Supplementary Material

Improving Nitrate-to-Ammonia Conversion on Electrodeposited Nickel Phosphide via Surface δ-FeOOH Modification

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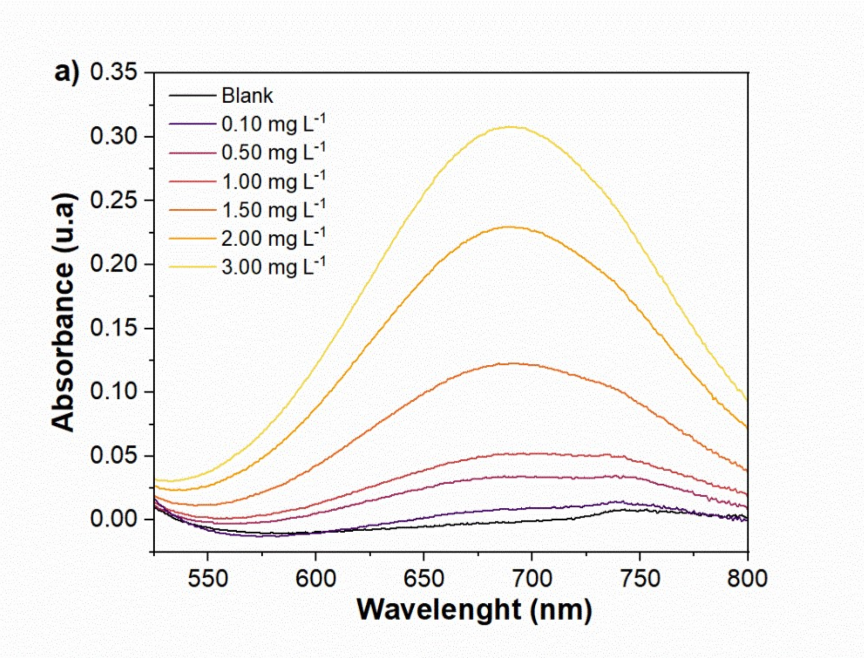
Figure S1. Calibration of the indophenol blue method for NH_3 quantification in alkaline (1.0 M KOH) using NH_4Cl standard solution: (a) UV-Vis spectra of the NH_3 standard solutions after incubation registered from 500 to 800 nm in 1.0 M KOH. (b) Calibration curve used to estimate NH_3 concentration in 1.0 M KOH.



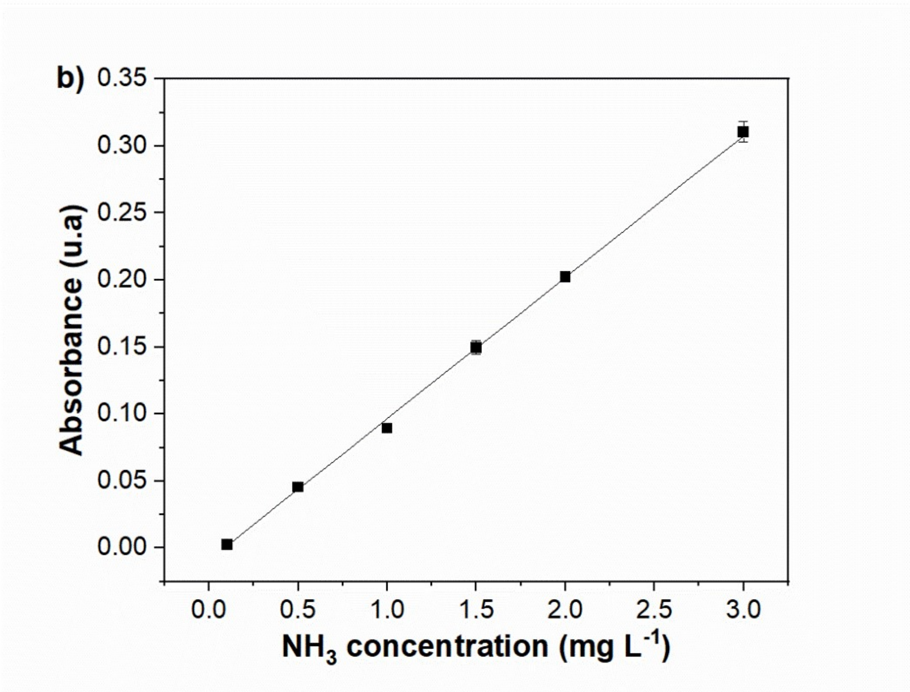


Figure S2. XRD profile of the CFP/ Ni_3P-amorphous and CFP/ Ni_3P-annealed electrodes.

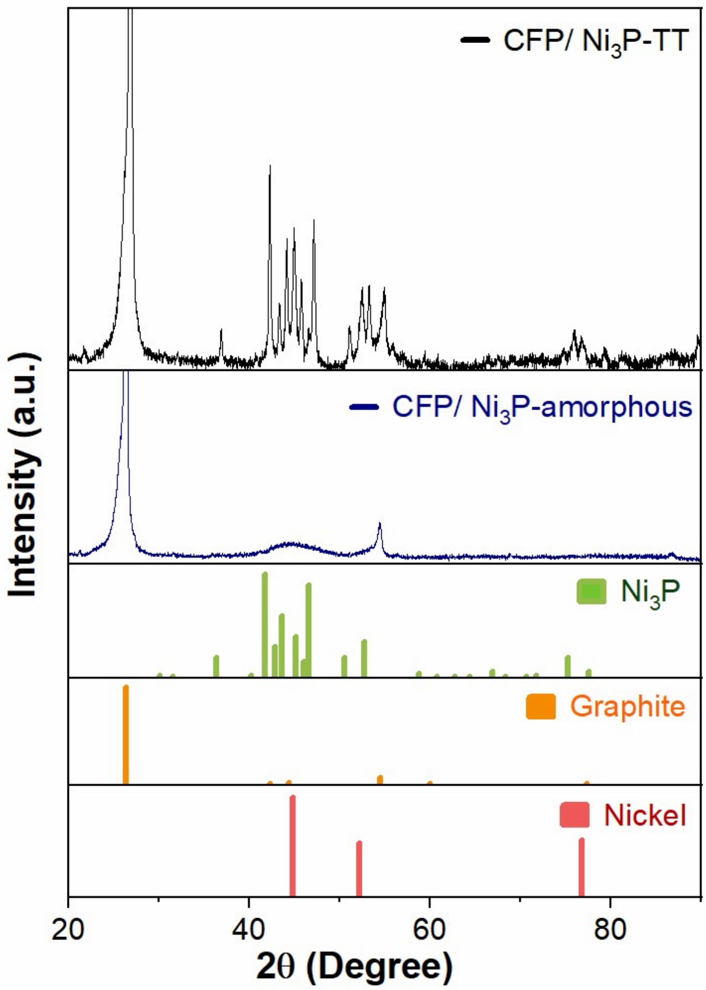


Figure S3. EDS-SEM mapping images for the CFP/Ni_3P/δ-FeOOH.

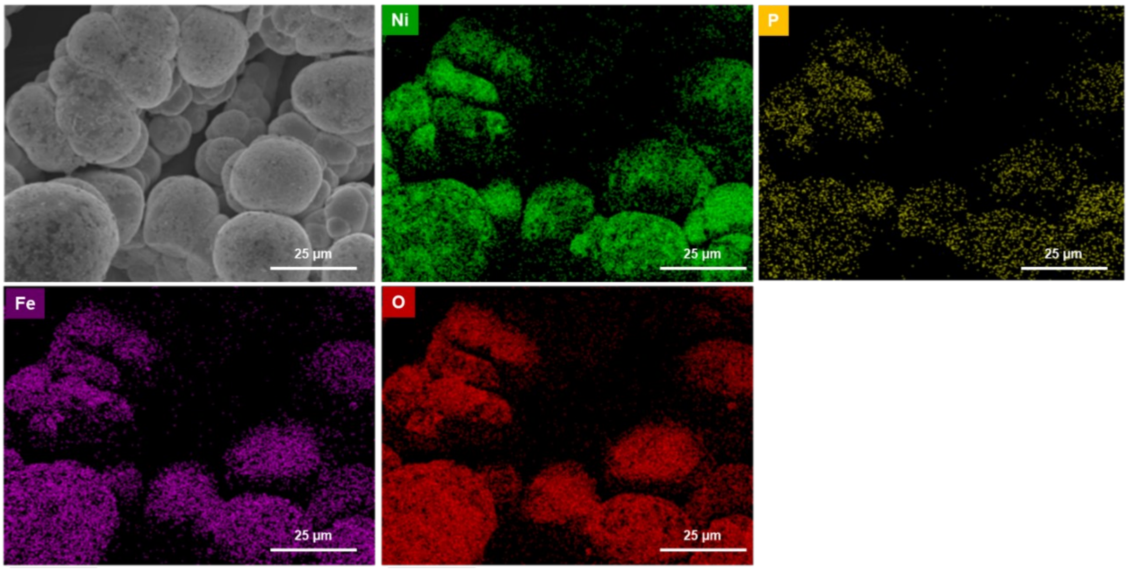


Figure S4. XPS survey spectrum of the CFP/Ni_3P/δ-FeOOH electrode.

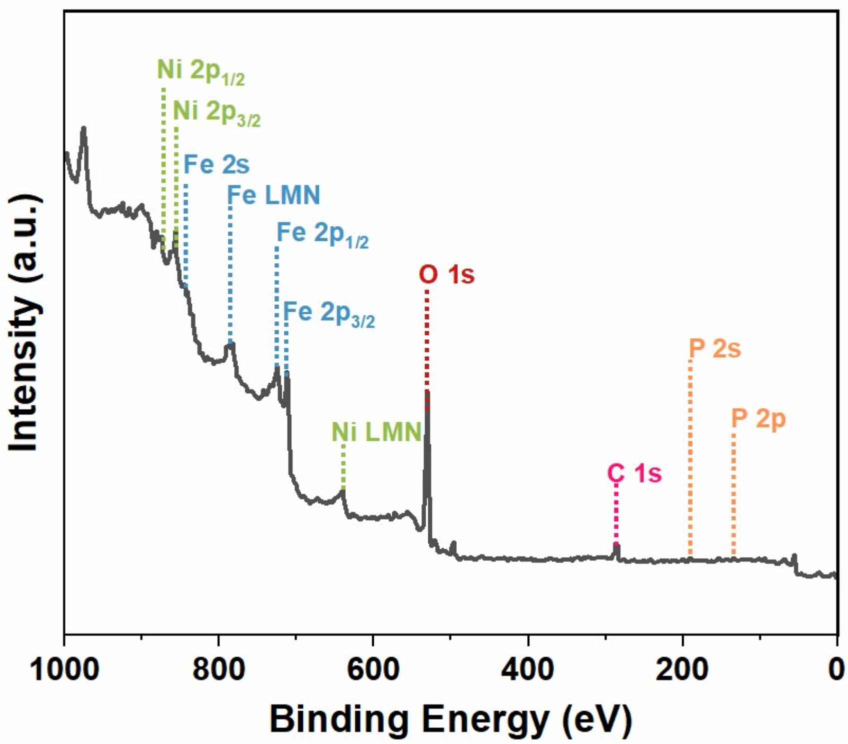


Figure S5. High-resolution Ni 2P and P 2p XPS spectra for the **a)** reference sample (initial Ni_3P surface) and the **b)** Ni_3P surface after 5 min Ar^+ bombardment.

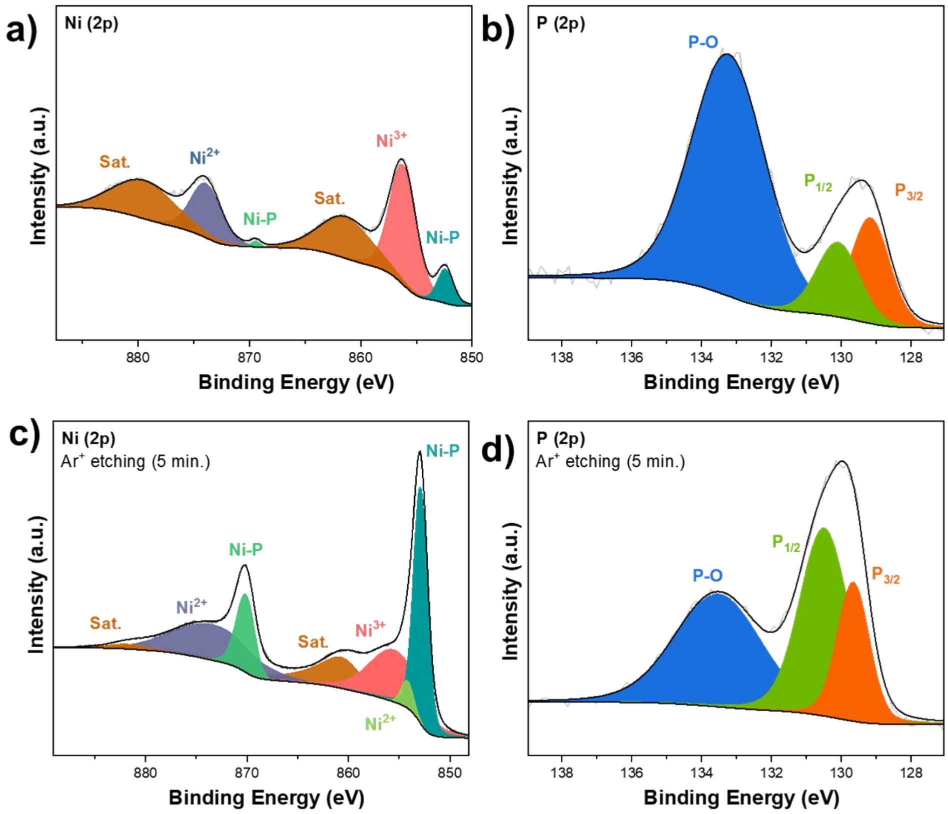


Figure S6. ECSA-normalized Linear sweep voltammetry curves registered in 1.0 M KOH + 0.1 M KNO_3 at 5 mVs^{-1}.

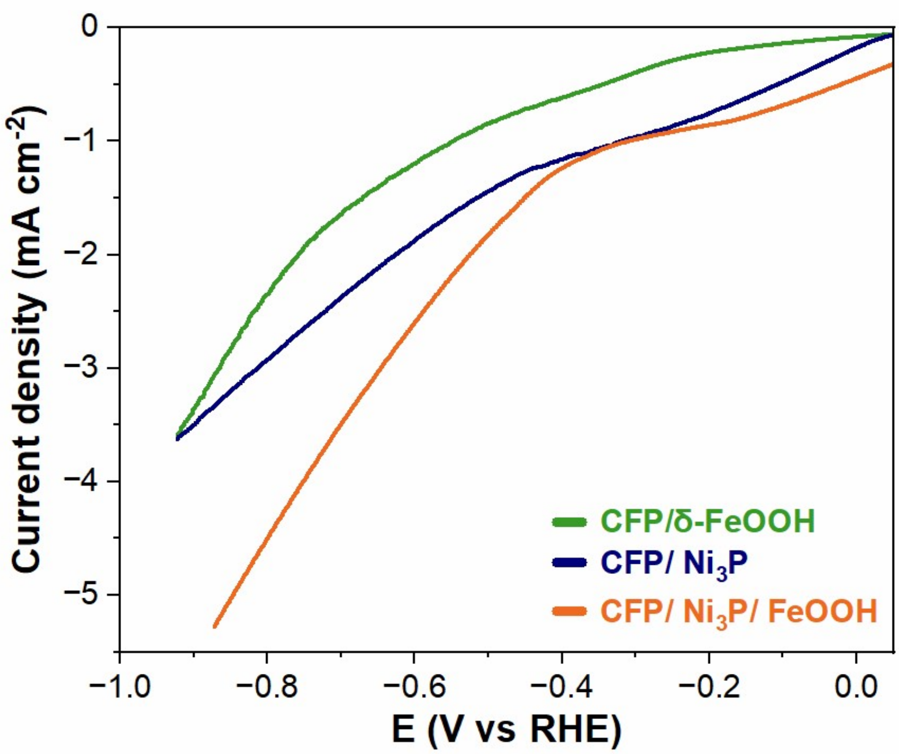
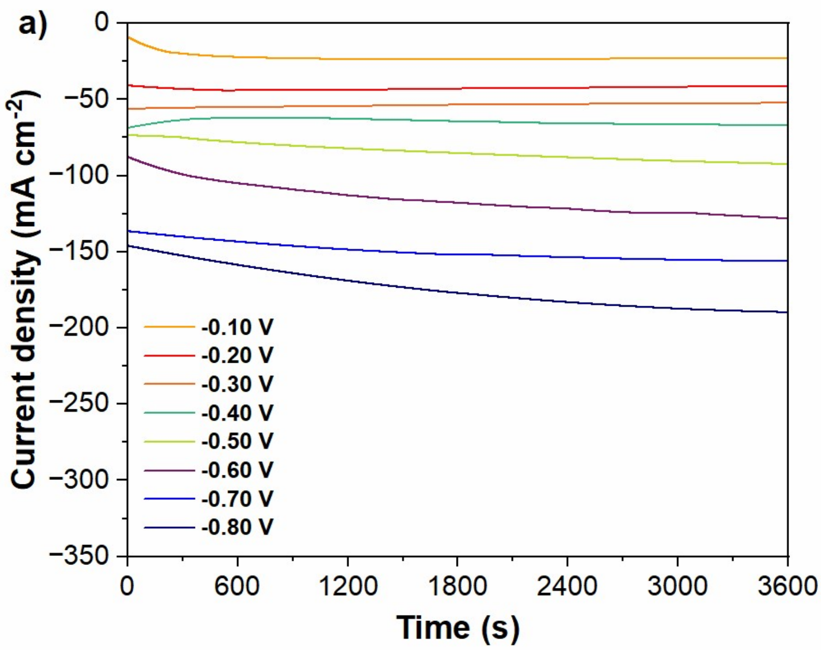


Figure S7. Chronoamperometry curves registered in 1.0 M KOH with 0.10 M KNO_3 at different applied potentials for the a) CFP/Ni_3P/δ-FeOOH and b) CFP/Ni_3P.



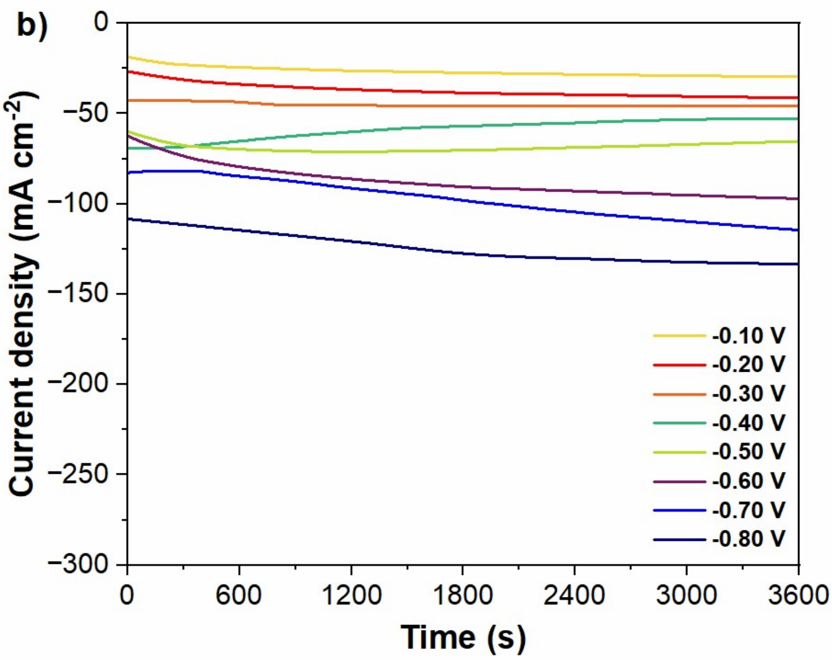


Figure S8. Cyclic voltammograms registered for 1.0 M KOH with different NO_2 concentrations (0.005 to 0.10 M). (b) Standard curve for NO_2- quantification.

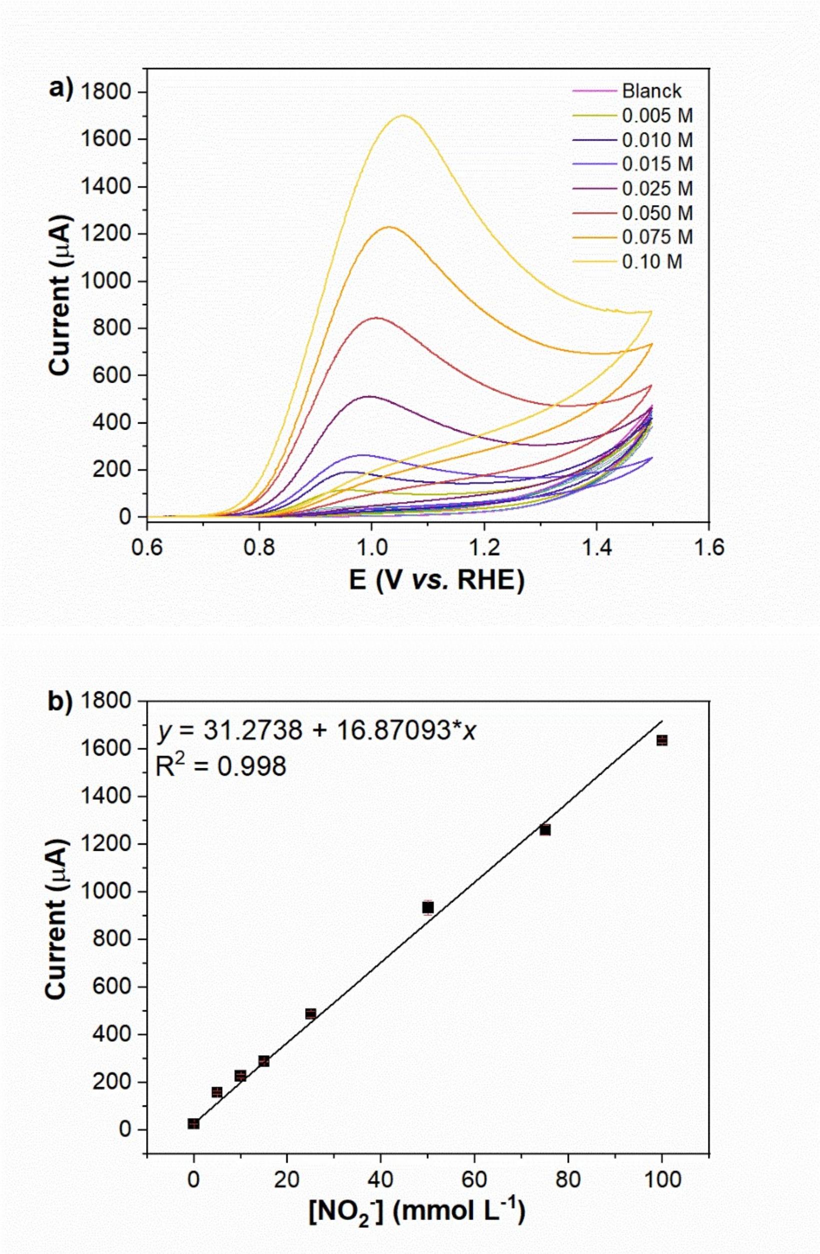


Figure S9. Chronoamperometry curves registered in 1.0 M KOH with 0.10 M KNO_3 at different applied potentials for the a) CFP/Ni_3P/δ-FeOOH and b) CFP/Ni_3P.

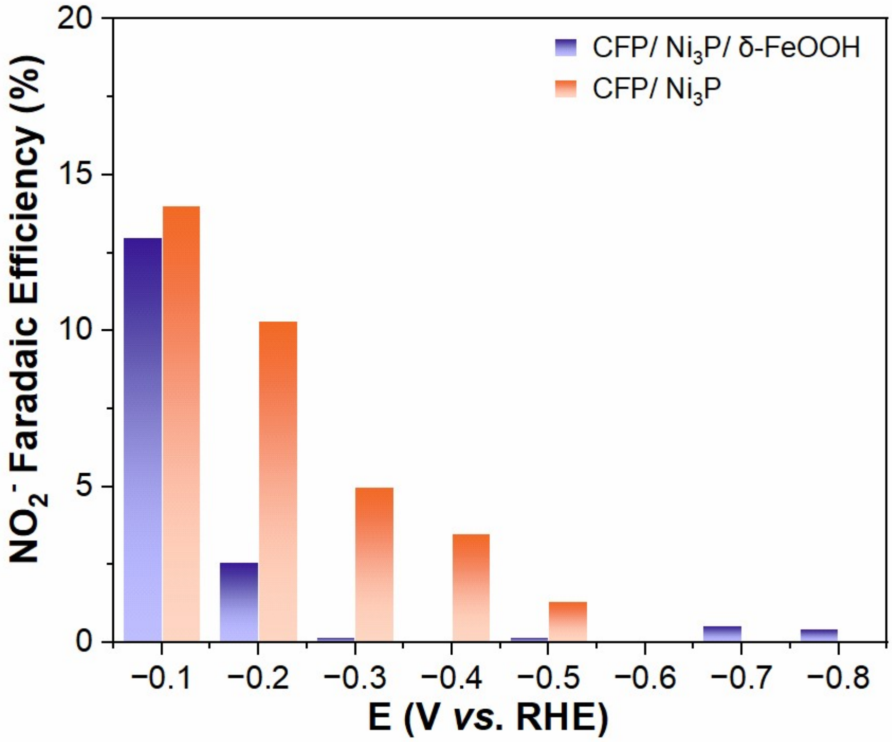


Figure S10. Ammonia yield rate at OCP (CFP/Ni_3P/δ-FeOOH) and at -0.30 V vs RHE of the individual CFP, CFP/Ni_3P, CFP/δ-FeOOH and CFP/Ni_3P/δ-FeOOH electrodes in KOH + 0.1 M KNO_3.

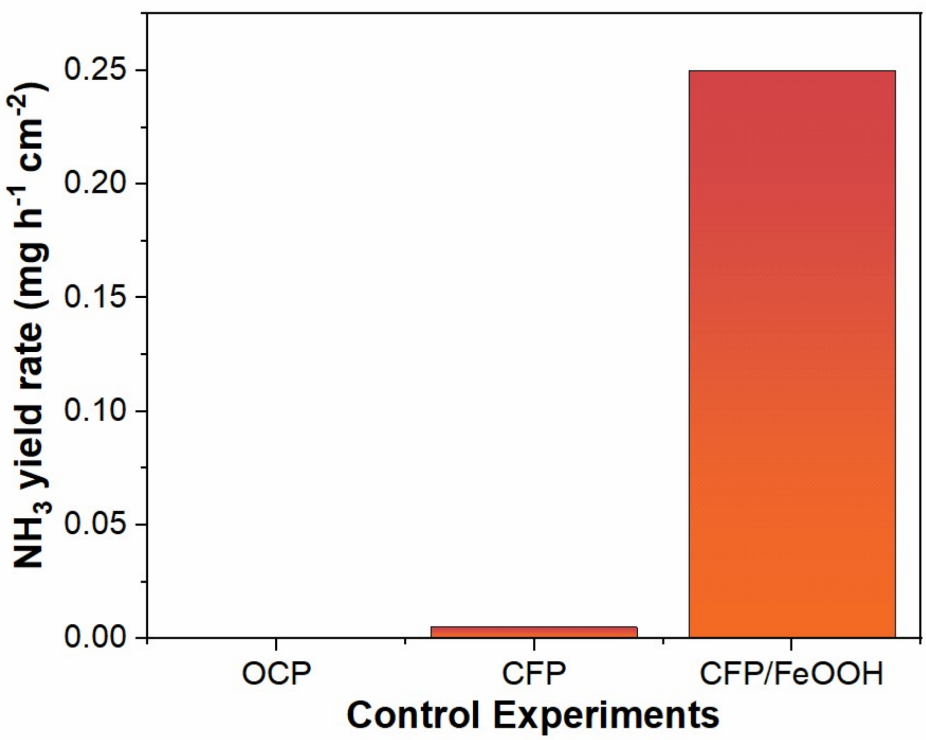


Figure S11. Comparison of NH_3 yield and applied potential for electroreduction of nitrate to ammonia under ambient conditions using alkaline electrolyte (1 M) [1–11].

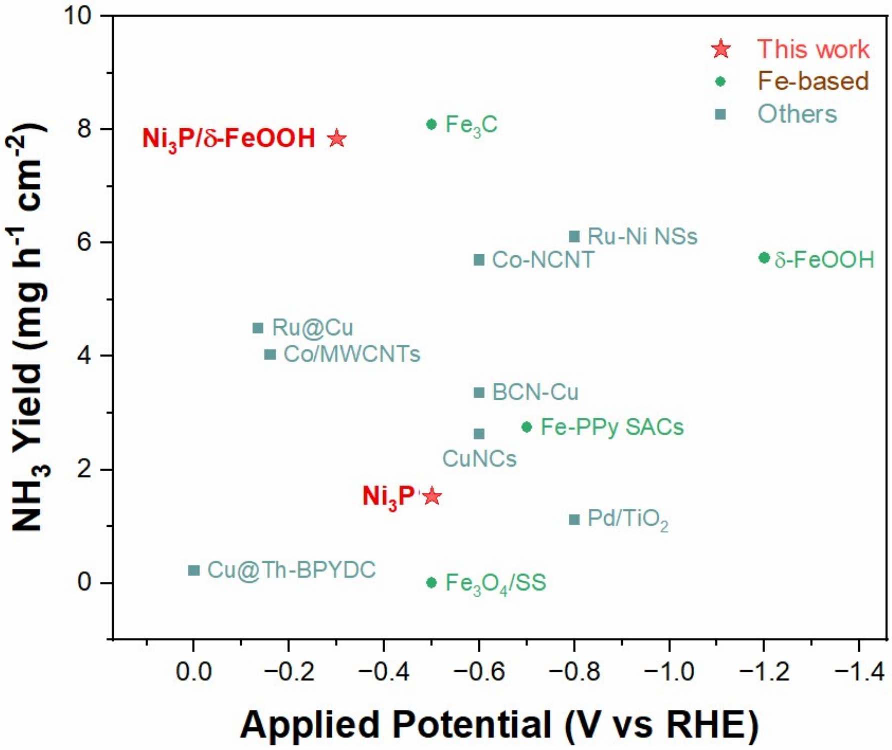


Figure S12. a) Linear sweep voltammetry curves registered with the CFP/Ni_3P/δ-FeOOH sample at 5 mVs^{-1} in 1.0 M KOH with different KNO_3 concentrations. b) NH_3 yield rate and Faradaic efficiency for the δ-FeOOH modified Ni_3P electrode in different KNO_3 concentrations at -0.30 V vs. RHE.

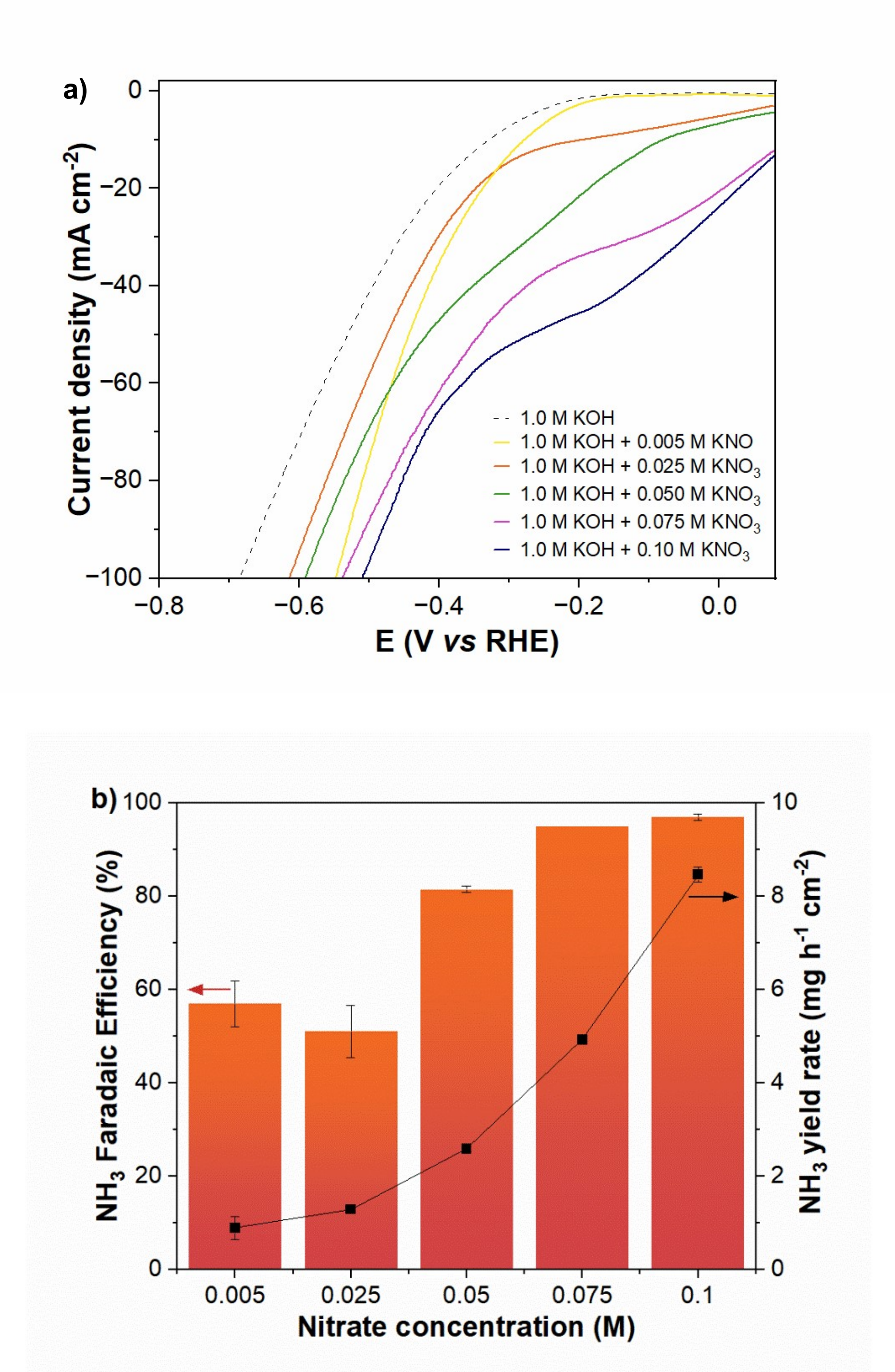
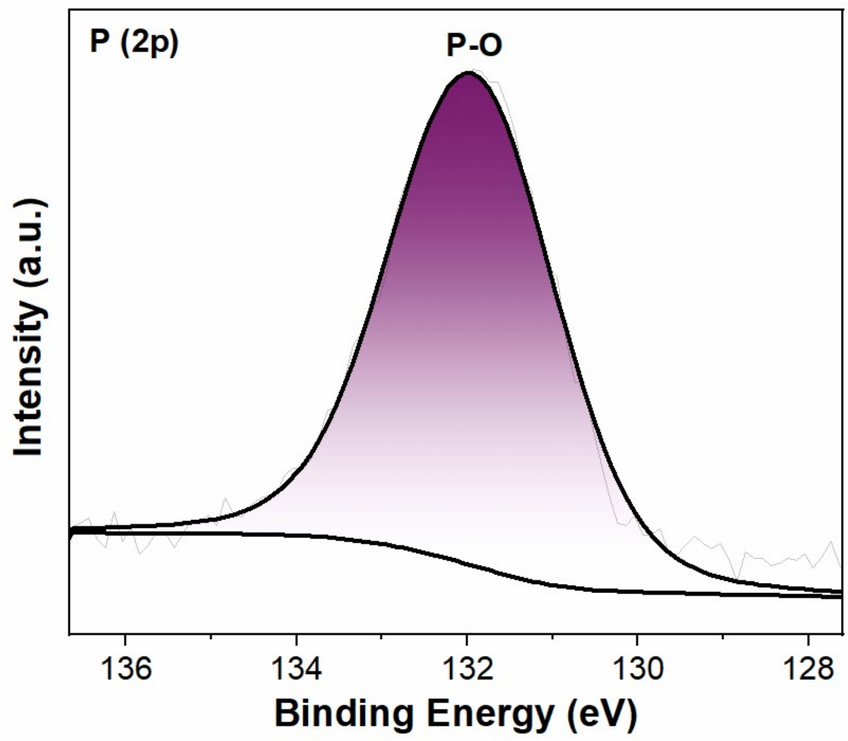


Figure S13. P 2p XPS spectra of the CFP/Ni_3P/δ-FeOOH sample after consecutive recycling cycles.



References

1 N. Zhang, G. Zhang, P. Shen, H. Zhang, D. Ma and K. Chu, *Adv Funct Mater*, 2023, **33**, 2211537.

2 K. Qu, X. Zhu, Y. Zhang, L. Song, J. Wang, Y. Gong, X. Liu and A. L. Wang, *Small*, 2024, 2401327.

3 J. Li, Y. Zhang, C. Liu, L. Zheng, E. Petit, K. Qi, Y. Zhang, H. Wu, W. Wang, A. Tiberj, X. Wang, M. Chhowalla, L. Lajaunie, R. Yu and D. Voiry, *Adv Funct Mater*, 2022, **32**, 2108316.

4 Y. Wang, L. Zhang, Y. Niu, D. Fang, J. Wang, Q. Su and C. Wang, *Green Chemistry*, 2021, **23**, 7594–7608.

5 X. You, J. Xu, Z. Zhuang, J. Xia, S. Wang, H. Wei, Y. Li, Y. Cai, H. Xiang and B. Yu, *Nano Res*, 2024, 1–10.

6 M. ; Jiang, X. ; Zhang, Y. ; Liu, Y. ; Zhao, L. Enhanced, J. Kim, M. Ye, X. Jiang, Y. Zhang, Y. Liu, Y. Liu and L. Zhao, *Nanomaterials 2024, Vol. 14, Page 102*, 2024, **14**, 102.

7 W. Luo, S. Wu, Y. Jiang, P. Xu, J. Zou, J. Qian, X. Zhou, Y. Ge, H. Nie and Z. Yang, *ACS Appl Mater Interfaces*, 2023, **15**, 18928–18939.

8 X. Zhao, X. Jia, Y. He, H. Zhang, X. Zhou, H. Zhang, S. Zhang, Y. Dong, X. Hu, A. V. Kuklin, G. V. Baryshnikov, H. Ågren and G. Hu, *Appl Mater Today*, 2021, **25**, 101206.

9 Z. Gao, Y. Lai, Y. Tao, L. Xiao, L. Zhang and F. Luo, *ACS Cent Sci*, 2021, **7**, 1066–1072.

10 Y. Guo, R. Zhang, S. Zhang, Y. Zhao, Q. Yang, Z. Huang, B. Dong and C. Zhi, *Energy Environ Sci*, 2021, **14**, 3938–3944.

11 J. Chen, Q. Zhou, L. Yue, D. Zhao, L. Zhang, Y. Luo, Q. Liu, N. Li, A. A. Alshehri, M. S. Hamdy, F. Gong and X. Sun, *Chemical Communications*, 2022, **58**, 3787–3790.