

Supporting Information

Metastable State Structure Promotes Surface Reconstruction of Spinel NiFe₂O₄ for Efficient Oxygen Evolution Reaction

Hong-Rui Zhu^a, Gui-Xiang Ding^b, Hui-Min Xu^a, Chen-Jin Huang^a, Vyacheslav Yu. Fominski^{c,*} Gao-Ren Li^{a,*}

^a*College of Materials Science and Engineering, Sichuan University, Chengdu 610065, China*

^b*College of Materials Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, China*

^c*National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe sh. 31, Moscow 115409, Russia*

*Corresponding authors (E-mails: VYFominskij@mephi.ru; ligaoren@scu.edu.cn)

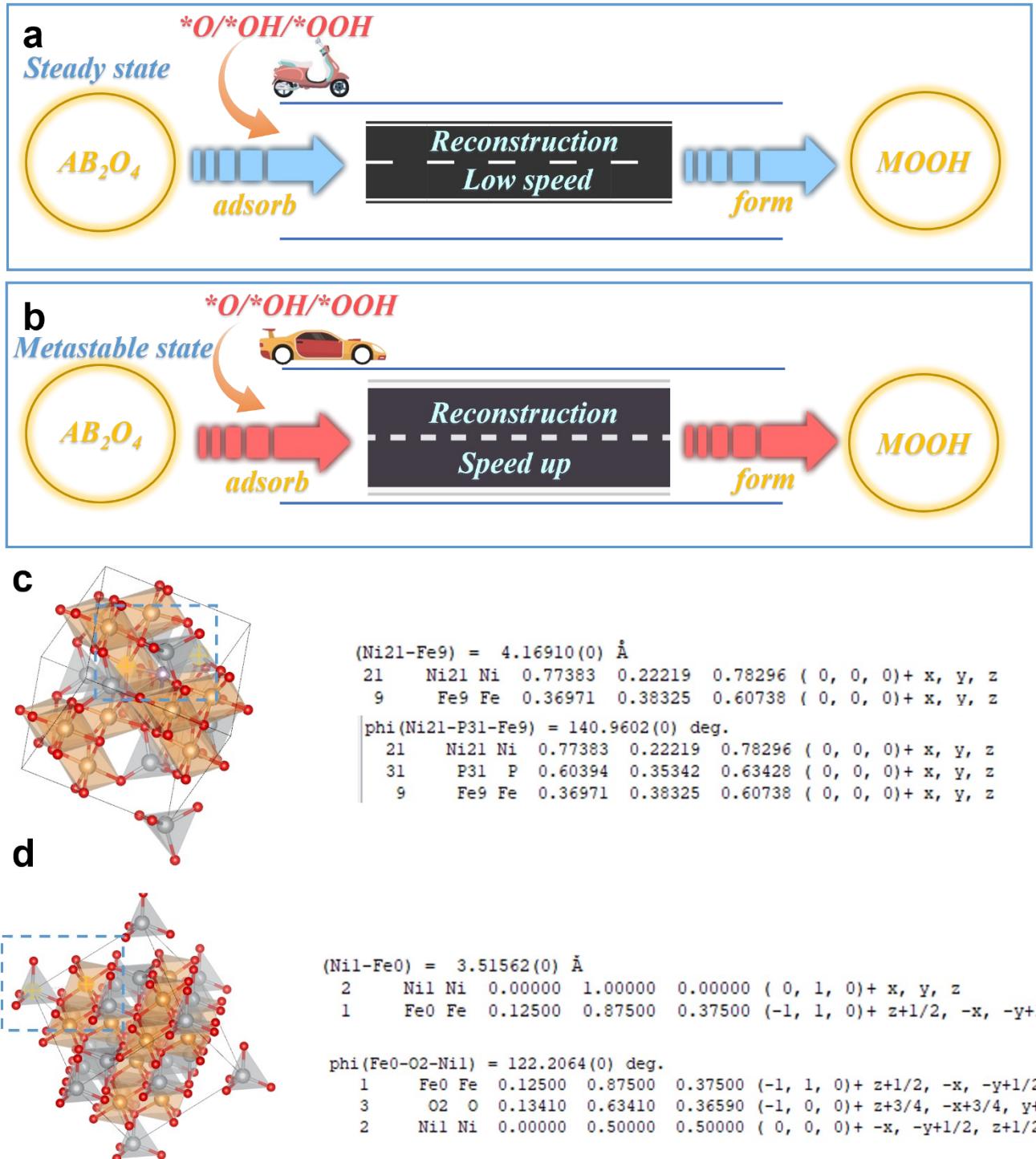


Figure S1. (a,b) Steady state spinel and metastable state spinel reconstruction at different rates to form the MOOH mechanism. (c) The lattice structure models of A-P-NFO and (d) C-NFO (The distances and angle between Ni and Fe atoms are labelled on the right based on the simulations of VESTA).

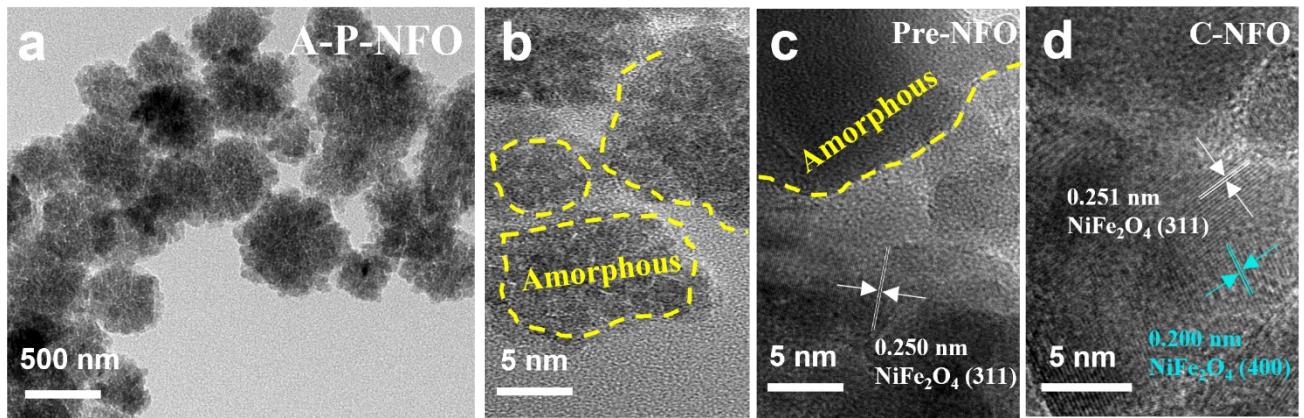


Figure S2. (a) TEM image of A-P-NFO; (b-d) HRTEM images of A-P-NFO, Pre-NFO and C-NFO.

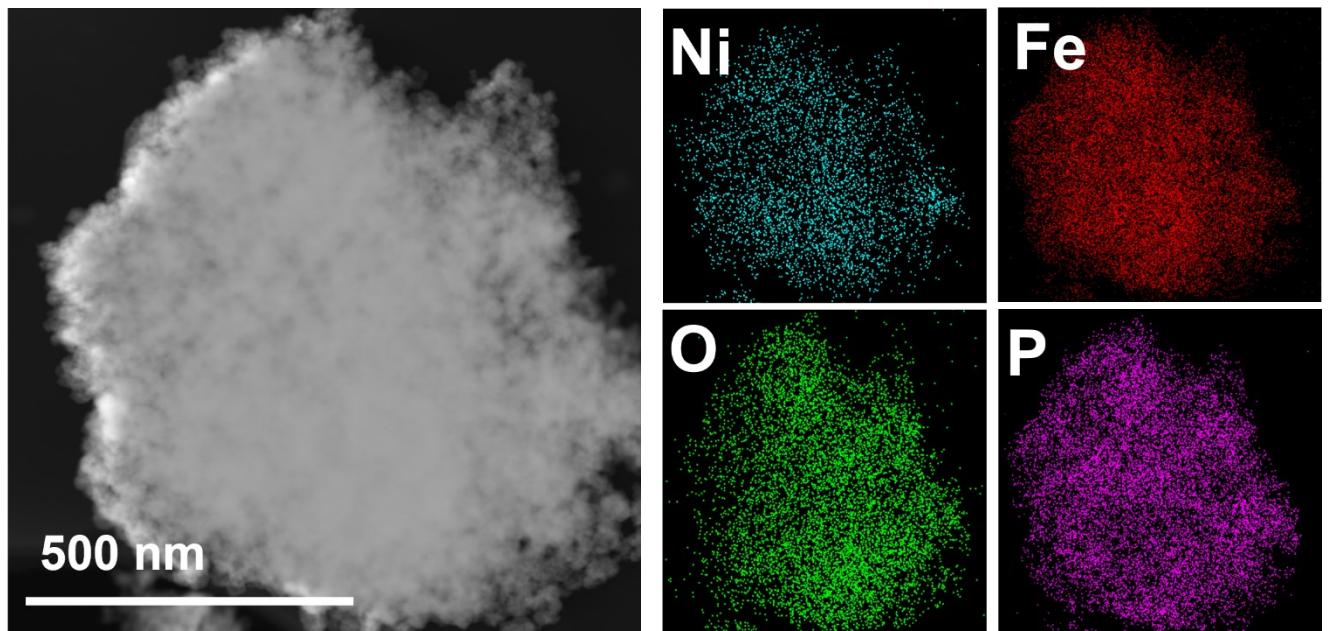


Figure S3. EDX mappings of the A-P-NFO.

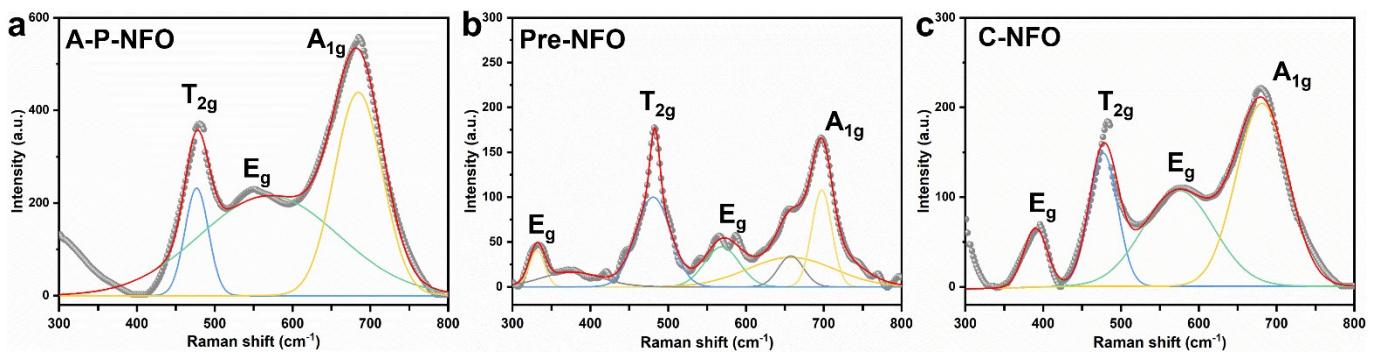


Figure S4. Peak fitting results for Raman spectra of (a) A-P-NFO, (b) Pre-NFO and (c) C-NFO.

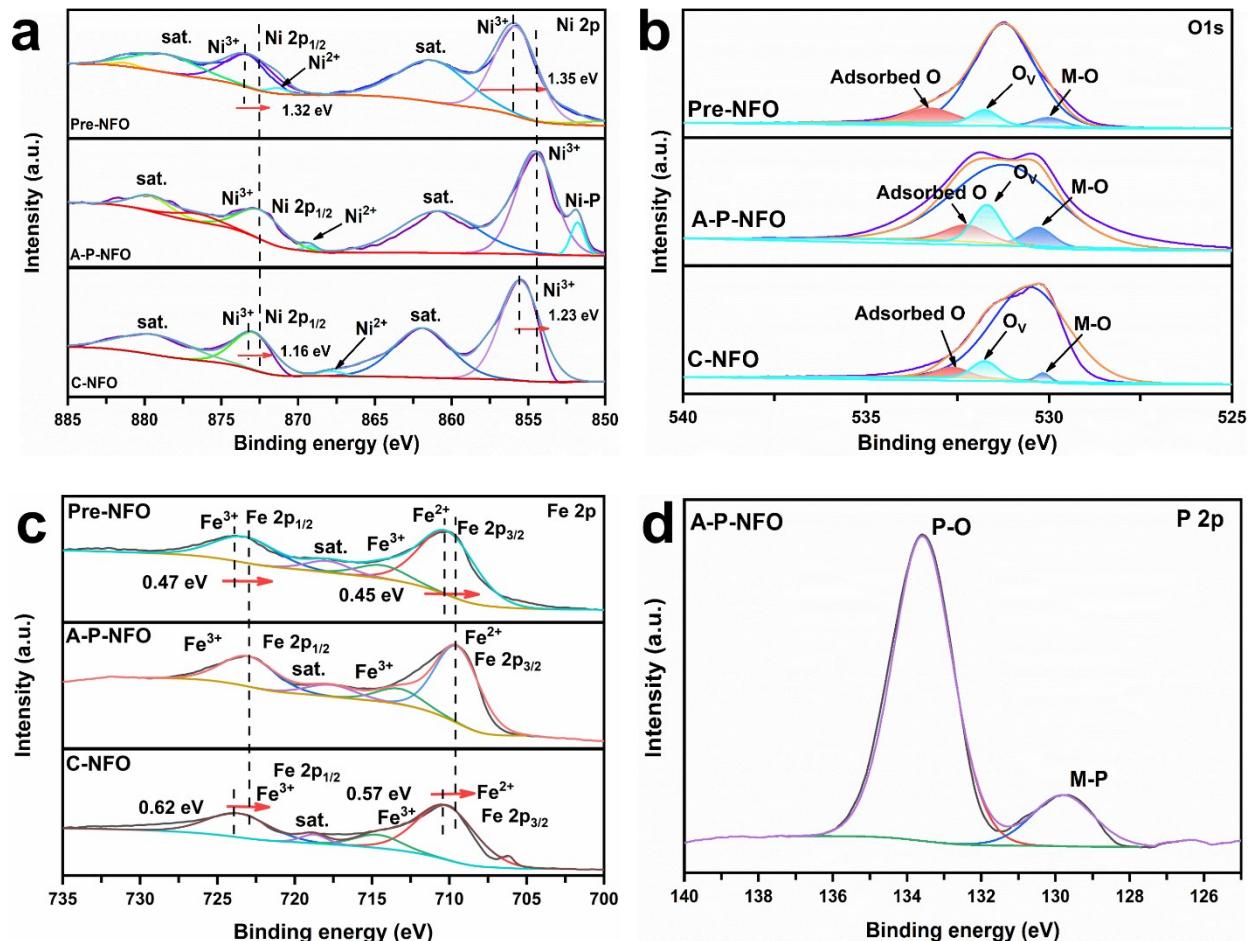


Figure S5. High-resolution XPS spectra of (a) Ni 2p, (b) O1s, (c) Fe 2p of Pre-NFO, NFO and A-P-NFO and (d)

P 2p of A-P-NFO.

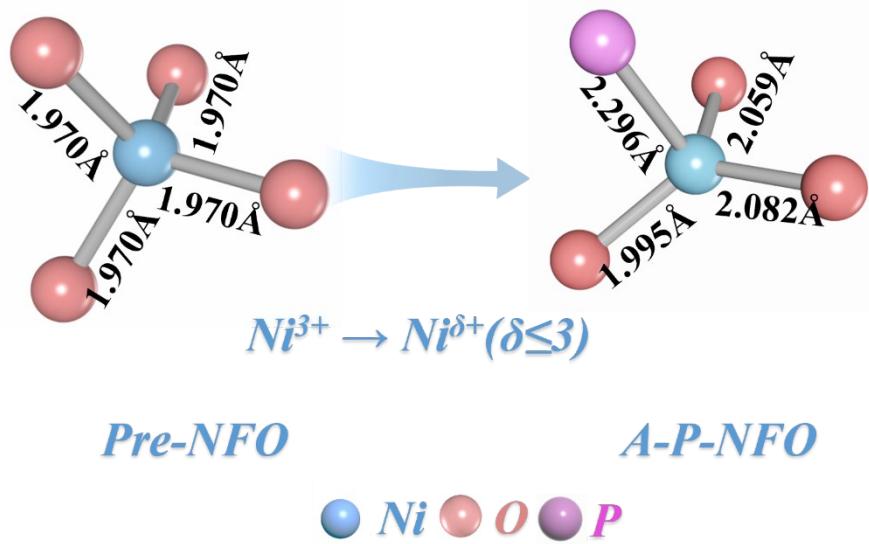


Figure S6. Theoretical models of NFO and A-P-NFO.

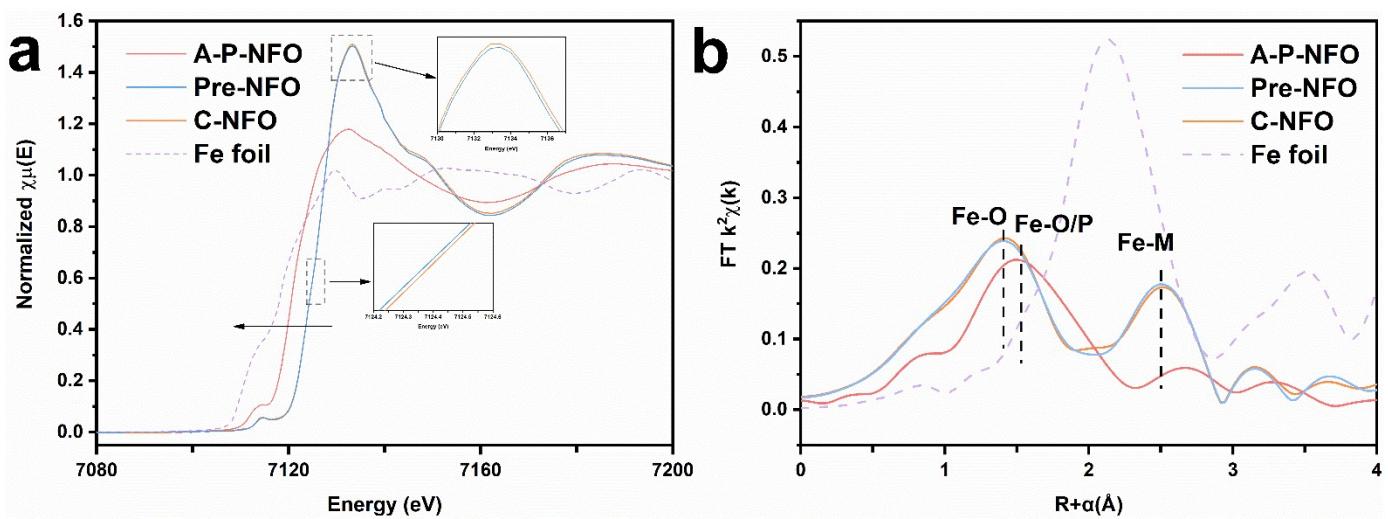


Figure S7. (a) XANES spectra of Fe-K edge of various catalysts; (b) Fe-K edge EXAFS spectra of various catalysts.

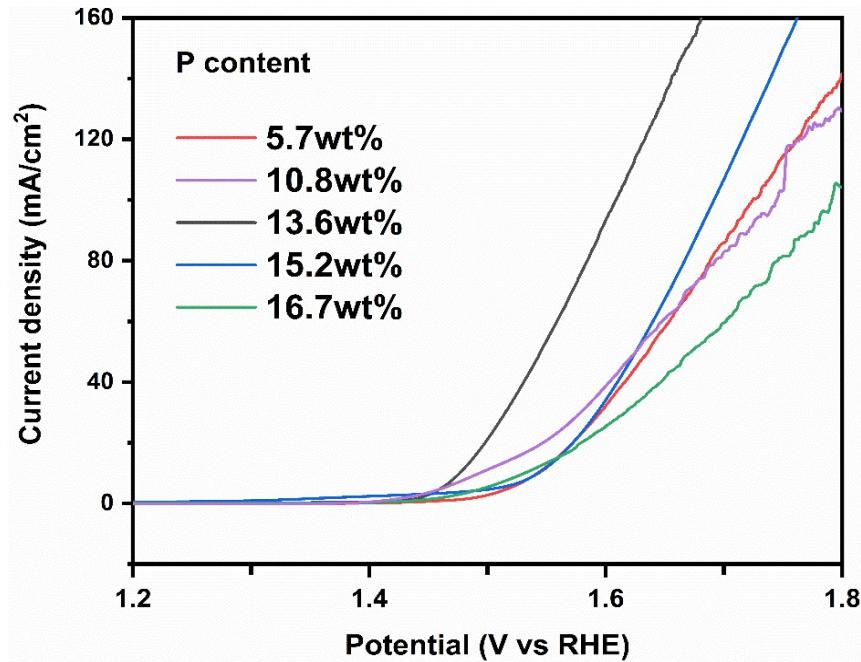


Figure S8. LSVs of A-P-NFO samples with different P contents.

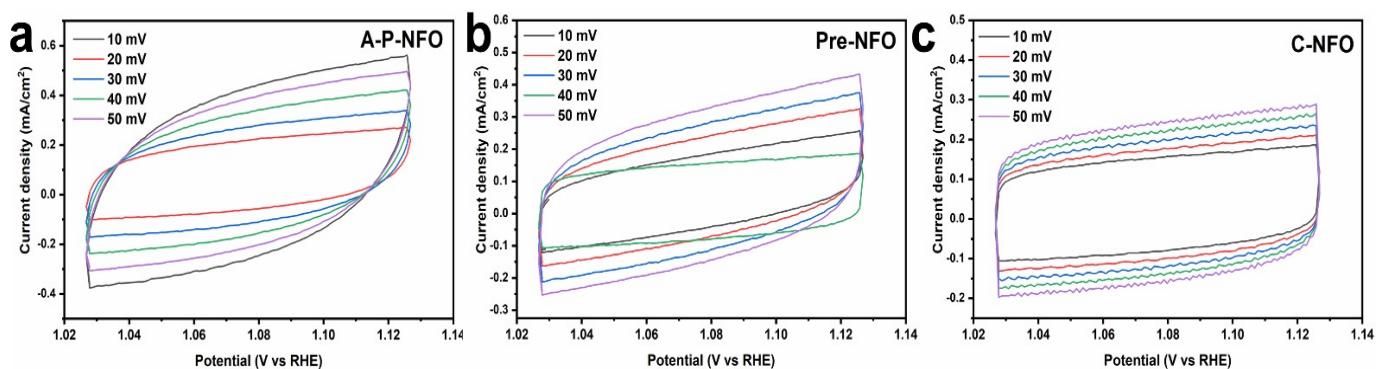


Figure S9. Cyclic voltammograms of different samples at scan rates ranging from 10 to 50 mV s^{-1} : (a) A-P-NFO, (b) Pre-NFO, and (c) NFO.

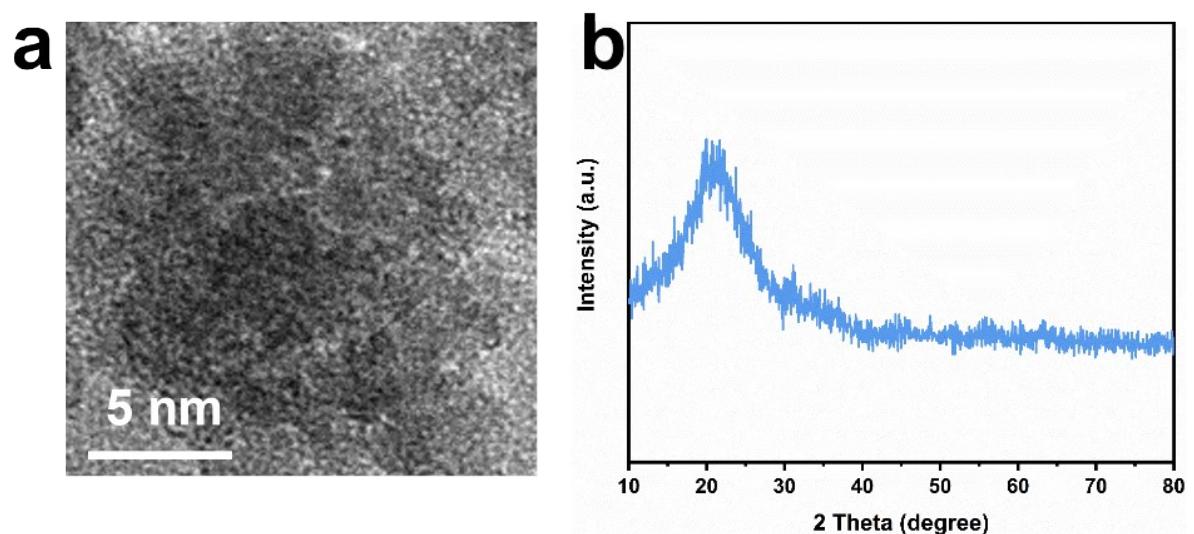


Figure S10. (a) TEM image and (b) XRD pattern of A-P-NFO after durability test.

Table S1. Elemental composition of the synthesized catalysts calculated from the weight percentages of Ni, Fe, O and P by ICP analysis.

| Sample | Ni (wt%) | Fe (wt%) | P (wt%) |
|---------|----------|----------|---------|
| A-P-NFO | 17.8 | 41.4 | 13.6 |
| Pre-NFO | 18.65 | 48.88 | / |
| C-NFO | 20.68 | 51.56 | / |

Table S2. The fitting results of the solution resistance (R_s) and charge transfer resistance (R_{ct}) of different samples by EIS.

| Sample | R_s (Ω) | R_{ct} (Ω) |
|---------|--------------------|-----------------------|
| A-P-NFO | 10.81 | 5.57 |
| Pre-NFO | 9.35 | 8.62 |
| C-NFO | 11.25 | 10.88 |

Table S3. OER catalytic performance of various electrocatalysts in 1 M KOH for comparison.

| Electrode | Overpotential (mV) (at 10 mA/cm ²) | Tafel slope (mV dec ⁻¹) | Stable (h) | Ref. |
|--|---|-------------------------------------|------------|------------------|
| A-P-NFO | 240 | 52 | 100 | This work |
| Ni ₂ P-NiFe ₂ O ₄ | 255 | 48.54 | 48 | [7] |
| HO _{oct} -NFO NC/IF | 260 | 36.1 | 50 | [8] |
| NiFe ₂ O _{4-x} /NMO-25 | 262 | 41.9 | 40 | [9] |
| NiFe _x /NiFe ₂ O ₄ @NC | 262 | 51.4 | 150 | [10] |
| AT NiFe ₂ O ₄ QDs | 262 | 53 | 9 | [11] |
| NiFe ₂ O ₄ /Ti ₃ C ₂ | 266 | 71.4 | 8.33 | [12] |
| NiCo LDH-TPA | 267 | 52.4 | 18 | [13] |
| Fe-Ni@NC-CNTs | 274 | 45.47 | 11.11 | [14] |
| NiFe ₂ O ₄ /NiFe(OH) _x | 276 | 68 | 12 | [15] |
| NiO/NiFe ₂ O ₄ | 279 | 42 | 450 | [16] |
| Ni ₃ S ₂ @FeNi-NFO/C | 280 | 33.9 | 12 | [17] |
| MoS ₂ @NiFe ₂ O ₄ | 290 | 68.7 | 24 | [18] |
| Ni/Fe ₃ O ₄ @ONC | 296 | 61 | 10 | [19] |
| M _x Ni _{1-x} Fe ₂ O ₄ | 381 | 46.4 | 2 | [20] |

References

- [1] X. Li, H. Zhang, Q. Hu, W. Zhou, J. Shao, X. Jiang, C. Feng, H. Yang, C. He, *Angew. Chem. Int. Ed.* **2023**, *62*, e202300478.
- [2] M. S. S. Clark, C. Pickard, P. Hasnip, M. Probert, K. Refson, M. Payne, *Zeitschrift Fur Kristallographie* **2005**, *220*, 567-570.
- [3] a)P. J. Hasnip, C. J. Pickard, *Comp. Phy. Commun.* **2006**, *174*, 24-29; b) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B Cond. Matt.* **1992**, *46*, 6671-6687.
- [4] D. Vanderbilt, *Phys. Rev. B Cond. Matt.* **1990**, *41*, 7892-7895.
- [5] M. P. M. Probert, *Phy. Rev. B* **2003**, *67*, 7.
- [6] V. H. Do, P. Prabhu, V. Jose, T. Yoshida, Y. Zhou, H. Miwa, T. Kaneko, T. Uruga, Y. Iwasawa, J. M. Lee, *Adv. Mater.* **2023**, *35*, e2208860.
- [7] Y. Li, Z. Zhang, Z. Zhang, J. He, M. Xie, C. Li, H. Lu, Z. Shi, S. Feng, *Appl. Catal. B-Environ. Energy* **2023**, *339*, 123141.
- [8] Y. Peng, C. Huang, J. Huang, M. Feng, X. Qiu, X. Yue, S. Huang, *Adv. Funct. Mater.* **2022**, *32*, 2201011.
- [9] J. Choi, D. Kim, W. Zheng, B. Yan, Y. Li, L. Y. S. Lee, Y. Piao, *Appl. Catal. B-Environ. Energy* **2021**, *286*.
- [10] J. Zhao, X. Zhang, M. Liu, Y.-Z. Jiang, M. Wang, Z.-Y. Li, Z. Zhou, *J. Mater. Chem. A* **2019**, *7*, 21338-21348.
- [11] H. Yang, Y. Liu, S. Luo, Z. Zhao, X. Wang, Y. Luo, Z. Wang, J. Jin, J. Ma, *ACS Catal.* **2017**, *7*, 5557-5567.
- [12] P. V. Shinde, P. Mane, B. Chakraborty, C. Sekhar Rout, *J. Colloid. Interface. Sci.* **2021**, *602*, 232-241.
- [13] W. Liu, D. Zheng, T. Deng, Q. Chen, C. Zhu, C. Pei, H. Li, F. Wu, W. Shi, S. W. Yang, Y. Zhu, X. Cao, *Angew. Chem. Int. Ed.* **2021**, *60*, 10614-10619.
- [14] X. Zhao, P. Pachfule, S. Li, J. R. J. Simke, J. Schmidt, A. Thomas, *Angew. Chem. Int. Ed.* **2018**, *57*, 8921-8926.
- [15] L. Yao, Z. Geng, W. Zhang, X. Wu, J. Liu, L. Li, X. Wang, X. Hou, K. Xu, K. Huang, S. Feng, *ACS Sus. Chem. Eng.* **2020**, *8*, 17194-17200.
- [16] H. Zhong, G. Gao, X. Wang, H. Wu, S. Shen, W. Zuo, G. Cai, G. Wei, Y. Shi, D. Fu, C. Jiang, L. W. Wang, F. Ren, *Small* **2021**, *17*, e2103501.
- [17] L. Xu, S. Ali Shah, H. Khan, R. Sayyar, X. Shen, I. Khan, A. Yuan, W. Yaseen, Z. Ali Ghazi, A. Naeem, H. Ullah, X. Li, C. Wang, *J. Colloid. Interface. Sci.* **2022**, *617*, 1-10.
- [18] M. Karpuraranjith, Y. Chen, B. Wang, J. Ramkumar, D. Yang, K. Srinivas, W. Wang, W. Zhang, R. Manigandan, *J. Colloid. Interface. Sci.* **2021**, *592*, 385-396.
- [19] G. Liu, R. Yao, Y. Zhao, M. Wang, N. Li, Y. Li, X. Bo, J. Li, C. Zhao, *Nanoscale* **2018**, *10*, 3997-4003.
- [20] V. Maruthapandian, M. Mathankumar, V. Saraswathy, B. Subramanian, S. Muralidharan, *ACS. Appl. Mater. Interfaces* **2017**, *9*, 13132-13141.