

Electronic Modulation and Surface Reconstruction of Cactus-Like $\text{CoB}_2\text{O}_4@FeOOH$ Heterojunction for Synergistically Triggering Oxygen Evolution Reaction

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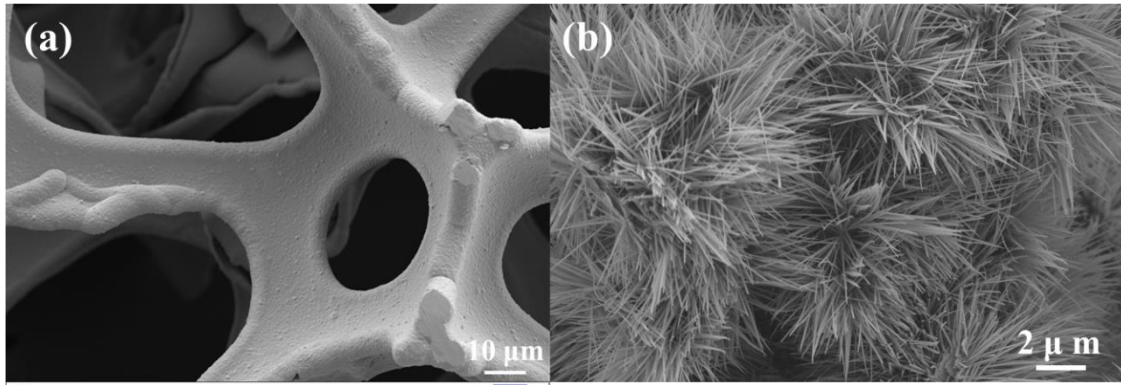


Figure S1 SEM images of (a) NF and (b) Co(OH)F/NF.

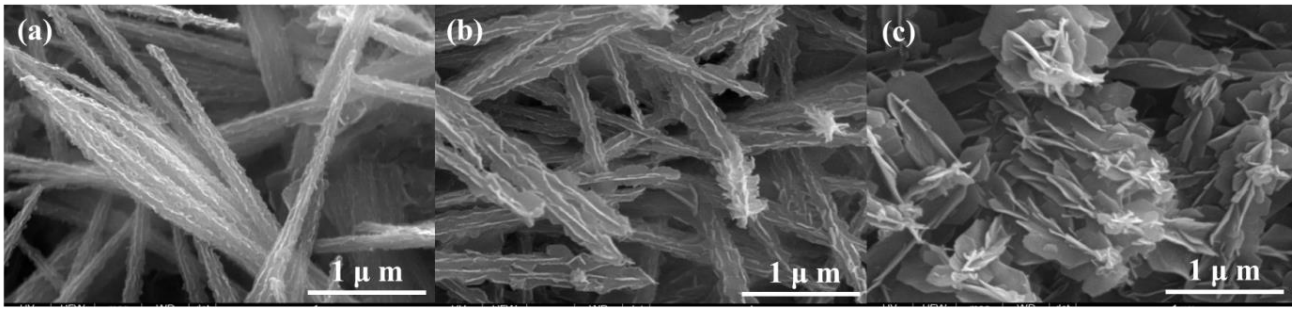


Figure S2 SEM images of the CoB₂O₄@FeOOH/NF with various electro-synthesis time ((a) 60 s, (b) 180 s and (c) 300 s).

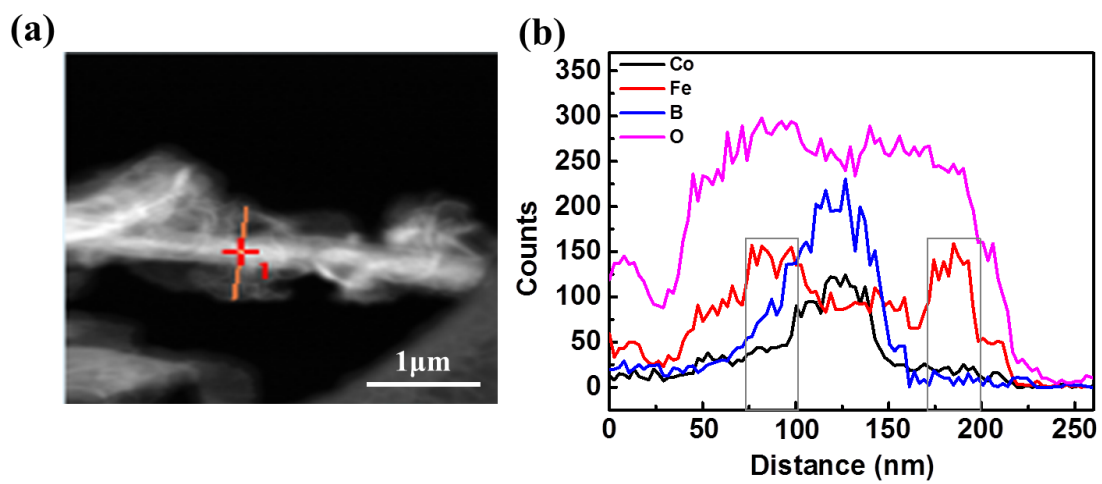


Figure S3 (a) and (b) elemental line scanning images of $\text{CoB}_2\text{O}_4@\text{FeOOH}/\text{NF}$.

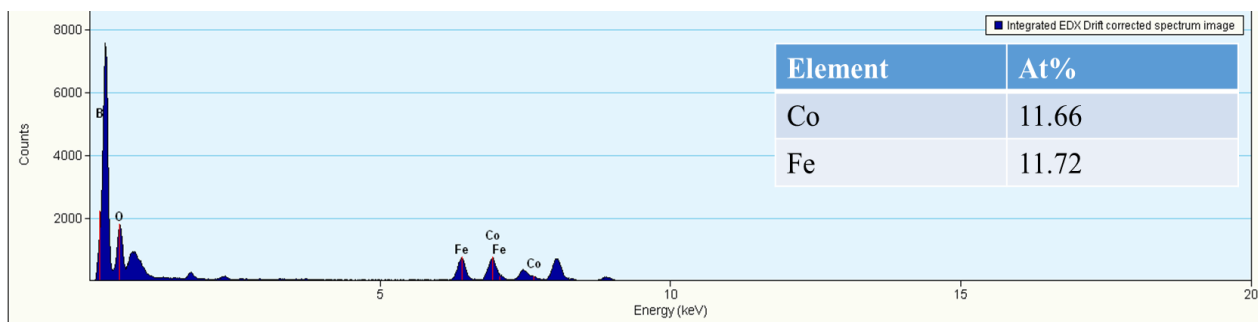


Figure S4 TEM-EDS spectrum of CoB₂O₄@FeOOH/NF.

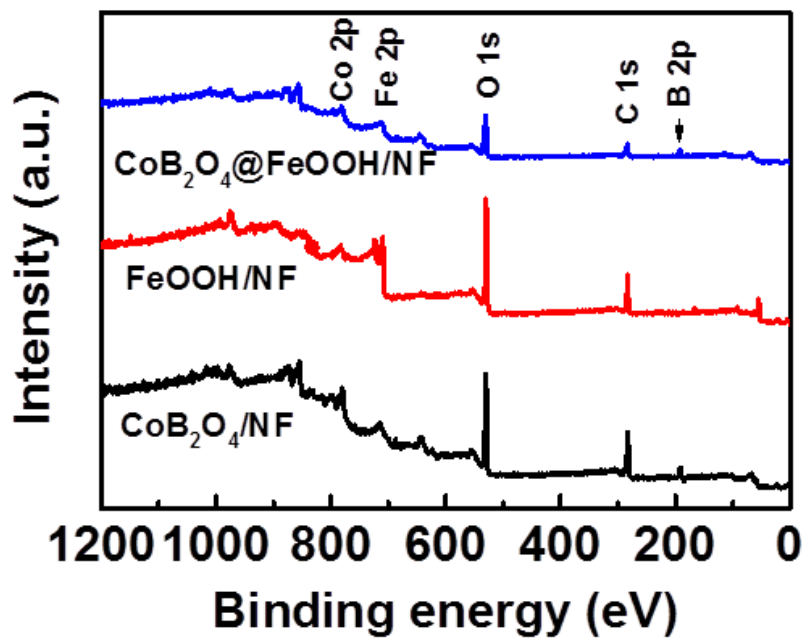


Figure S5 The survey XPS spectra of CoB₂O₄ /NF, FeOOH/NF and CoB₂O₄@FeOOH/NF.

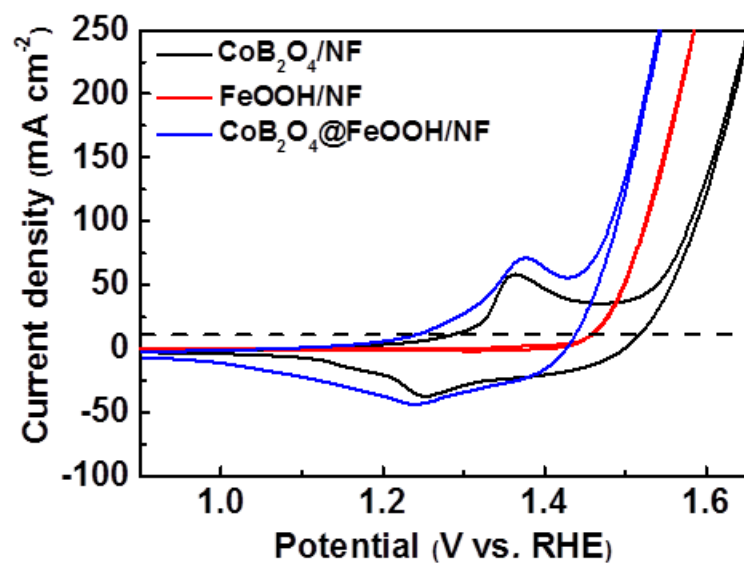


Figure S6 CV curves of CoB₂O₄ /NF, FeOOH/NF and CoB₂O₄@FeOOH/NF.

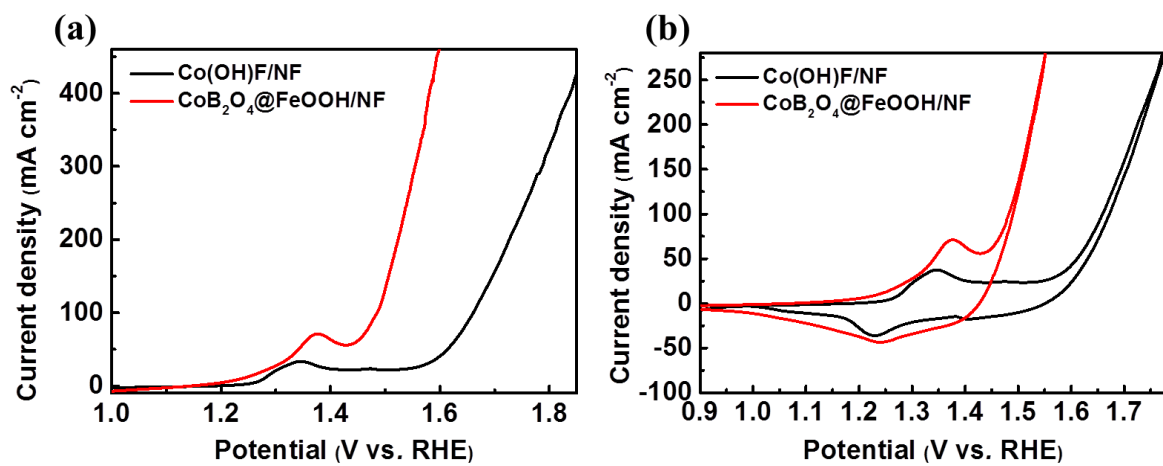


Figure S7 (a) LSV curves and (b) CV curves of Co(OH)F/NF and CoB₂O₄@FeOOH/NF.

Table S1 Comparison of OER activities for reported catalysts

Catalysts	Substrate	η_{10} (mV)	η_{100} (mV)	Stability	Ref
CoB₂O₄@FeOOH/NF	Ni Foam	205	260	100 h	This work
FeOOH/Cr-NiCo ₂ O ₄ /NF	Ni Foam	217	268	20 h	[1]
FeOOH(Se)/IF	Iron foam	287	364	15 h	[2]
CoP/FeOOH	-	290	-	20 h	[3]
NiV-LDH@FeOOH/NF	Ni Foam	-	297	20 h	[4]
Co@Co-Bi/Ti	Ti mesh	329	373	20000s	[5]
Co-Fe-Bi/NF	Ni Foam	307	-	40 h	[6]
CC@CoO@FeOOH-NWAs	Carbon Cloth	255	-	20 h	[7]
Co-B@Co-Bi	-	291	-	25 h	[8]
FeOOH@NiCo ₂ O ₄	-	203	259	10 h	[9]
FeOOH/Co/FeOOHHNTAs-NF	Ni Foam	239	305	50 h	[10]

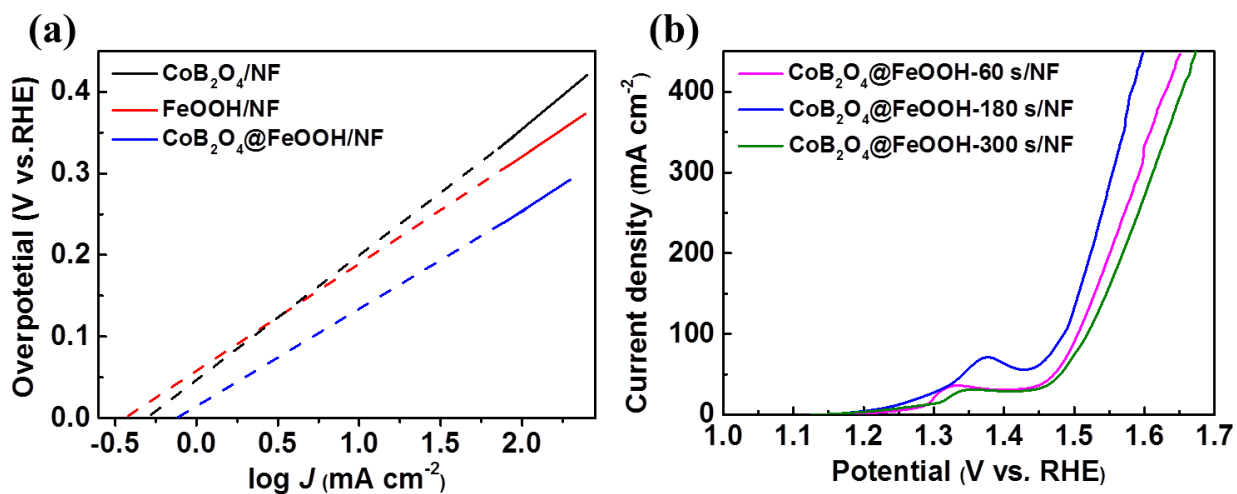


Figure S8 (a) The exchange current density of $\text{CoB}_2\text{O}_4/\text{NF}$, FeOOH/NF and $\text{CoB}_2\text{O}_4@\text{FeOOH}/\text{NF}$, (b) LSV curves of catalysts with different electro-synthesis time for $\text{CoB}_2\text{O}_4@\text{FeOOH}/\text{NF}-60$, $\text{CoB}_2\text{O}_4@\text{FeOOH}/\text{NF}-180$, $\text{CoB}_2\text{O}_4@\text{FeOOH}/\text{NF}-300$.

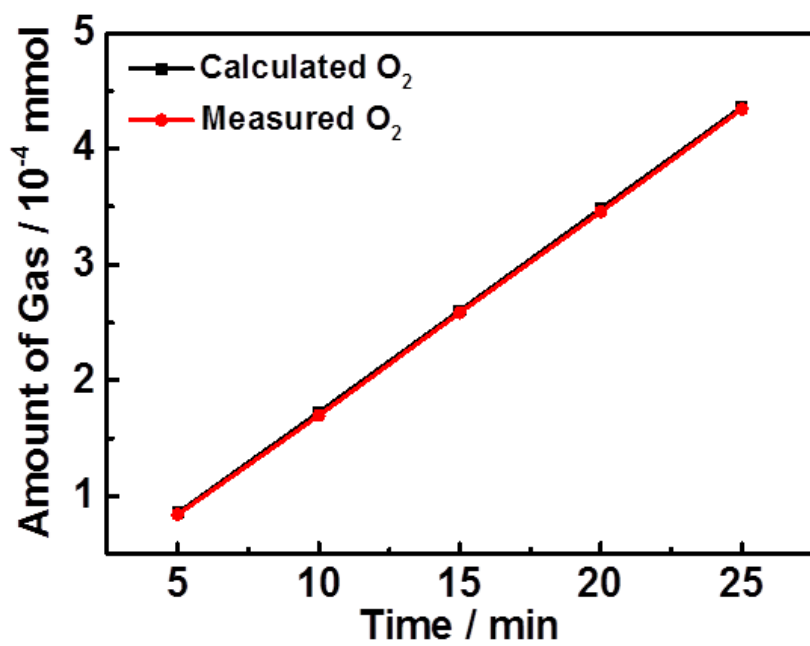


Figure S9 Faradaic efficiency of the CoB₂O₄@FeOOH/NF catalyst for O₂ evolution.

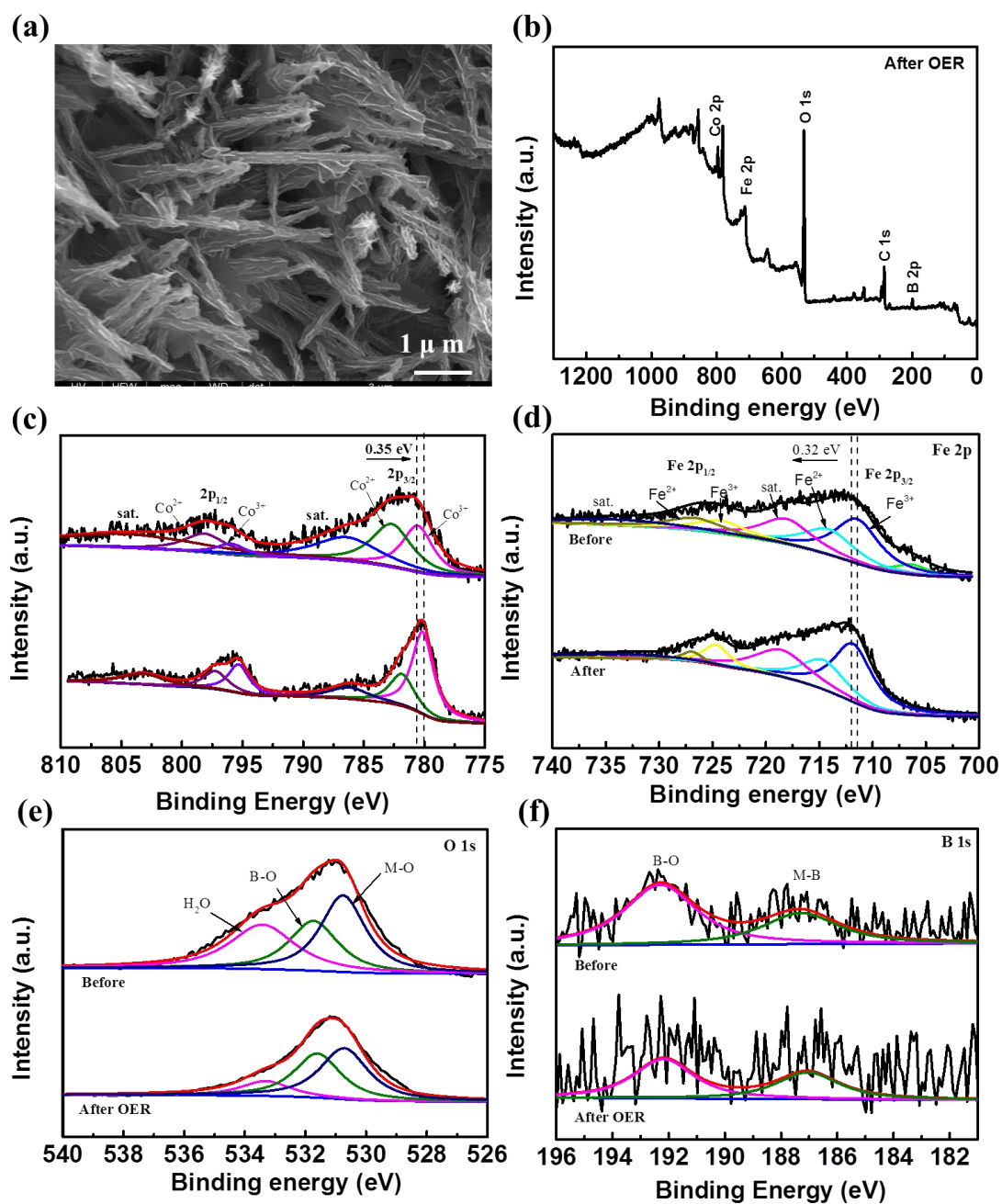


Figure S10 (a) SEM image of $\text{CoB}_2\text{O}_4@FeOOH/NF$ after durability test. (b) The survey XPS of $\text{CoB}_2\text{O}_4@FeOOH/NF$ after durability test. Comparison of XPS spectra of (c) Co 2p, (d) Fe 2p, (e) O 1s and (f) B 1s before and after OER durability test.

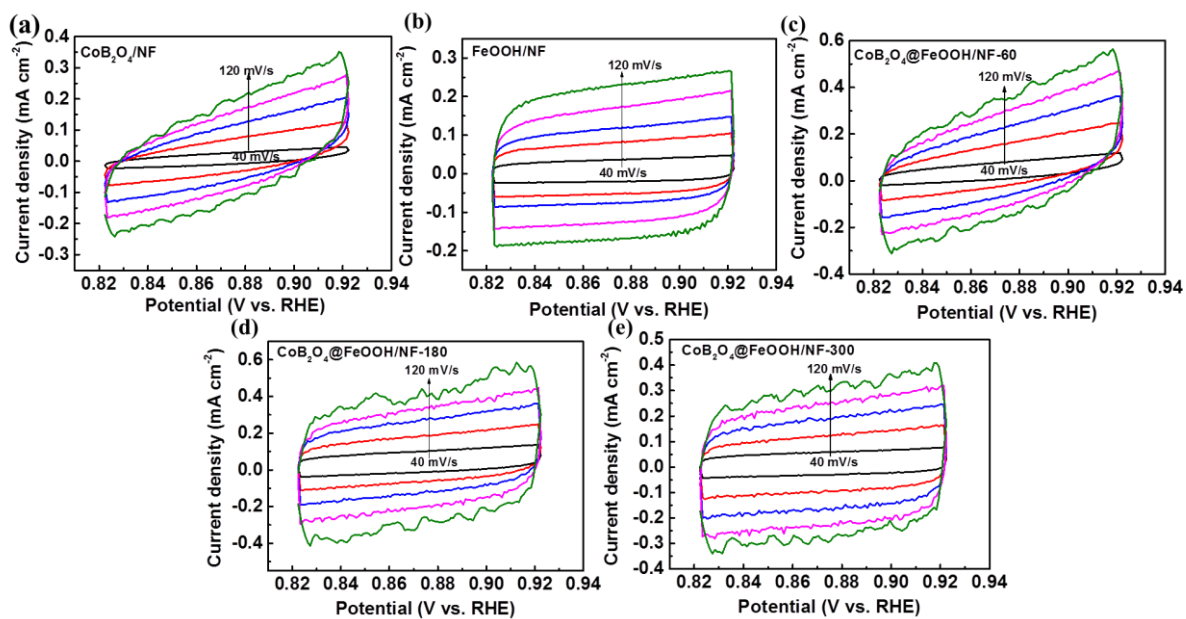


Figure S11 CV curves of CoB₂O₄ /NF, FeOOH/NF and CoB₂O₄@FeOOH/NF recorded from 0.8224 to 0.9224 V (vs. RHE) at different scan rates (40, 60, 80, 100, 120 mV s⁻¹).

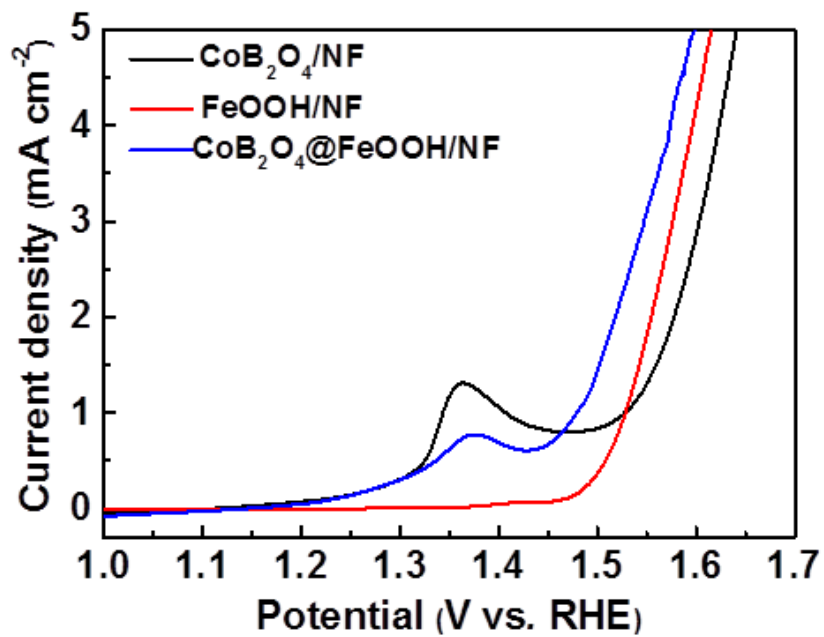


Figure S12 OER polarization curves standardized by ECSA of CoB₂O₄/NF, FeOOH/NF and CoB₂O₄@FeOOH/NF.

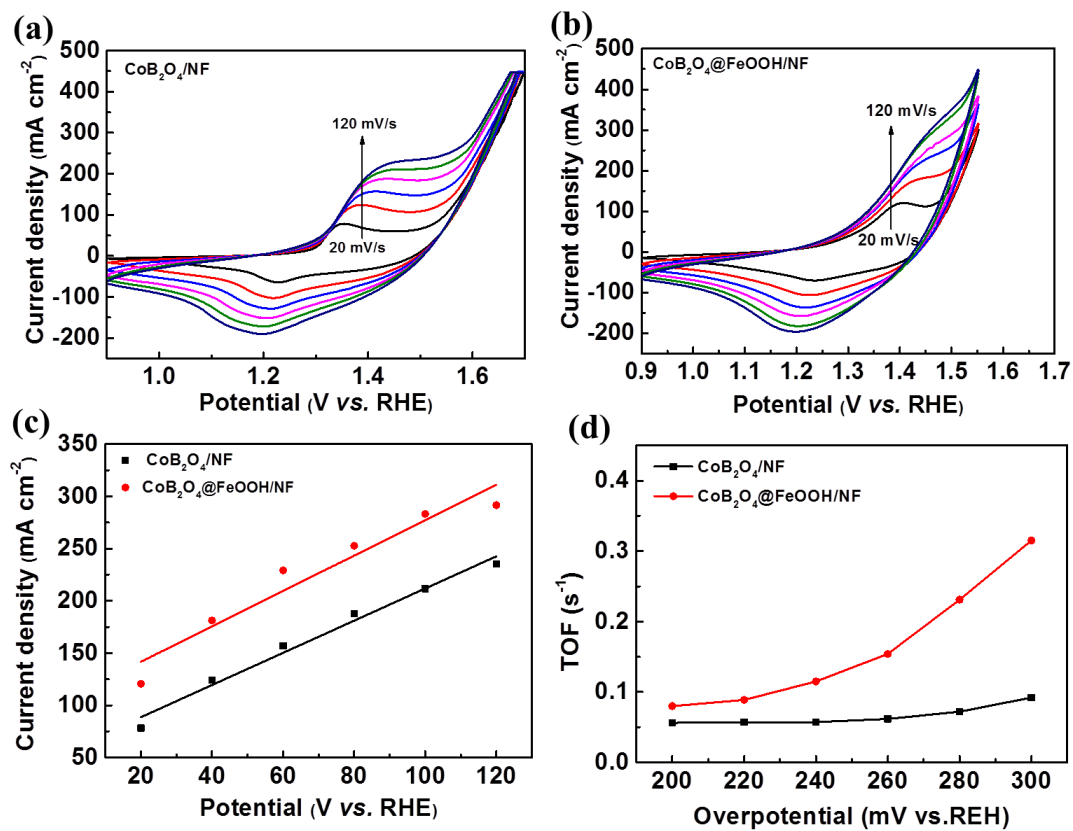


Figure S13 Cyclic voltammograms of (a) $\text{CoB}_2\text{O}_4/\text{NF}$ and (b) $\text{CoB}_2\text{O}_4@\text{FeOOH}/\text{NF}$ at various scan rates (c) Linear relationship of the peak current density for oxidation wave as a function of scan rate for $\text{CoB}_2\text{O}_4/\text{NF}$ and $\text{CoB}_2\text{O}_4@\text{FeOOH}/\text{NF}$. (d) Plot of TOF for $\text{CoB}_2\text{O}_4/\text{NF}$ and $\text{CoB}_2\text{O}_4@\text{FeOOH}/\text{NF}$

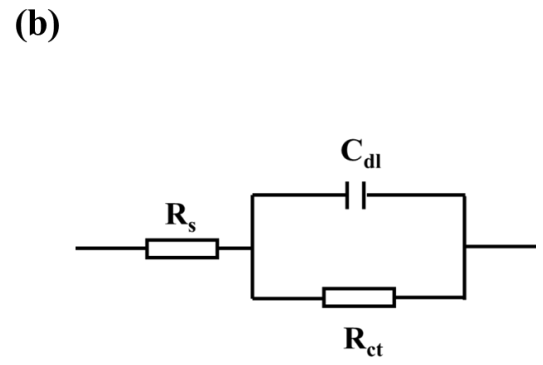
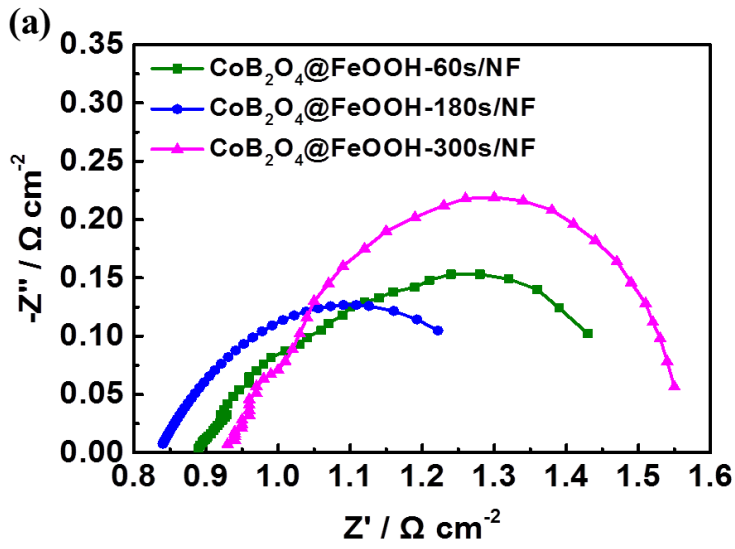


Figure S14 (a) Nyquist plots of CoB₂O₄@FeOOH/NF with different deposition times (60, 180 and 300 s) at potential of 1.5 V (vs. RHE), (b) A simplified Randles circuit by fitting the plots.

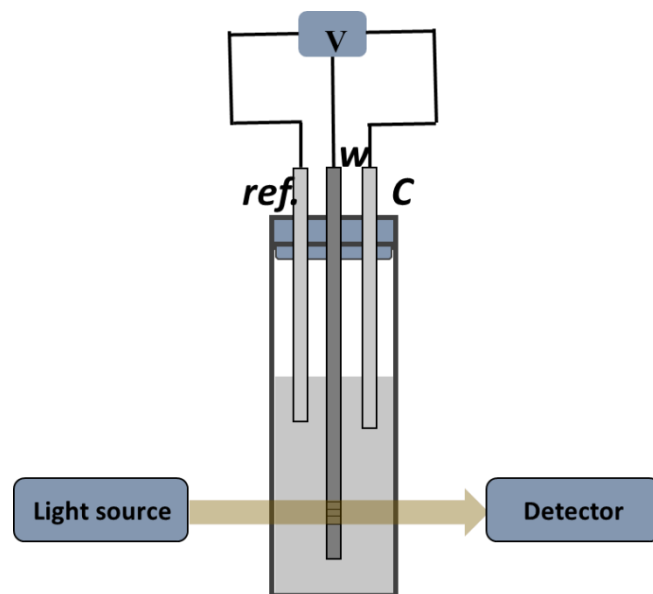


Figure S15 In-situ UV-vis experiment. W is working electrode, ref. is reference electrode and c is counter electrode.

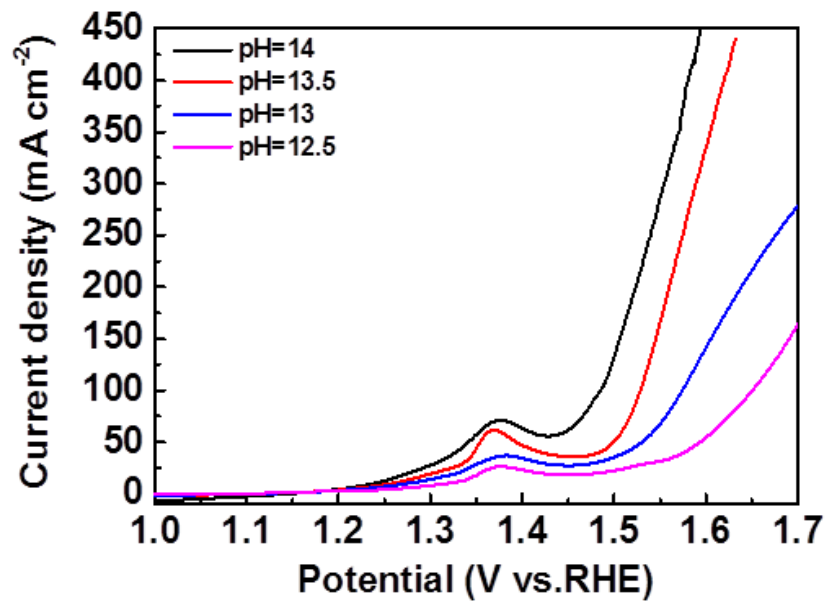


Fig. S16 LSV curves of CoB₂O₄@FeOOH/NF in a KOH solution with different PH range.

Table S2 Comparison of reported electrocatalysts for overall water splitting

Catalysts	Cell Voltages (V)		Stability (h)	Reference
	η_{50}	η_{100}		
CoB ₂ O ₄ @FeOOH/NF Pt/C/NF	1.537	1.576	125@300 mA cm ⁻²	This work
NC/Ni ₃ Mo ₃ N/NF NiMoO ₄ ·xH ₂ O/NF	1.58	1.71	50 h@500 mA cm ⁻²	[11]
NiFe(OH) _x @Ni ₃ S ₂ /MoS ₂ -CC Ni ₃ S ₂ /MoS ₂ -CC	-	1.71	48 h@20 mA cm ⁻²	[12]
NiFeCo LDH NiFeCo phosphide	1.44	1.58	70 h@50 mA cm ⁻²	[13]
Co _{1-x} Fe _x -LDH Ni _{1-x} Fe _x -LDH	1.59	1.88	24 h@25 mA cm ⁻²	[14]
FeOOH/Cr-NiCo ₂ O ₄ /NF FeOOH/Cr-NiCo ₂ O ₄ /NF	1.62	1.65	10 h@20 mA cm ⁻²	[1]
Ni ₅ P ₄ /NiP ₂ /NiFe LDH/NF Ni ₅ P ₄ /NiP ₂ /NF	1.60	1.68	50 h@50 mA cm ⁻²	[15]
NiFe LDH-NiSe/NF NiFe LDH-NiSe/NF	-	1.84	75 h@12 mA cm ⁻²	[16]
NiFe(OH) _x /FeS/IF MoNi ₄ /MoO ₂ /NF	-	1.68	70 h@300 mA cm ⁻²	[17]
Ni@NCNTs/NF-L NiFe-L	1.52	2.1	10 h@100 mA cm ⁻²	[18]
NiFe(OH) _x /FeS/IF MoNi ₄ /MoO ₂ /NF	1.50	1.68	70 h@300 mA cm ⁻²	[19]
NiFe LDH-MoS _x /INF 20%PtC/INF	-	1.72	20 h@100 mA cm ⁻²	[20]
Co ₅ Mo _{1.0} O NSs@NF Co ₅ Mo _{1.0} O NSs@NF	-	1.90	30 h@10 mA cm ⁻²	[21]
NiFe LDHs/NiCo ₂ O ₄ /NF NiFe LDHs/NiCo ₂ O ₄ /NF	1.81	1.95	24 h@15 mA cm ⁻²	[22]
NiFe-HD/pre-NF CoP/P-NiO/NF	-	1.62	85 h at 100 mA cm ⁻²	[23]

Reference

- 1 T. Liu, P. Diao, *Nano Res.*, 2020, **13**, 3299-3309.
- 2 S. Niu, W. J. Jiang, Z. X. Wei, T. Tang, J. M. Ma, J. S. Hu, L. J. Wan, *J. Am. Chem. Soc.*, 2019, **141**, 7005-7013
- 3 J. Cheng, B. Shen, Y. Song, J. Liu, Q. Ye, M. Mao, Y. Cheng, *Chem. Eng. J.*, 2022, **428**, 131130-131137
- 4 W. Bao, L. Xiao, J. Zhang, Z. Deng, C. Yang, T. Ai, X. Wei, *Chem. Commun.*, 2020, **56**, 9360-9363.
- 5 C. Xie, Y. Wang, D. Yan, L. Tao, S. Wang, *Nanoscale*, 2017, **9**, 16059-16065.
- 6 U. P. Suryawanshi, M. P. Suryawanshi, U. V. Ghorpade, S. W. Shin, J. Kim, J. H. Kim, *Appl. Surf. Sci.*, 2019, **495**, 143462-143469.
- 7 Y. Wang, Y. Ni, B. Liu, S. Shang, S. Yang, M. Cao, C. Hu, *Electrochim. Acta*, 2017, **257**, 356-363.
- 8 T. Tan, P. Han, H. Cong, G. Cheng, W. Luo, *ACS Sustain. Chem. Eng.*, 2019, **7**, 5620-5625.
- 9 X. Cao, Y. Sang, L. Wang, G. Ding, R. Yu, B. Geng, *Nanoscale*, 2020, **12**, 19404-19412.
- 10 J. X. Feng, H. Xu, Y. T. Dong, S. H. Ye, Y. X. Tong, G. R. Li, *Angew. Chem. Int. Ed.*, 2016, **55**, 3694-3698.
- 11 Y. Chen, J. Yu, J. Jia, F. Liu, Y. Zhang, G. Xiong, R. Zhang, R. Yang, D. Sun, H. Liu, W. Zhou, *Appl. Catal. B-Environ.*, 2020, **272**, 118956-118964.
- 12 X. H. Wang, Y. Ling, B. L. Li, X. L. Li, G. Chen, B. X. Tao, L. J. Li, N. B. Li, H. Q. Luo, *J. Mater. Chem. A*, 2019, **7**, 2895-2900.
- 13 J. Lee, H. Jung, Y. S. Park, N. Kwon, S. Woo, N. C. S. Selvam, G. S. Han, H. S. Jung, P. J. Yoo, S. M. Choi, J. W. Han, B. Lim, *Appl. Catal. B-Environ.*, 2021, **294**, 120246-120255.
- 14 G. Rajeshkhanna, T. I. Singh, N. H. Kim, J. H. Lee, *ACS Appl. Mater. Interfaces.*, 2018, **10**, 42453-42468.
- 15 L. Yu, H. Q. Zhou, J. Y. Sun, I. K. Mishra, D. Luo, F. Yu, Y. Yu, S. Chen, F. Ren, *J. Mater. Chem. A*, 2018, **6**, 13619-13623.
- 16 S. Dutta, A. Indra, F. Yi, T. Song, U. Paik, *ACS Appl. Mater. Interfaces*, 2017, **9**, 33766-33775.
- 17 M. Li, L. M. Tao, X. Xiao, X. W. Lv, X. X. Jiang, M. K. Wang, Z. Q. Peng, S. Yan, *ChemCatChem*, 2018, **10**, 4119-4125.
- 18 H. F. Yuan, F. Liu, G. B. Xue, H. Liu, Y. J. Wang, Y. W. Zhao, X. Y. Liu, X. L. Zhang, L. L. Zhao, Z. Liu, H. Liu, W. J. Zhou, *Appl. Catal. B- Environ.*, 2021, **283**, 119647-119657.
- 19 S. Niu, W. J. Jiang, T. Tang, L. P. Yuan, H. Luo, J. S. Hu, *Adv. Funct. Mater.*, 2019, **29**, 1902180-1902189
- 20 H. Zhang, G. Shen, X. Liu, B. Ning, C. Shi, L. Pan, X. Zhang, Z.-F. Huang, J.-J. Zou, *Chin. J. Catal.*, 2021, **42**, 1732-1741.
- 21 Y. Zhang, Q. Shao, S. Long, X. Huang, *Nano Energy*, 2018, **45**, 448-455.
- 22 Z. Wang, S. Zeng, W. Liu, X. Wang, Q. Li, Z. Zhao, F. Geng, *ACS Appl. Mater. Interfaces*, 2017,

9, 1488-1495.

23 B. Wu, Z. Yang, X. Dai, X. Yin, Y. Gan, F. Nie, Z. Ren, Y. Cao, Z. Li, X. Zhang, Dalton Trans., 2021, **50**, 12547-12554.