

Supplementary Information

Electronically Modulated Nickel Boron by CeO_x Doping as a Highly Efficient Electrocatalyst toward Overall Water Splitting

Huimin Wang,^a Huixiang Liu,^b Tao Feng,^a Lincai Wang,^{*a} Wenyi Yuan,^a Qing Huang^a and Yanhui Guo^{*b}

a. Shanghai Collaborative Innovation Centre for WEEE Recycling, Shanghai Polytechnic University, Shanghai, 201209, P.R. China.

b. Department of Materials Science, Fudan University, Shanghai, 200433, P.R. China.

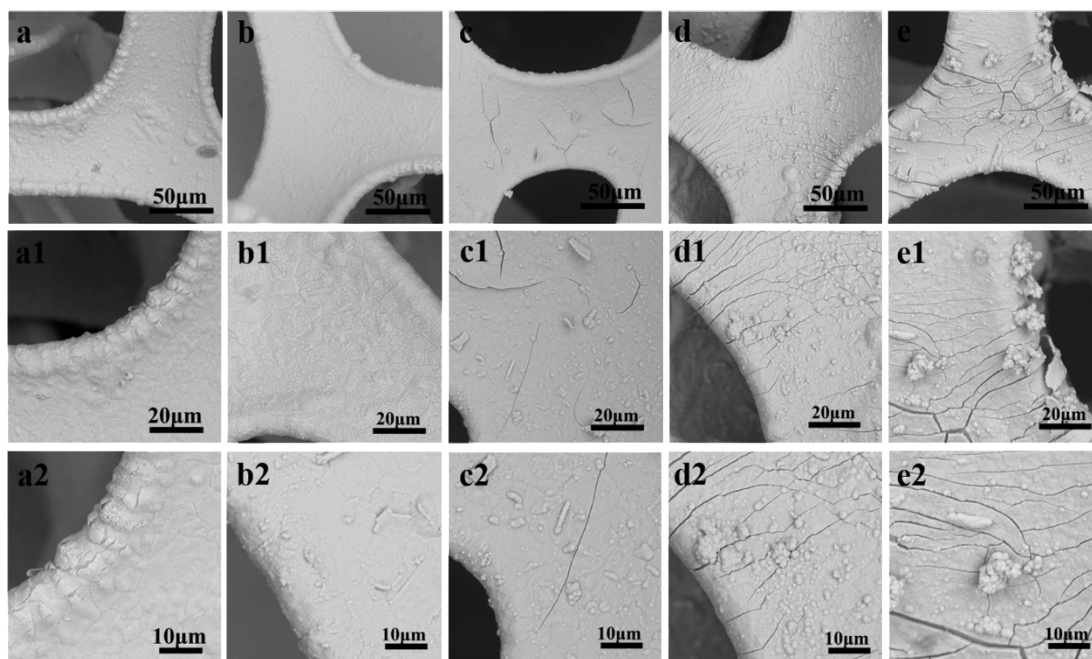


Fig. S1 SEM images of $\text{CeO}_x\text{-NiB@NF}$ after electroless plating at 30 °C for (a) 30 min; (b) 60 min; (c) 90 min; (d) 120 min and (e) 150 min.

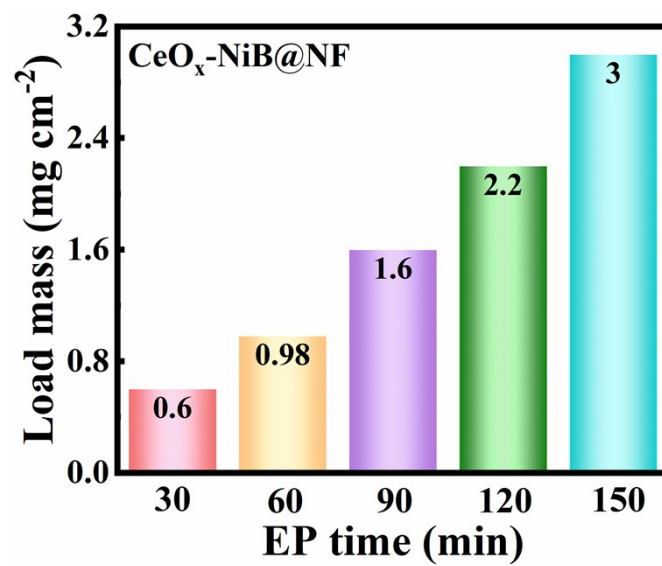


Fig. S2 Loading mass of CeO_x-NiB@NF at different EP times.

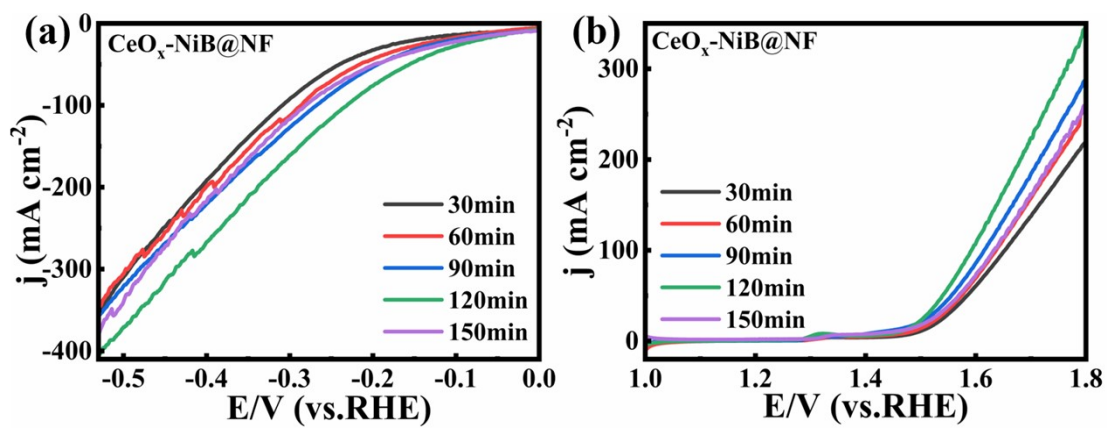


Fig. S3. (a)-(b) LSV curves for HER and OER of $\text{CeO}_x\text{-NiB@NF}$ at different EP times.

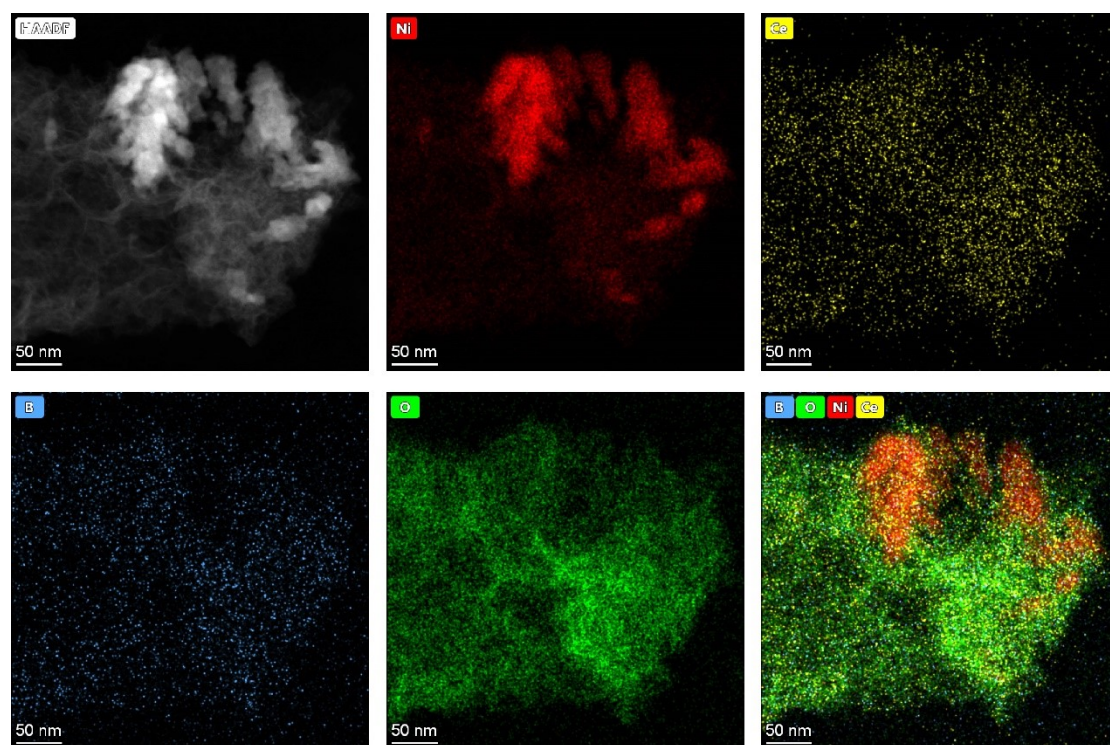


Fig. S4 HAADF image and corresponding elemental mapping images of Ni, Ce, B and O of $\text{CeO}_x\text{-NiB}$ peeled from $\text{CeO}_x\text{-NiB@NF}$.

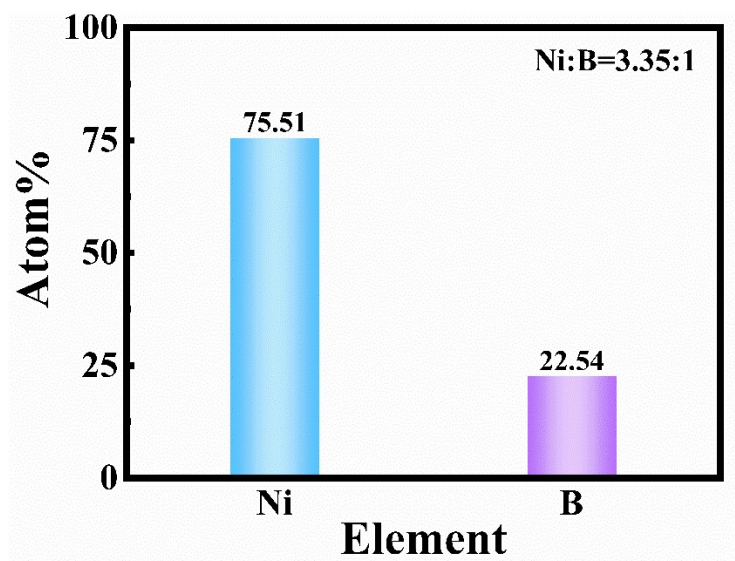


Fig. S5 Atom% of Ni and B in Ni-B@NF sample.

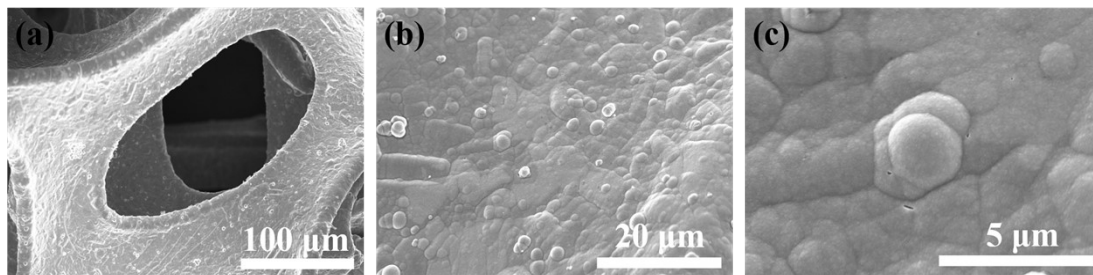


Fig. S6 FESEM images of Ni-B@NF.

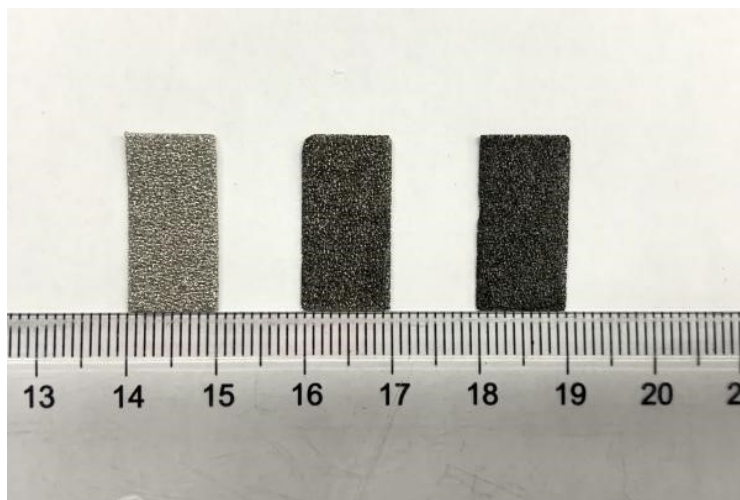


Fig. S7 Optical photos of NF, Ni-B@NF and CeO_x-NiB@NF.

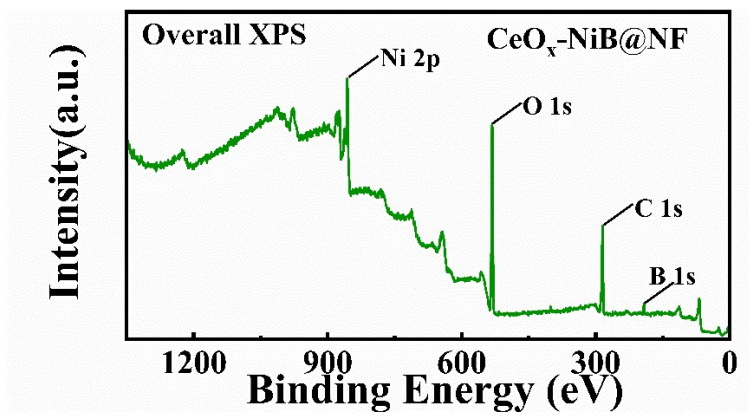


Fig. S8 Overall XPS spectra of CeO_x-NiB@NF.

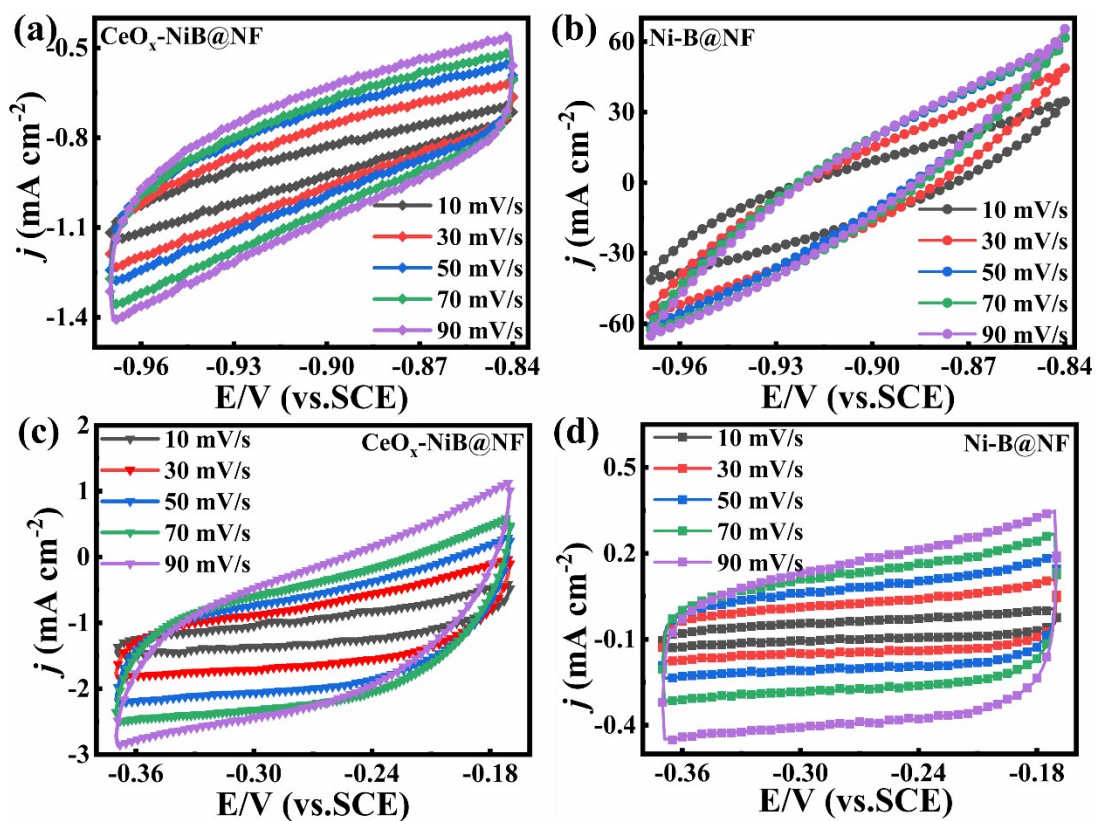


Fig. S9. (a-b) Cyclic voltammograms of Ni-B@NF and CeO_x-NiB@NF electrodes at different scan rates in 1.0 M KOH for HER; (c-d) Cyclic voltammograms of Ni-B@NF and CeO_x-NiB@NF electrode at different scan rates in 1.0 M KOH for OER.

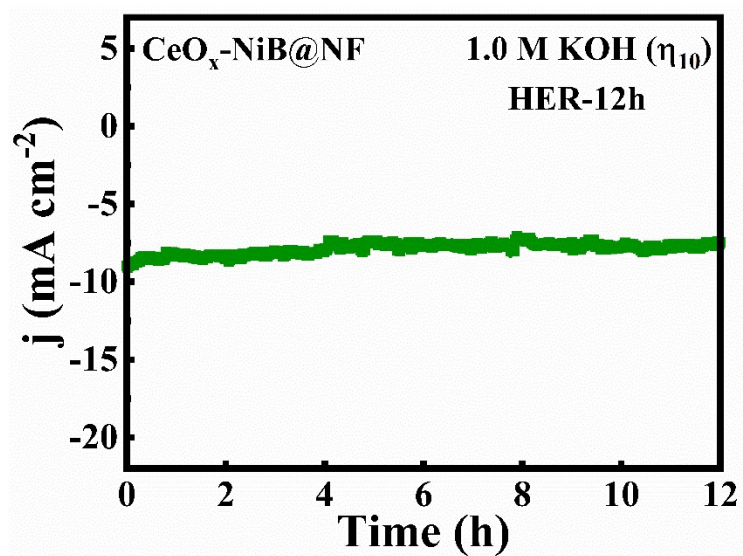


Fig. S10 Chronoamperometry measurements of long-term stability of CeO_x-NiB@NF at around 10 mA·cm⁻² for 12 h.

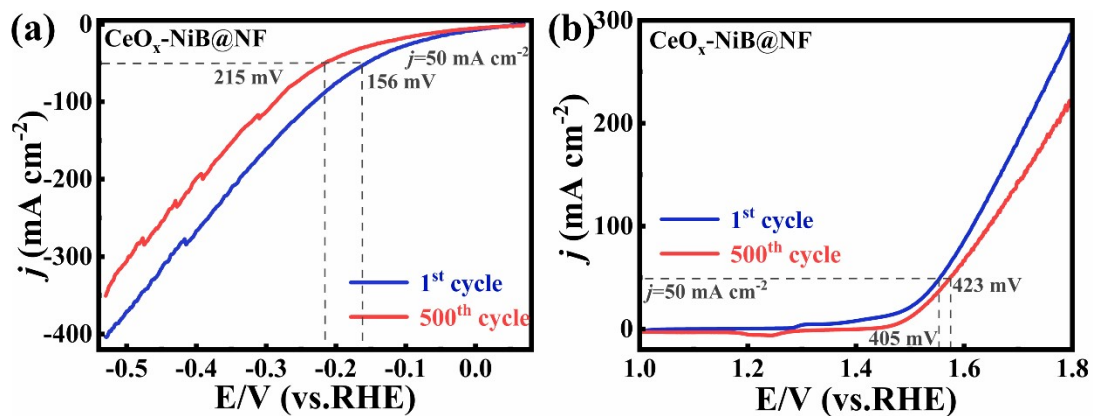


Fig. S11. (a) LSV curves for $\text{CeO}_x\text{-NiB@NF}$ electrode toward HER before and after 500 continuous CV scan cycles; (b) LSV curves for $\text{CeO}_x\text{-NiB@NF}$ electrode toward OER before and after 500 continuous CV scan cycles.

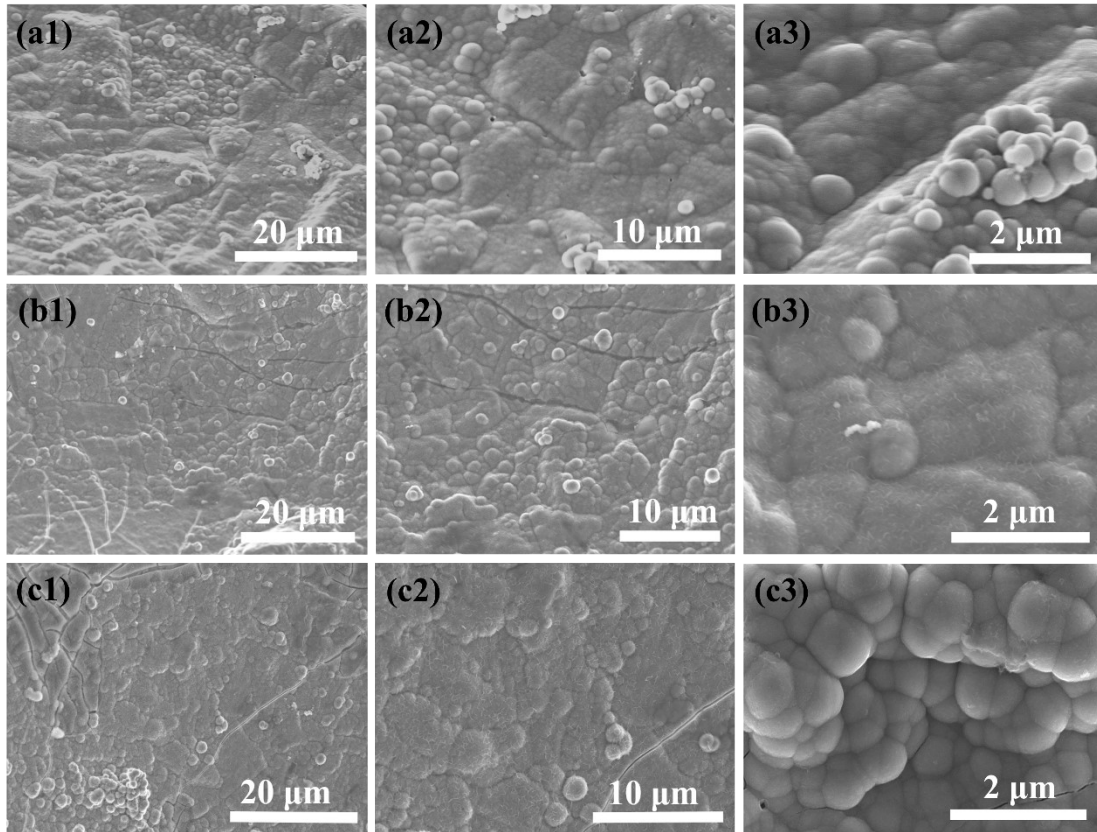


Fig. S12. (a-c) The FESEM images of original, post-HER and post-OER $\text{CeO}_x\text{-NiB@NF}$ electrode.

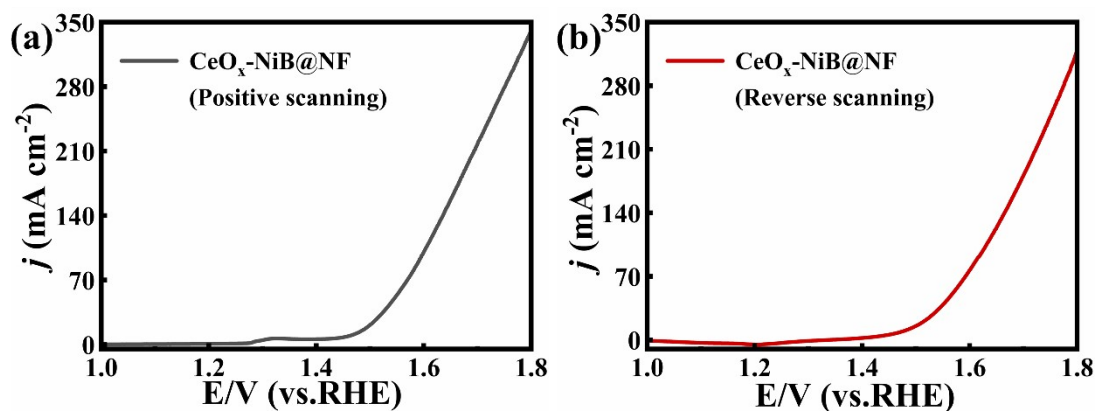


Fig. S13. (a)-(b) LSV curves for OER of CeO_x-NiB@NF at different scanning directions.

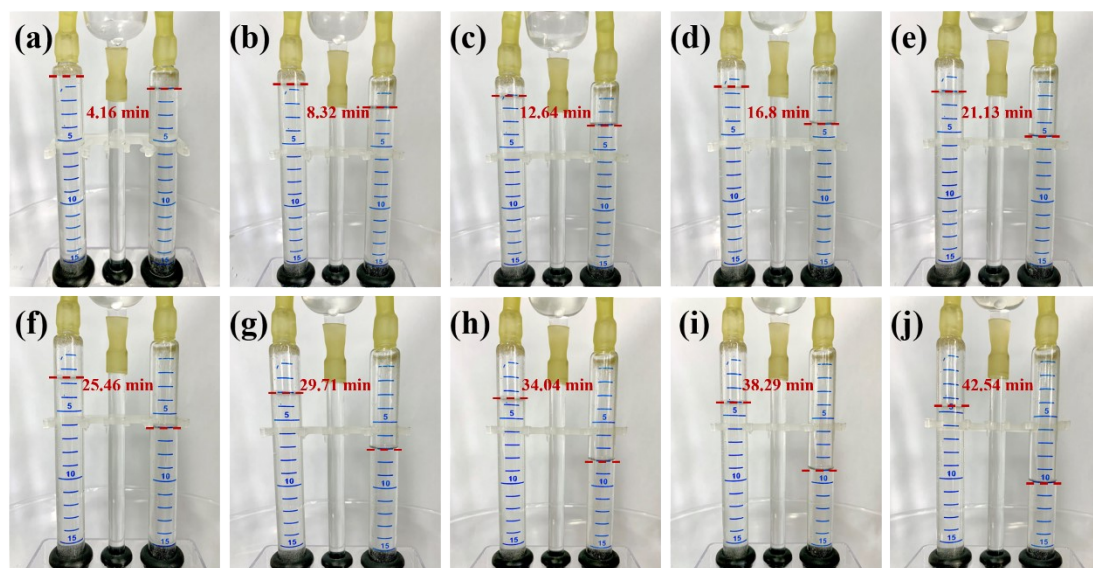


Fig. S14 Intuitive diagram of the amount of H_2 and O_2 produced over time of $CeO_x-NiB@NF$.

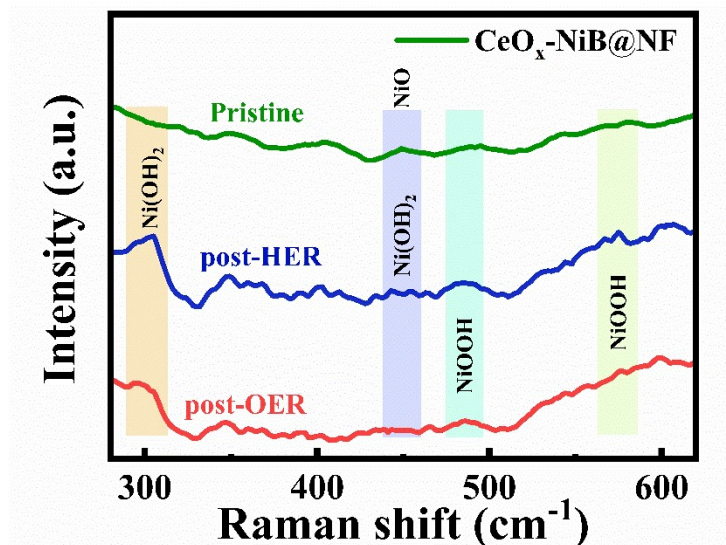


Fig. S15 Raman spectrum with 532 nm excitation before and after HER or OER cycles.

Table S1 Atom% of Ni, Ce and B in CeO_x-NiB@NF sample.

Elements	Ni	Ce	B	Ni:Ce:B
EDS results	37.9	0.51	4.2	9.02:0.12:1
ICP results	25	0.437	3.2	7.8:0.136:1

Table S2 Comparison of the HER catalytic performance of CeO_x-NiB@NF and other electrocatalyst electrodes in 1.0 M KOH.

Catalysts	Electrolyte	j (mA·cm ⁻²)	Potential (mV)	Reference
CeO _x -NiB@NF	1M KOH	10	19	This work
CoP/EEBP	1M KOH	10	118	1
FeNi/PNG	1M KOH	10	132	2
Ni _x Fe _{1-x} B	1M KOH	10	63.5	3
hcp-Co@NC	1M KOH	10	90	4
CoP-5	1M KOH	10	21.1	5
FeOOH/Ni ₃ N	1M KOH	10	67	6
N-NiVFeP/ NF	1M KOH	10	79	7
U-Fe-β-Ni(OH) ₂ /NF	1M KOH	10	121	8
NiMoS	1M KOH	10	78	9
NiTe@RuO ₂	1M KOH	10	19	10
NiRu@C	1M KOH	10	33	11
Fe-Ni ₃ S ₂ @ FeNi ₃	1M KOH	10	105	12
Co/N-CNT/VN	1M KOH	10	63.4	13
RuCo@CDs	1M KOH	10	11	14
Co ₄ N-CeO ₂ /GP	1M KOH	10	24	15
Rh SAC-CuO NAs/CF	1M KOH	10	44	16
Co ₅ Mo ₁₀ S _x /CC	1M KOH	10	36	17
MP-MO _x	1M KOH	10	26	18
Ir-NiCo LDH	1M KOH	10	21	19

Table S3 Comparison of the OER catalytic performance of CeO_x-NiB@NF and other electrocatalyst electrodes in 1.0 M KOH.

Catalysts	Electrolyte	j (mA·cm ⁻²)	Potential (mV)	Reference
CeO _x -NiB@NF	1M KOH	10	274	This work
CoP/EEBP	1M KOH	10	335	1
FeNi/PNG	1M KOH	10	353	2
Ni _x Fe _{1-x} B	1M KOH	10	282	3
hcp-Co@NC	1M KOH	10	290	4
CoP-5	1M KOH	10	320	5
FeOOH/Ni ₃ N	1M KOH	10	244	6
N-NiVFeP/ NF	1M KOH	10	229	7
U-Fe-β-Ni(OH) ₂ /NF	1M KOH	10	218	8
NiMoS	1M KOH	10	260	9
NiTe@RuO ₂	1M KOH	10	274	10
NiRu@C	1M KOH	10	250	11
Fe-Ni ₃ S ₂ @ FeNi ₃	1M KOH	10	213	12
Co/N-CNT/VN	1M KOH	10	240	13
RuCo@CDs	1M KOH	10	257	14
Co ₄ N-CeO ₂ /GP	1M KOH	10	239	15
Rh SAC-CuO NAs/CF	1M KOH	10	197	16
Co ₅ Mo ₁₀ S _x /CC	1M KOH	10	153	17
MP-MO _x	1M KOH	10	197	18
Ir-NiCo LDH	1M KOH	10	192	19

Table S4 Comparison of the overall water splitting performance of CeO_x-NiB@NF and other electrocatalyst electrodes in 1.0 M KOH.

Catalysts	Electrolyte	j (mA·cm ⁻²)	Potential (V)	Reference
CeO _x -NiB@NF CeO _x -NiB@NF	1M KOH	10	1.424	This work
Ni _{0.33} Co _{0.67} MoS ₄ /CFC Ni _{0.33} Co _{0.67} MoS ₄ /CFC	1M KOH	10	1.55	20
FeNi ₃ -FeNi ₃ N/NF FeNi ₃ -FeNi ₃ N/NF	1M KOH	10	1.5	21
CoO/MoO _x CoO/MoO _x	1M KOH	10	1.53	22
NiS ₂ /MoS ₂ -CC NiS ₂ /MoS ₂ -CC	1M KOH	10	1.605	23
NiFeOH/CoS _x /NF NiFeOH/CoS _x /NF	1M KOH	10	1.563	24
MoS ₂ /NiS ₂ MoS ₂ /NiS ₂	1M KOH	10	1.59	25
Ru ₁ Co ₂ NPs Ru ₁ Co ₂ NPs	1M KOH	10	1.59	26
S-CoO _x S-CoO _x	1M KOH	10	1.63	27
Ni ₂ P/Co ₂ P Ni ₂ P/Co ₂ P	1M KOH	10	1.57	28
RuNi-NCNFs RuNi-NCNFs	1M KOH	10	1.564	29
Ni _x Fe _{1-x} B-2 Ni _x Fe _{1-x} B-2	1M KOH	10	1.57	3

References

1. T. Liang, Y. Liu, P. Zhang, C. Liu, F. Ma, Q. Yan and Z. Dai, *Chem. Eng. J.*, 2020, **395**, 124976.
2. H. Wang, X. Feng, M. Zhou, X. Bo and L. Guo, *ACS Appl. Nano Mater.*, 2020, **3**, 6336-6343.
3. W. Hong, S. Sun, Y. Kong, Y. Hu and G. Chen, *J. Mater. Chem. A*, 2020, **8**, 7360-7367.
4. N. Li, H. Tan, X. Ding, H. Duan, W. Hu, G. Li, Q. Ji, Y. Lu, Y. Wang, F. Hu, C. Wang, W. Cheng, Z. Sun and W. Yan, *Appl. Catal., B*, 2020, **266**, 118621.
5. J. H. Jeong, S. Kunwar, S. Pandit and J. Lee, *ACS Appl. Nano Mater.*, 2020, **3**, 6507-6515.
6. J. Guan, C. Li, J. Zhao, Y. Yang, W. Zhou, Y. Wang and G. Li, *Appl. Catal., B*, 2020, **269**, 118600.
7. H. Fan, W. Chen, G. Chen, J. Huang, C. Song, Y. Du, C. Li and K. Ostrikov, *Appl. Catal., B*, 2020, **268**, 118440.
8. X. Qiao, H. Kang, Y. Li, K. Cui, X. Jia, H. Liu, W. Qin, M. Pupucevski and G. Wu, *ACS Appl. Mater. Interfaces*, 2020, **12**, 36208-36219.
9. C. Wang, X. Shao, J. Pan, J. Hu and X. Xu, *Appl. Catal., B*, 2020, **268**, 118435.
10. H. Sun, J. Yang, J. Li, Z. Li, X. Ao, Y. Liu, Y. Zhang, Y. Li, C. Wang and J. Tang, *Appl. Catal., B*, 2020, **272**, 118988.
11. Q. Yang, P. Jin, B. Liu, L. Zhao, J. Cai, Z. Wei, S. Zuo, J. Zhang and L. Feng, *J. Mater. Chem. A*, 2020, **8**, 9049-9057.
12. W. Zhang, Q. Jia, H. Liang, L. Cui, D. Wei and J. Liu, *Chem. Eng. J.*, 2020, **396**, 125315.
13. C. Huang, D. Wu, P. Qin, K. Ding, C. Pi, Q. Ruan, H. Song, B. Gao, H. Chen and P. K. Chu, *Nano Energy*, 2020, **73**, 104788.
14. T. Feng, G. Yu, S. Tao, S. Zhu, R. Ku, R. Zhang, Q. Zeng, M. Yang, Y. Chen, W. Chen, W. Chen and B. Yang, *J. Mater. Chem. A*, 2020, **8**, 9638-9645.
15. H. Sun, C. Tian, G. Fan, J. Qi, Z. Liu, Z. Yan, F. Cheng, J. Chen, C. P. Li and M. Du, *Adv. Funct. Mater.*, 2020, **30**, 1910596.
16. H. Xu, T. Liu, S. Bai, L. Li, Y. Zhu, J. Wang, S. Yang, Y. Li, Q. Shao and X. Huang, *Nano Lett.*, 2020, **20**, 5482-5489.
17. Y. Lu, X. Guo, L. Yang, W. Yang, W. Sun, Y. Tuo, Y. Zhou, S. Wang, Y. Pan, W. Yan, D. Sun and Y. Liu, *Chem. Eng. J.*, 2020, **394**, 124849.
18. J. Deng, S. Chen, N. Yao, Q. Wang, J. Li and Z. Wei, *Appl. Catal., B*, 2020, **277**, 119175.
19. R. Fan, Q. Mu, Z. Wei, Y. Peng and M. Shen, *J. Mater. Chem. A*, 2020, **8**, 9871-9881.
20. L. Hang, T. Zhang, Y. Sun, D. Men, X. Lyu, Q. Zhang, W. Cai and Y. Li, *J. Mater. Chem. A*, 2018, **6**, 19555-19562.
21. S. Liang, M. Jing, T. Thomas, J. Liu, H. Guo, J. P. Attfield, A. Saad, H. Shen and M. Yang, *Sustainable Energy Fuels*, 2020, **4**, 6245-6250.
22. X. Yan, L. Tian, S. Atkins, Y. Liu, J. Murowchick and X. Chen, *ACS Sustainable Chem. Eng.*, 2016, **4**, 3743-3749.
23. X. Wang, L. Li, Z. Wang, L. Tan, Z. Wu, Z. Liu, S. Gai and P. Yang, *Electrochim. Acta*, 2019, **326**, 134983.
24. R. Bose, V. R. Jothi, K. Karuppasamy, A. Alfantazi and S. C. Yi, *J. Mater. Chem. A*, 2020, **8**, 13795-13805.
25. J. Lin, P. Wang, H. Wang, C. Li, X. Si, J. Qi, J. Cao, Z. Zhong, W. Fei and J. Feng, *Adv. Sci.*,

-
- 2019, **6**, 1900246.
26. Y. Bao, J. Dai, J. Zhao, Y. Wu, C. Li, L. Ji, X. Zhang and F. Yang, *ACS Appl. Energy Mater.*, 2020, **3**, 1869-1874.
27. X. Yu, Z. Yu, X. Zhang, P. Li, B. Sun, X. Gao, K. Yan, H. Liu, Y. Duan, M. Gao, G. Wang and S. Yu, *Nano Energy*, 2020, **71**, 104652.
28. H. Liu, M. Jin, D. Zhan, J. Wang, X. Cai, Y. Qiu and L. Lai, *Appl. Catal., B*, 2020, **272**, 118951.
29. M. Li, H. Wang, W. Zhu, W. Li, C. Wang and X. Lu, *Adv. Sci.*, 2020, **7**, 1901833.