

# Supporting Information for

## Electrocatalytic nitrate-to-ammonia conversion on CoO/CuO nanoarray through Zn-nitrate battery

Shanshan Chen<sup>a</sup>, Gaocan Qi<sup>b\*</sup>, Ruilian Yin<sup>c</sup>, Qian Liu<sup>d</sup>, Ligang Feng<sup>e</sup>, Xincai Feng<sup>f</sup>,  
Guangzhi Hu<sup>g</sup>, Jun Luo<sup>f</sup>, Xijun Liu<sup>h\*</sup>, and Wenxian Liu<sup>c\*</sup>

<sup>a</sup> Institute for New Energy Materials & Low-Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China.

<sup>b</sup> School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China.

<sup>c</sup> College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, China.

<sup>d</sup> Institute for Advanced Study, Chengdu University, Chengdu 610106, Sichuan, China.

<sup>e</sup> School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China.

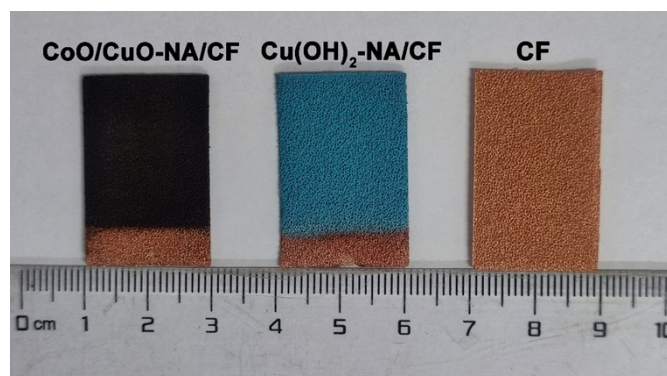
<sup>f</sup> ShenSi Lab, Shenzhen Institute for Advanced Study, University of Electronic Science and Technology of China, Longhua District, Shenzhen 518110, China.

<sup>g</sup> Institute for Ecological Research and Pollution Control of Plateau Lakes, School of Ecology and Environmental Science Yunnan University, Kunming 650091, China.

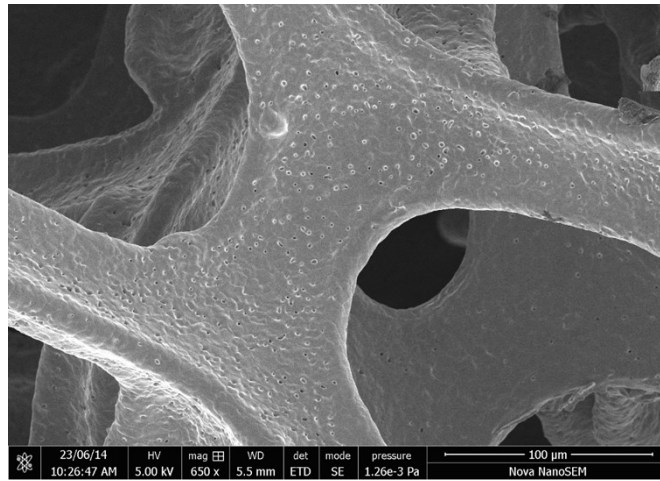
<sup>h</sup> State Key Laboratory of Featured Metal Materials and Life-cycle Safety for Composite Structures, MOE Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, School of Resources, Environment and Materials, Guangxi University, Nanning 530004, China.

**Authors to whom correspondence should be addressed:** [gaocanqi@tjut.edu.cn](mailto:gaocanqi@tjut.edu.cn);  
[xjliu@gxu.edu.cn](mailto:xjliu@gxu.edu.cn); [liuwx@zjut.edu.cn](mailto:liuwx@zjut.edu.cn)

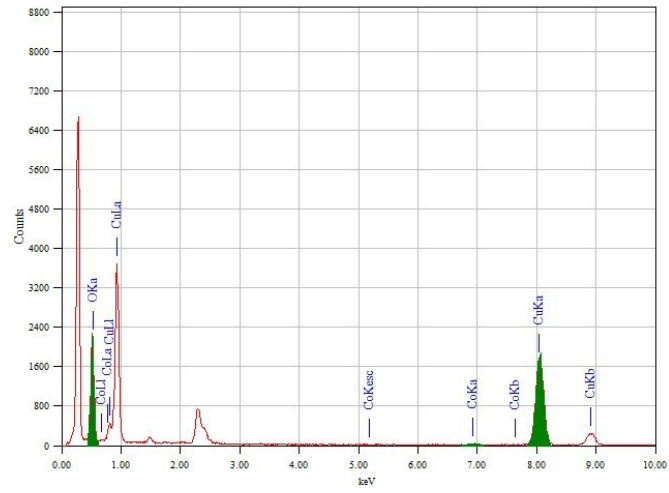
## Figures and Table



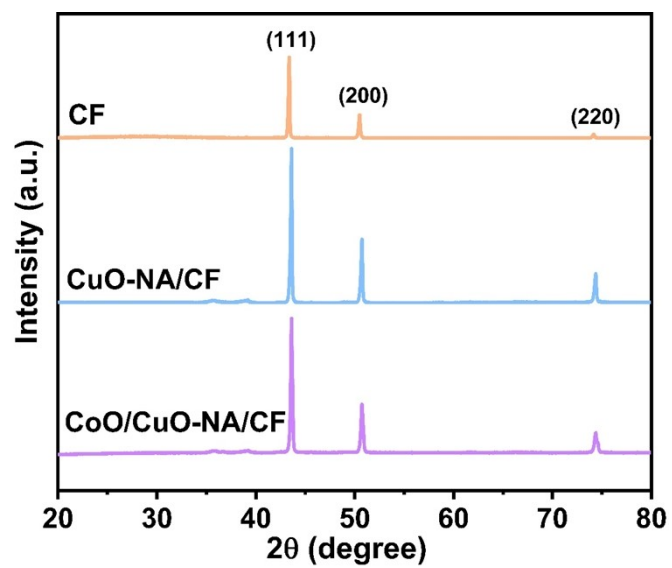
**Fig. S1** Photograph of different samples.



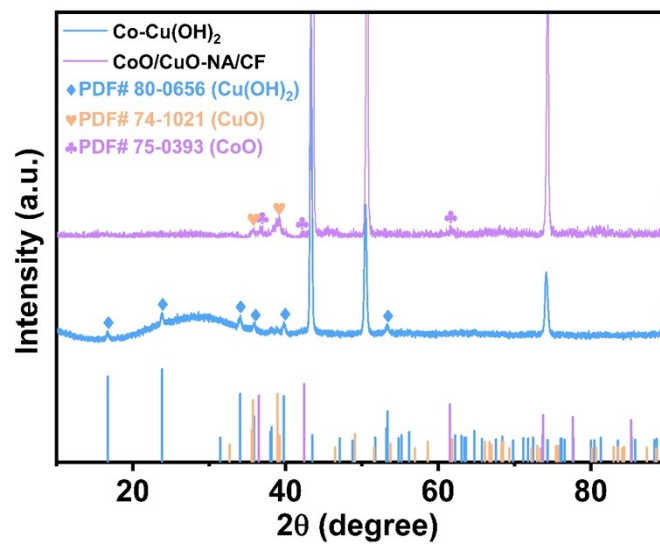
**Fig. S2** SEM images of CF.



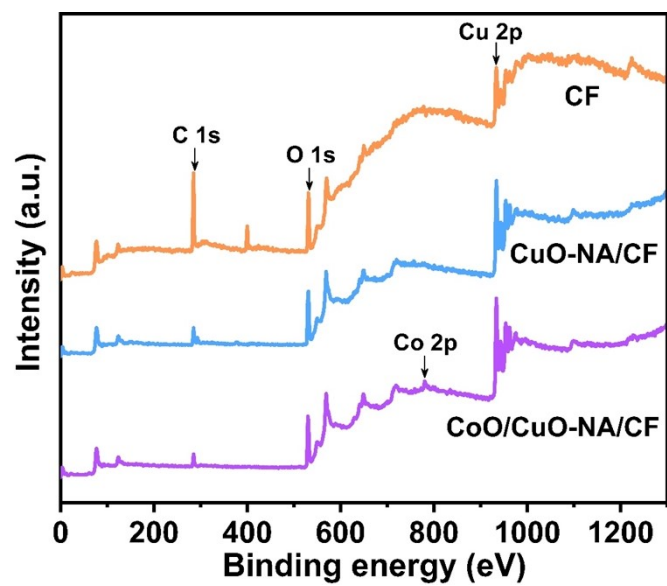
**Fig. S3** EDX spectrum of CoO/CuO-NA/CF.



**Fig. S4** XRD patterns of CF, CuO-NA/CF, and CoO/CuO-NA/CF.

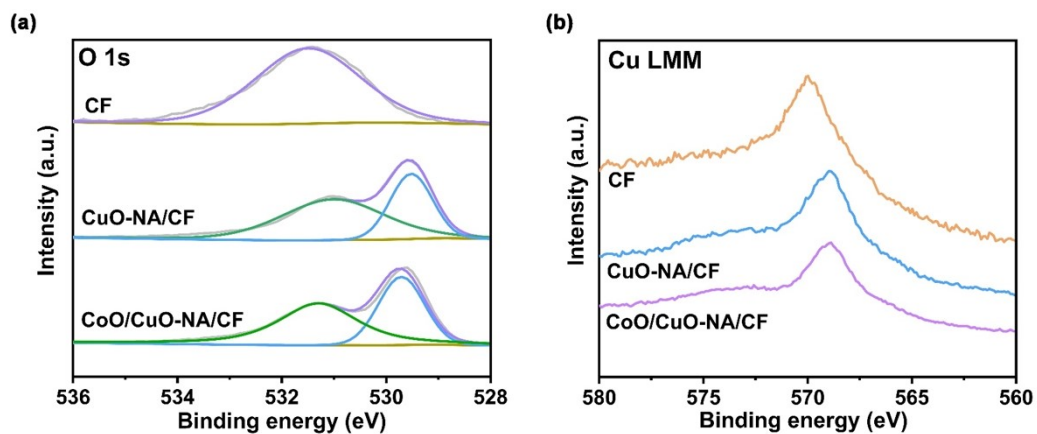


**Fig. S5** XRD patterns of Co-Cu(OH)<sub>2</sub> and CoO/CuO-NA/CF.

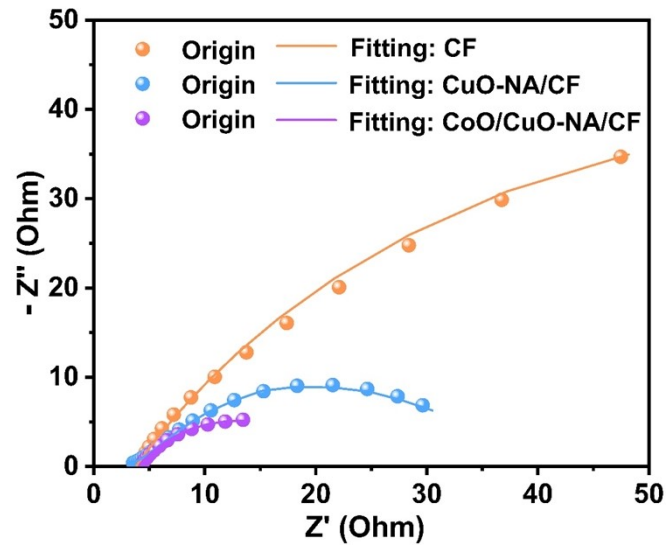


**Fig. S6** XPS survey spectrum of CF, CuO-NA/CF, and CoO/CuO-NA/CF.

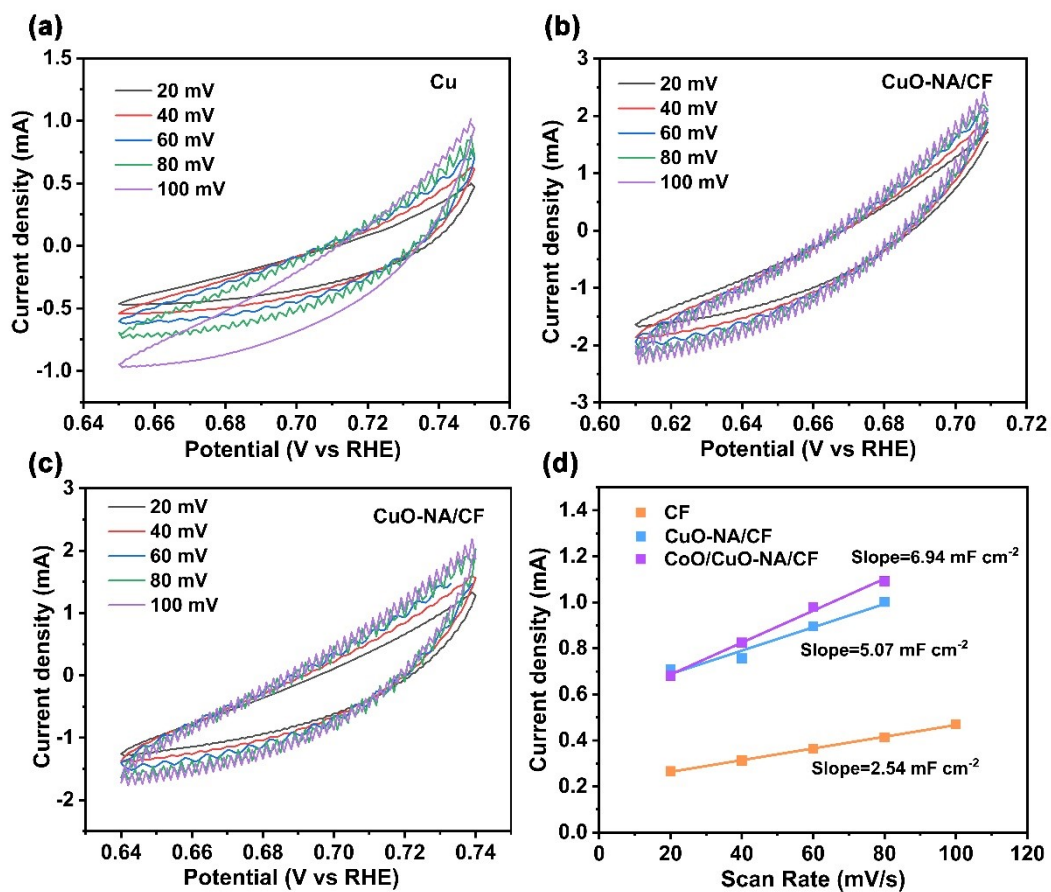




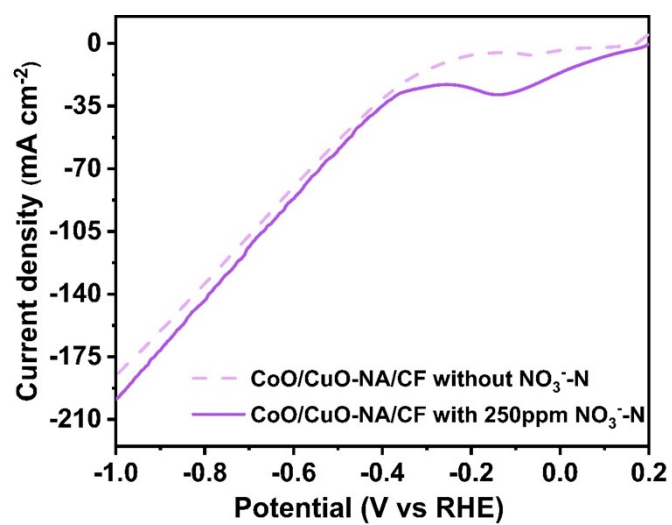
**Fig. S7** (a) XPS spectra in O 1s region and (b) Cu LMM Auger XPS spectra of CF, CuO-NA/CF, and CoO/CuO-NA/CF.



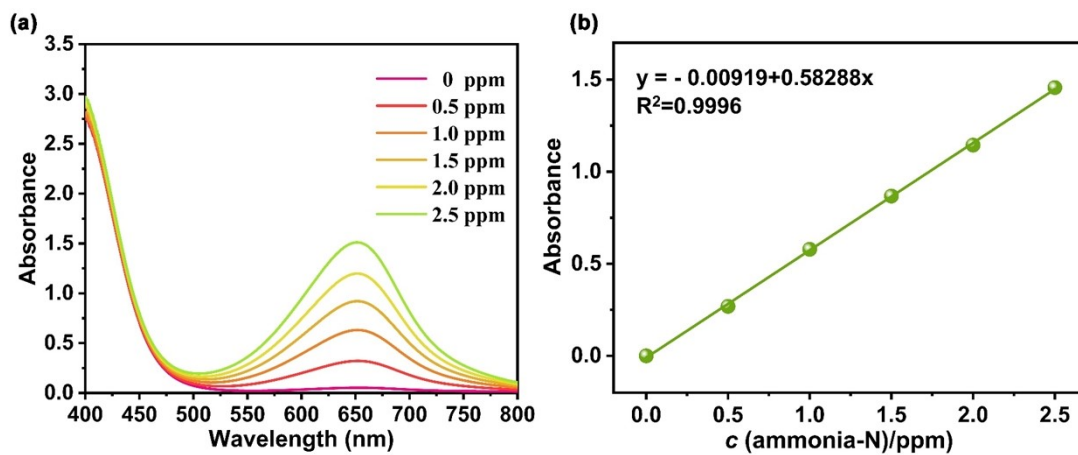
**Fig. S8** EIS measurements of CF, CuO-NA/CF, and CoO/CuO-NA/CF.



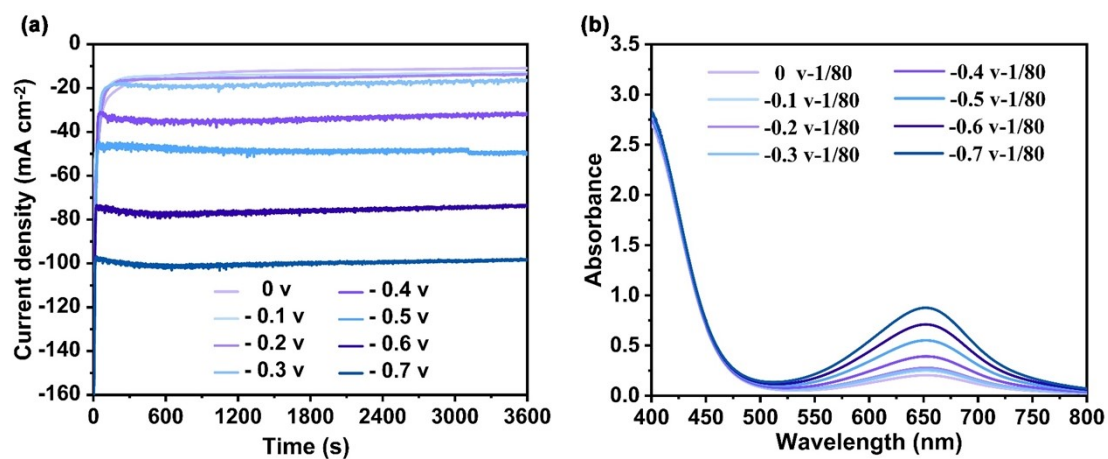
**Fig. S9** ECSA measurements of CF, CuO-NA/CF, and CoO/CuO-NA/CF.



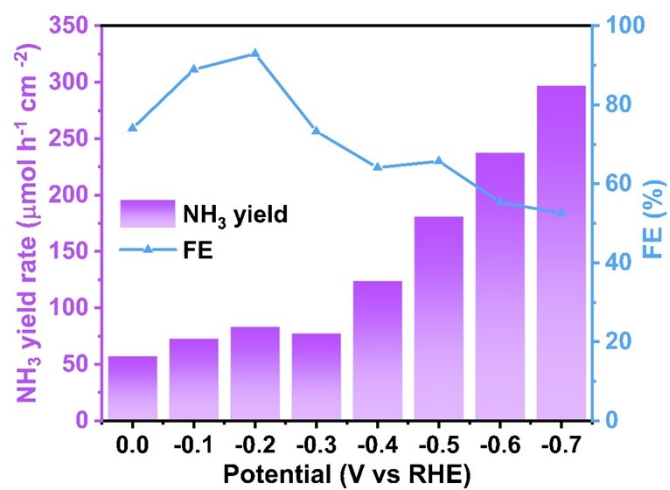
**Fig. S10** LSV curves CoO/CuO-NA/CF in 0.5 M NaOH with and without 250 ppm NO<sub>3</sub><sup>-</sup>-N.



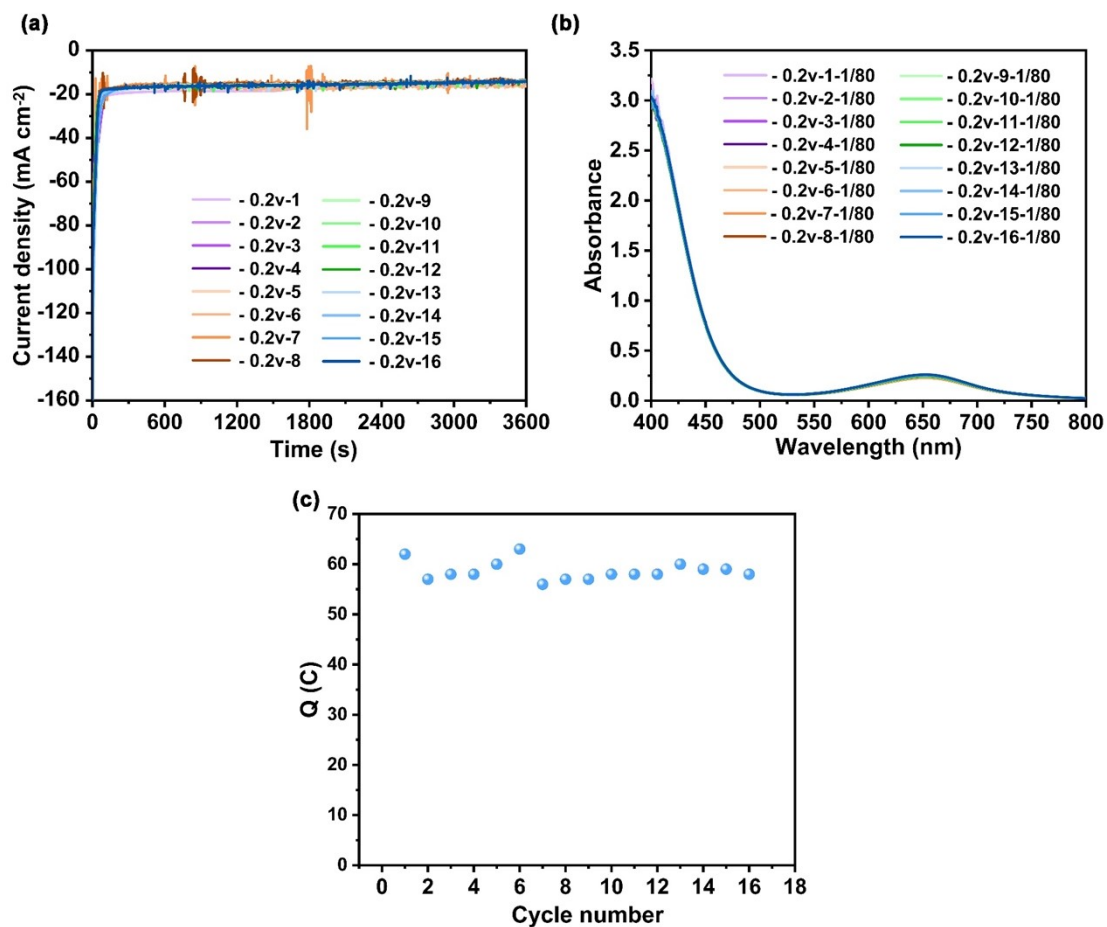
**Fig. S11** (a) The concentration-absorbance calibration curves of NH<sub>3</sub>. (b) The calibration curves show good linearity.



**Fig. S12** Chronoamperometry curves for CoO/CuO-NA/CF in Ar-saturated 0.5 M NaOH electrolytes containing 250 ppm NO<sub>3</sub><sup>-</sup>-N.

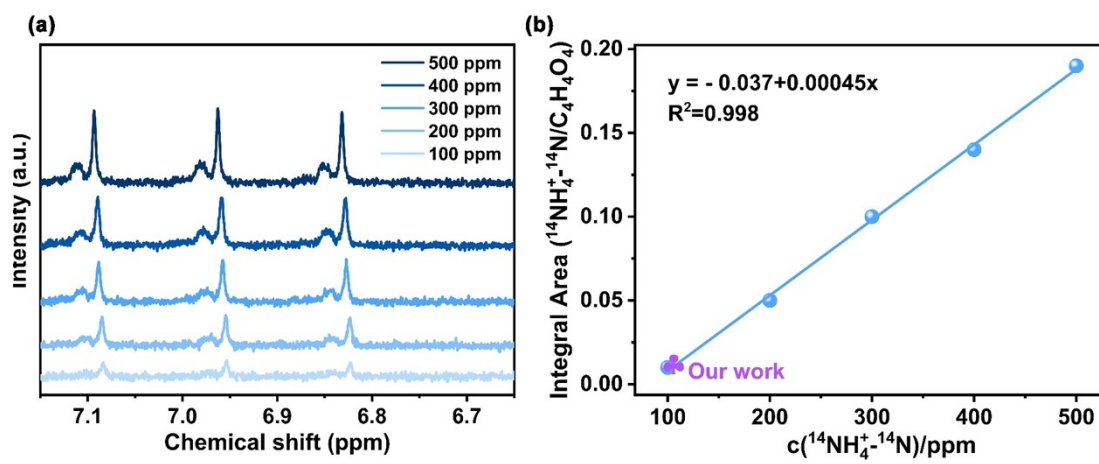


**Fig. S13** NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> conversion FE<sub>NH<sub>3</sub></sub> and NH<sub>3</sub> yield for CoO/CuO-NA/CF.

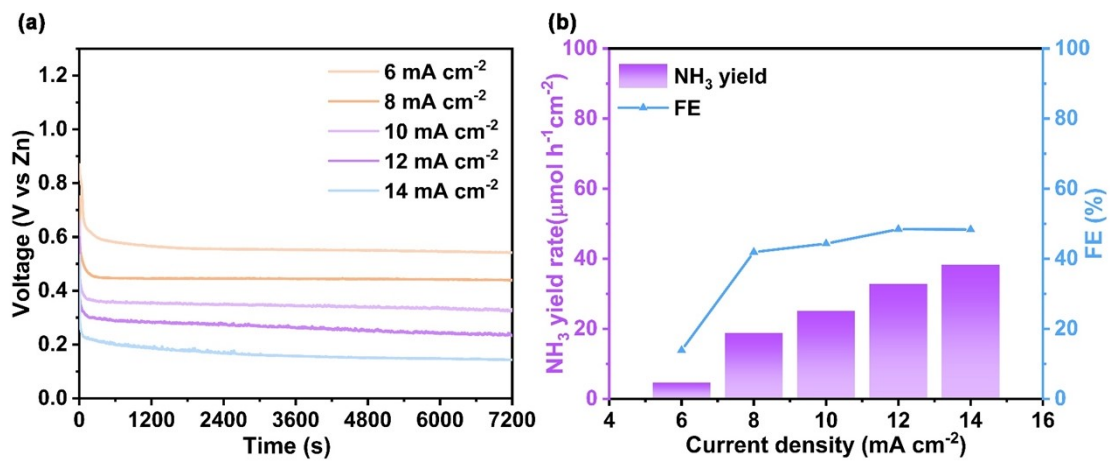


**Fig. S14** (a) Chronoamperometry curves of CoO/CuO-NA/CF. (b) UV-Vis absorption spectra and (c) Q values for electrogenerated NH<sub>3</sub> during recycling tests at -0.2 V vs. RHE.

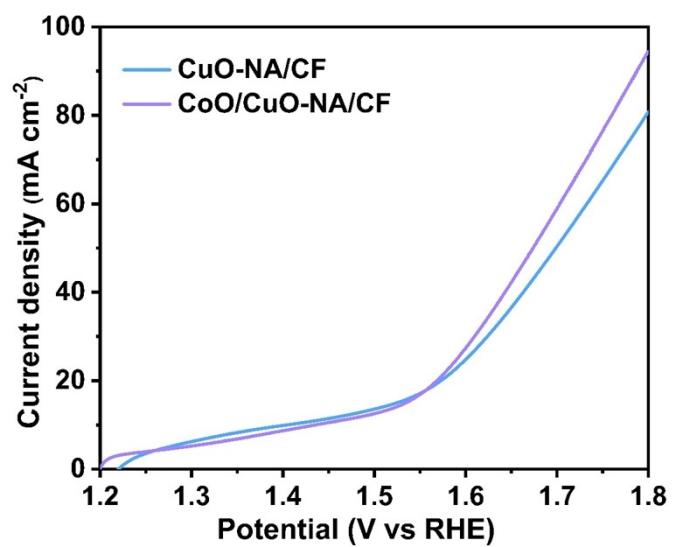




**Fig. S15**  $^1\text{H}$  NMR spectra  $^{14}\text{NH}_4^+ - ^{14}\text{N}$  with different concentrations.



**Fig. S16** Chronoamperometry curves (a) and  $FE_{NH_3}$  and yield of  $NH_3$  (b) for CuO-NA/CF-based Zn- $NO_3^-$  battery at in Ar-saturated 0.5 M NaOH electrolytes containing 500 ppm  $NO_3^-$ -N.



**Fig. S17** LSV curves of OER for CuO-NA/CF and CoO/CuO-NA/CF.

**Table S1** Comparison of NH<sub>3</sub> yield and power density of our battery with other Zn-NO<sub>3</sub><sup>-</sup> battery systems.

Catalyst	Power density (mW cm <sup>-2</sup> )	FE (%)	NH <sub>3</sub> yield	Rechargeability	Ref.
CoO/CuO-NA/CF	4.3	82.0	60.3 μmol h <sup>-1</sup> cm <sup>-2</sup>	Yes	This work
Pd/TiO <sub>2</sub>	0.87	81.3	32 mmol h <sup>-1</sup> cm <sup>-2</sup>	No	[2]
NiCo <sub>2</sub> O <sub>4</sub> /CC	3.94	96.1	48.5 μmol h <sup>-1</sup> cm <sup>-2</sup>	No	[1]
ZnCo <sub>2</sub> O <sub>4</sub> NSA/CC	4.62	90	91.75 μmol h <sup>-1</sup> cm <sup>-2</sup>	No	[3]
Co <sub>2</sub> AlO <sub>4</sub> /CC	3.43	95	750 μg h <sup>-1</sup> cm <sup>-2</sup>	No	[4]
CeO <sub>2-x</sub> @NC/GP	3.44	96.09	145.08 μmol h <sup>-1</sup> cm <sup>-2</sup>	No	[5]
Fe/Ni <sub>2</sub> P	3.25	85	22.6 μmol cm <sup>-2</sup> h <sup>-1</sup>	Yes	[6]
Co <sub>2</sub> B@Co <sub>3</sub> O <sub>4</sub> /TM	3.21	97.2	0.74 mg h <sup>-1</sup> cm <sup>-2</sup>	No	[7]
MP-Cu	7.56	93	76 μmol cm <sup>-2</sup> h <sup>-1</sup>	No	[8]
NiCoBDC	3.66	99.4%	66.2 μmol h <sup>-1</sup> cm <sup>-2</sup>	No	[9]
CoNi-Vp-1.0	1.05	76.23 %	12.227 μmol h <sup>-1</sup> cm <sup>-2</sup>	No	[10]

## References

1. Q. Liu, L. Xie, J. Liang, Y. Ren, Y. Wang, L. Zhang, L. Yue, T. Li, Y. Luo, N. Li, B. Tang, Y. Liu, S. Gao, A. A. Alshehri, I. Shakir, P. O. Agboola, Q. Kong, Q. Wang, D. Ma and X. Sun, *Small*, 2022, **18**, 2106961.
2. Y. Guo, R. Zhang, S. Zhang, Y. Zhao, Q. Yang, Z. Huang, B. Dong and C. Zhi, *Energy Environ. Sci.*, 2021, **14**, 3938-3944.
3. Z. Li, J. Liang, Q. Liu, L. Xie, L. Zhang, Y. Ren, L. Yue, N. Li, B. Tang, A. A. Alshehri, M. S. Hamdy, Y. Luo, Q. Kong and X. Sun, *Materials Today Physics*, 2022, **23**, 100619.
4. Z. Deng, J. Liang, Q. Liu, C. Ma, L. Xie, L. Yue, Y. Ren, T. Li, Y. Luo, N. Li, B. Tang, A. Ali Alshehri, I. Shakir, P. O. Agboola, S. Yan, B. Zheng, J. Du, Q. Kong and X. Sun, *Chem. Eng. J.*, 2022, **435**, 135104.
5. Z. Li, Z. Deng, L. Ouyang, X. Fan, L. Zhang, S. Sun, Q. Liu, A. A. Alshehri, Y. Luo, Q. Kong and X. Sun, *Nano Res.*, 2022, **15**, 8914-8921.
6. R. Zhang, Y. Guo, S. Zhang, D. Chen, Y. Zhao, Z. Huang, L. Ma, P. Li, Q. Yang, G. Liang and C. Zhi, *Adv. Energy Mater.*, 2022, **12**, 2212236.
7. L. Xie, S. Sun, L. Hu, J. Chen, J. Li, L. Ouyang, Y. Luo, A. A. Alshehri, Q. Kong, Q. Liu and X. Sun, *ACS Appl. Mater. Interfaces.*, 2022, **14**, 49650-49657.
8. W. Wen, P. Yan, W. Sun, Y. Zhou and X. Y. Yu, *Adv. Funct. Mater.*, 2022, **33**, 2212236.
9. J. Ma, Y. Zhang, B. Wang, Z. Jiang, Q. Zhang and S. Zhuo, *ACS Nano*, 2023, **17**, 6687-6697.
10. Y. Gao, K. Wang, C. Xu, H. Fang, H. Yu, H. Zhang, S. Li, C. Li and F. Huang, *Appl. Catal. B.*, 2023, **330**, 122627.