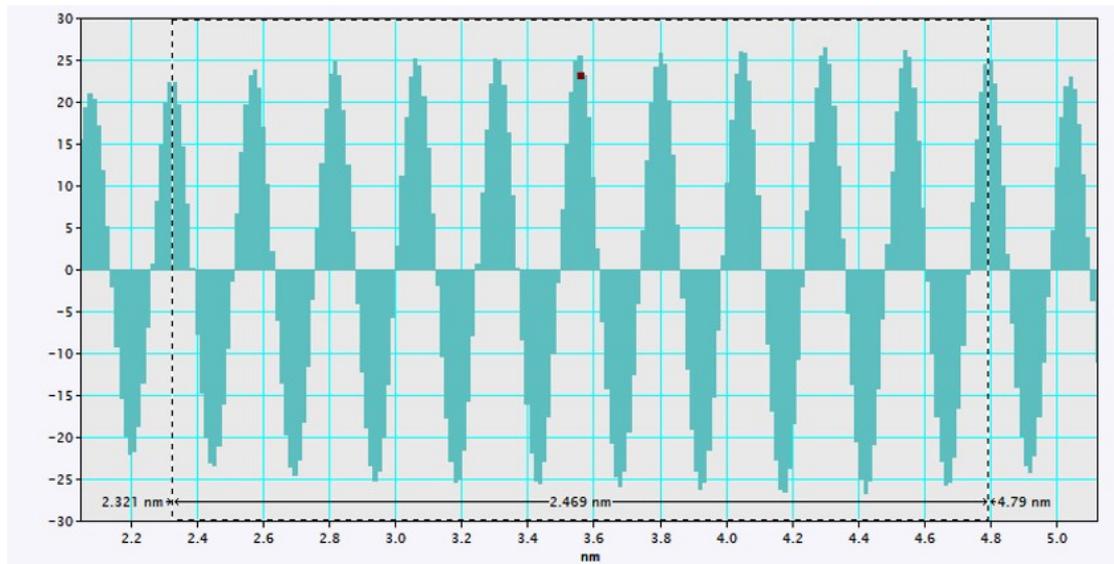


Fig. S4 Corresponding interplanar spacing profile of Co₃O₄ in TA-Fe/Co₃O₄.

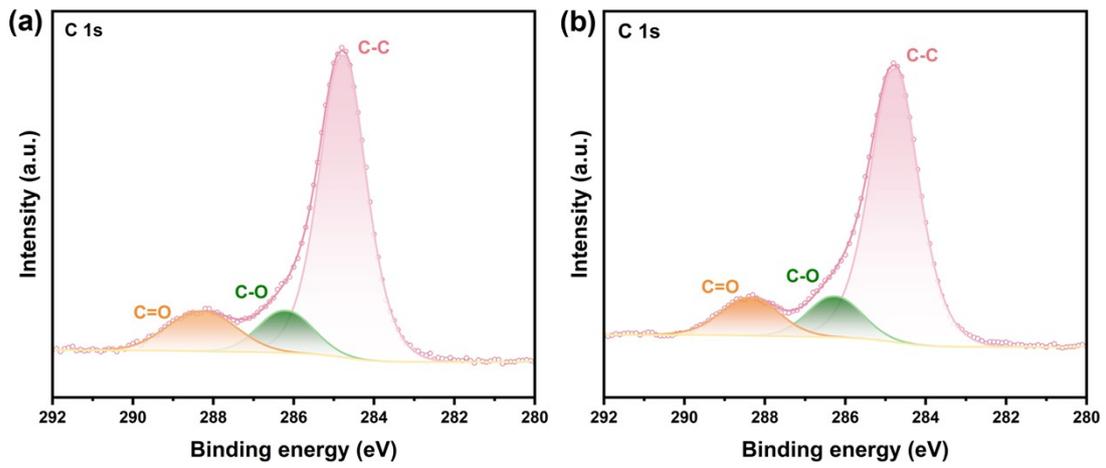


Fig. S5 C 1s XPS spectra of (a) Co_3O_4 and (b) TA-Fe/ Co_3O_4 .

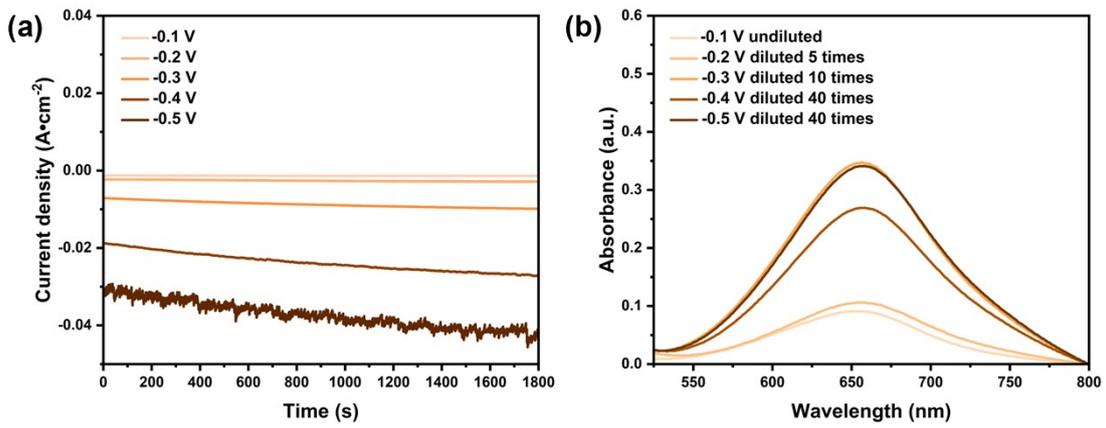


Fig. S6 (a) I-t curves and (b) corresponding UV-vis spectra of the electrolyte after electrolysis of Co_3O_4 at different potentials.

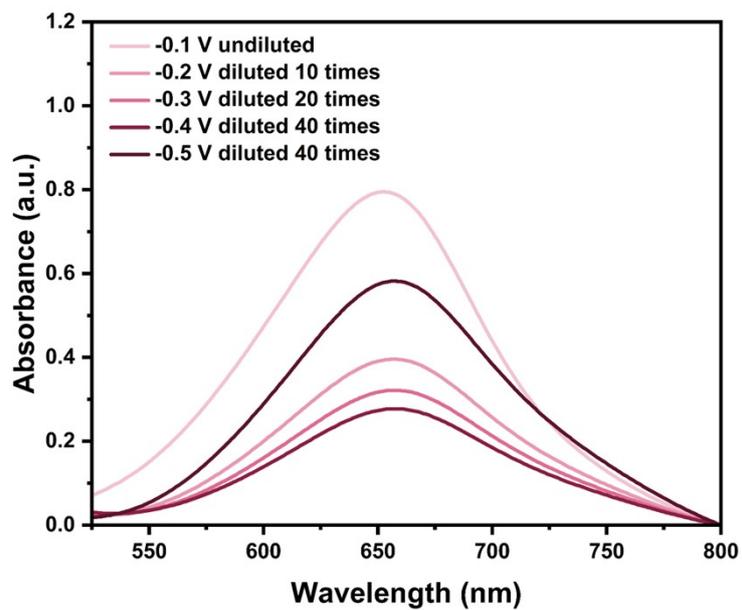


Fig. S7 UV-vis spectra of the electrolyte after electrolysis of TA-Fe/Co₃O₄ at different potentials.

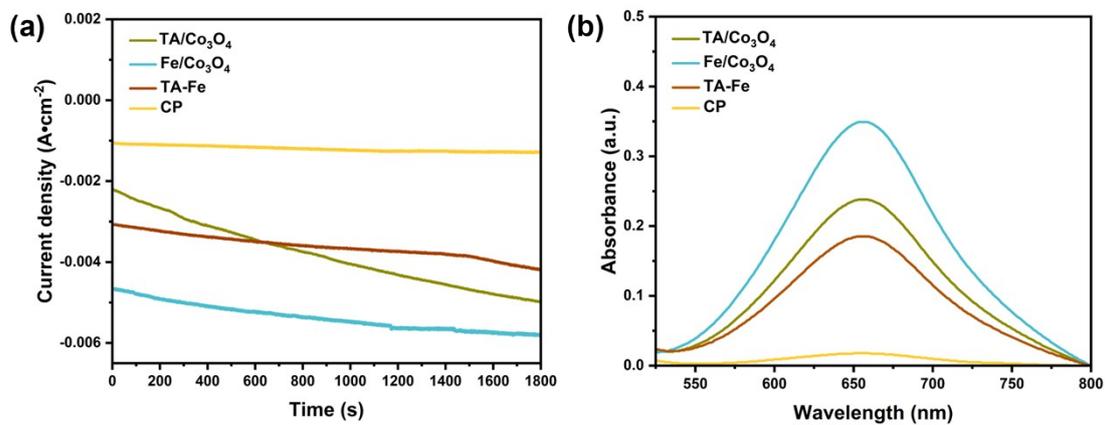


Fig. S8 (a) I-t curves and (b) corresponding UV-vis spectra of the electrolyte after electrolysis of TA/Co₃O₄, Fe/Co₃O₄, TA-Fe, and CP at -0.2 V vs. RHE.

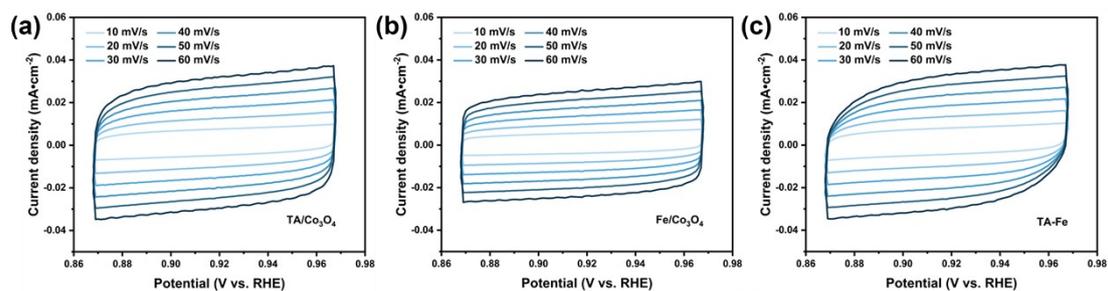


Fig. S9 CV curves at different scan rates of (a) TA/Co₃O₄, (b) Fe/Co₃O₄, and (c) TA-Fe.

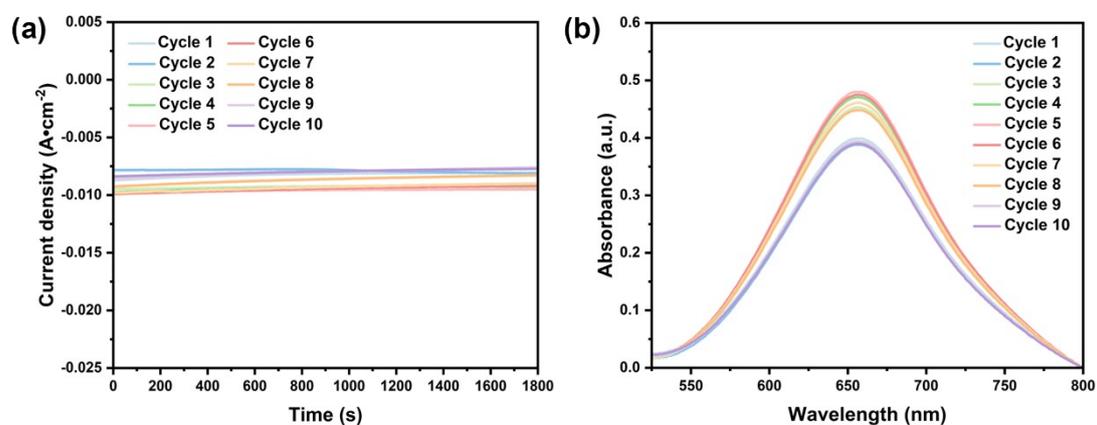


Fig. S10 (a) IT curves and (b) corresponding UV-vis absorbance spectra of the electrolyte after electrolysis of the stability test of TA-Fe/Co₃O₄ for 10 cycles at -0.2 V vs. RHE.

Table S1. ICP-OES test results of TA-Fe/Co₃O₄.

Catalysts	Co (wt.%)	Fe (wt.%)
TA-Fe/Co ₃ O ₄	54.59	8.50

Table S2. Valence state distribution of Co in the catalyst (%).

Catalysts	Co ³⁺	Co ²⁺	Co ³⁺ / Co ²⁺
-----------	------------------	------------------	-------------------------------------

Co ₃ O ₄	36.98	63.02	0.59
TA-Fe/Co ₃ O ₄	34.16	65.84	0.52

Table S3. Comparison of catalytic activity for TA-Fe/Co₃O₄ with other NO₃RR electrocatalysts

Catalysts	Electrolytes	Highest NH ₃ yield rate/ μmol h ⁻¹ cm ⁻²	Highest FE/%	Ref.
TA-Fe/Co ₃ O ₄	1 M KOH+0.1 M NO ₃ ⁻	206.50 (-0.5 V vs. RHE)	94.36 (-0.2 V vs. RHE)	This work
FOSP-Cu-0.1	0.5 M Na ₂ SO ₄ +0.1 M NO ₃ ⁻	101.4 (-0.266 V vs. RHE)	93.91 (-0.266 V vs. RHE)	1
Cu-Co ₃ O ₄ /NF	0.2 M K ₂ SO ₄ +2 mM NO ₃ ⁻	137 (-0.83V vs. RHE)	92.4 (-0.53V vs. RHE)	2
RuOx-Co ₃ O ₄	0.1 M NaSO ₄ +0.5 M NO ₃ ⁻	210.5 (-0.6V vs. RHE)	89.7 (-0.6 V vs. RHE)	3
Co-Fe ₂ P@NiP ₂	0.2 M Na ₂ SO ₄ +50 mM NO ₃ ⁻	395 (-0.7V vs. RHE)	97.2 (-0.6V vs. RHE)	4
Co ₃ O ₄ /TiO ₂ /Ti	1 M NaOH + 20 mM NO ₃ ⁻	93.3 (-0.4V vs. RHE)	80.0 (-0.3V vs. RHE)	5
Cu ₂ O NCs	1 M NaOH + 14 mM NO ₃ ⁻	149 (-0.3V vs. RHE)	94 (-0.3V vs. RHE)	6
CoNiO ₂	0.1 M NaOH +500 ppm NO ₃ ⁻	246.5 (-0.65V vs. RHE)	97.7 (-0.45V vs. RHE)	7
B-Co ₃ O ₄ /TM	0.1 M NaOH+0.1 M NO ₃ ⁻	561.7 (-0.8V vs. RHE)	94.7 (-0.7V vs.RHE)	8
Cu/Cu ₂ O@C	0.1 M KOH+0.1 M NO ₃ ⁻	158.66 (-0.6V vs.RHE)	76.97 (-0.6V vs.RHE)	9
Ru@C ₃ N ₄ /Cu	0.5 M Na ₂ SO ₄ +200 ppm NO ₃ ⁻	249	91.3	10

Catalysts	Electrolytes	Highest NH ₃ yield rate/ μmol h ⁻¹ cm ⁻²	Highest FE/%	Ref.
		(-0.9V vs. RHE)	(-0.8V vs. RHE)	

Table S4. Comparison of the catalytic activity of different catalysts at -0.2 V vs. RHE.

Catalysts	Electrolytes	NH ₃ Yield rate/ μmol h ⁻¹ cm ⁻²	FE/%
CP		0.12	2.12
Co ₃ O ₄		4.456	36.54
TA/Co ₃ O ₄	1M KOH +0.1M KNO ₃	10.47	58.90
Fe/Co ₃ O ₄		15.46	61.70
TA-Fe		8.02	47.59
TA-Fe/Co ₃ O ₄		35.09	94.36

References

- 1 Y. Zhao, Y. Liu, Z. Zhang, Z. Mo, C. Wang and S. Gao, *Nano Energy*, 2022, **97**, 107124.
- 2 X. Hu, M. Zhang, C. Lai, M. Cheng, F. Xu, D. Ma, L. Li, H. Yan, H. Sun, X. Fan and B. Wang, *Chem. Eng. J.*, 2024, **493**, 152543.
- 3 Y. Liu, X. Jiang, Y. Zhang, H. Li, W. Huang, Y. Yang, M. Ye and Y. Liu, *Dalton Trans.*, 2024, **53**, 162-170.
- 4 Y. Zheng, Y. Tan, X. Yu, H. Yao, S. Hu, J. Hu, Z. Chen and X. Guo, *Small*, 2024, **20**, 2312136.
- 5 K. L. Gomes, M. E. G. Winkler, M. P. Sales, J. B. Souza Junior, J. A. Bonacin and R. Nagao, *ACS Appl. Energy Mater.*, 2025, **8**, 15993-16001.
- 6 I. Messias, M. E. G. Winkler, G. F. Costa, T. Mariano, J. B. Souza Junior, I. T. Neckel, M. C. Figueiredo, N. Singh and R. Nagao, *ACS Appl. Energy Mater.*, 2024, **7**, 9034-9044.
- 7 Y. Zhang, J. Xiong, B. Liu and S. Yan, *Cell Rep. Phys. Sci.*, 2024, **5**, 101994.
- 8 Z. Deng, H. Liu, H. Wang, C. Ma, J. Du and B. Zheng, *Inorg. Chem. Front.*, 2024, **11**, 2339-2345.
- 9 G. Li, S. Xue, H. Zhu, Z. Liang, F. Zhao, Q. Hua, X. Ren, W. Xiong, L. Gao and A. Liu, *Ionics*, 2023, **29**, 2515-2522.
- 10 Y. Zheng, M. Qin, X. Yu, H. Yao, W. Zhang, G. Xie and X. Guo, *Small*, 2023, **19**, 2302266.