

Supporting Information for

Engineering thiospinel-based hollow heterostructured nanoarrays for boosting electrocatalytic oxygen evolution reaction

Kun Wang, Qing Wang, Lei Jin, Bingji Huang, Hui Xu*, Xingyue Qian, Haiqun

Chen*, Guangyu He*

*Key Laboratory of Advanced Catalytic Materials and Technology, Advanced
Catalysis and Green Manufacturing Collaborative Innovation Center, Changzhou
University, Changzhou, Jiangsu Province 213164, China.*

*Corresponding authors: xuhui006@cczu.edu.cn (H. Xu); hqchen@cczu.edu.cn (H.
Chen); hegy@cczu.edu.cn (G. He)*

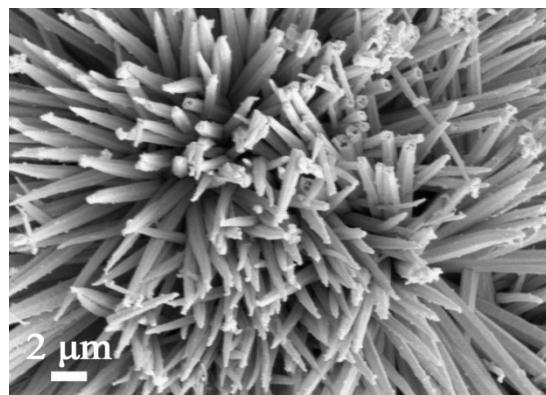


Fig.S1 SEM image of $\text{Ni}_3\text{S}_2/\text{NiCo}_2\text{S}_4@\text{NF}$.

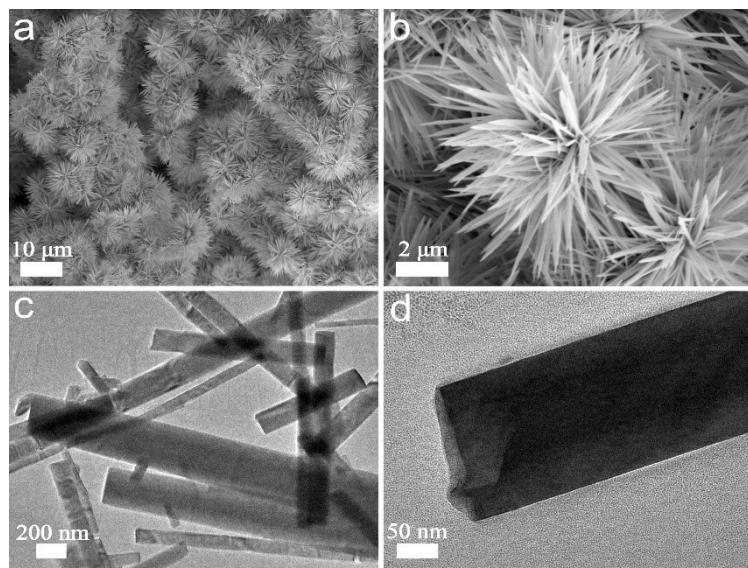


Fig.S2 (a, b) SEM images and (c, d) TEM images of the NiCo-LDH@NF.

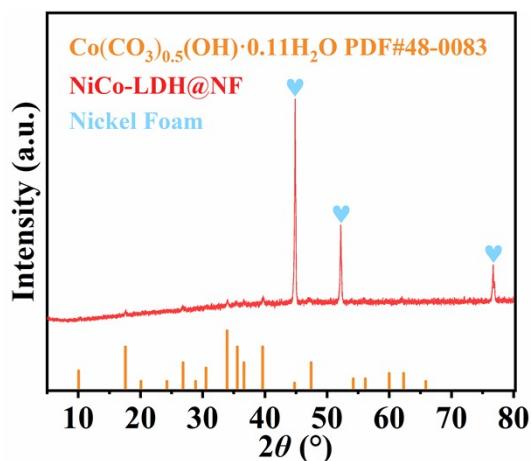


Fig.S3 XRD pattern of NiCo-LDH@NF.

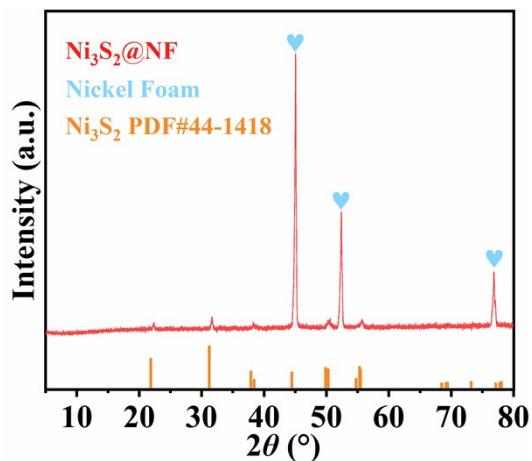


Fig.S4 XRD pattern of Ni₃S₂@NF.

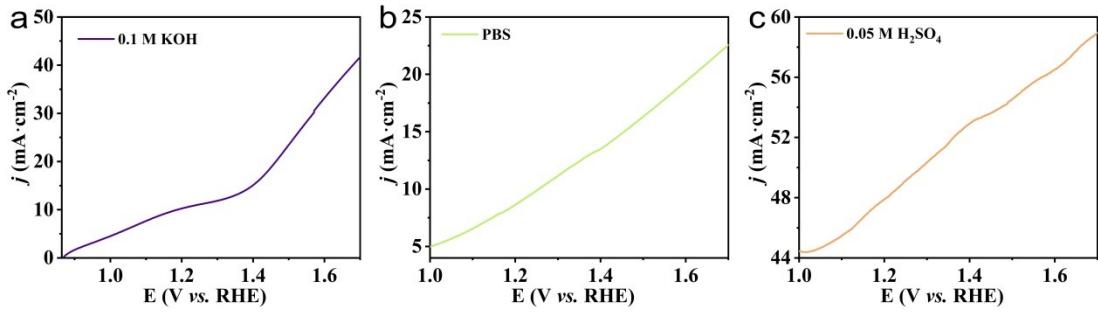


Fig.S5 OER polarization curves of $\text{Ni}_3\text{S}_2/\text{NiCo}_2\text{S}_4@\text{NF}$ in (a) 0.1 M KOH, (b) PBS and (c) 0.05 M H_2SO_4 electrolyte.

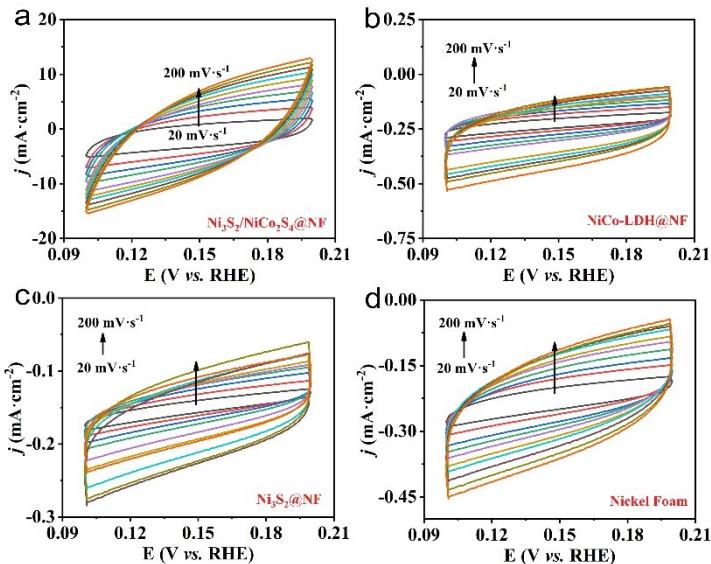


Fig.S6 Cyclic voltammograms in a capacitive current region at a scan rate ranging from 20 to 200 $\text{mV}\cdot\text{s}^{-1}$, (a) $\text{Ni}_3\text{S}_2/\text{NiCo}_2\text{S}_4@\text{NF}$, (b) $\text{NiCo-LDH}@\text{NF}$, (c) $\text{Ni}_3\text{S}_2@\text{NF}$ and (d) NF.

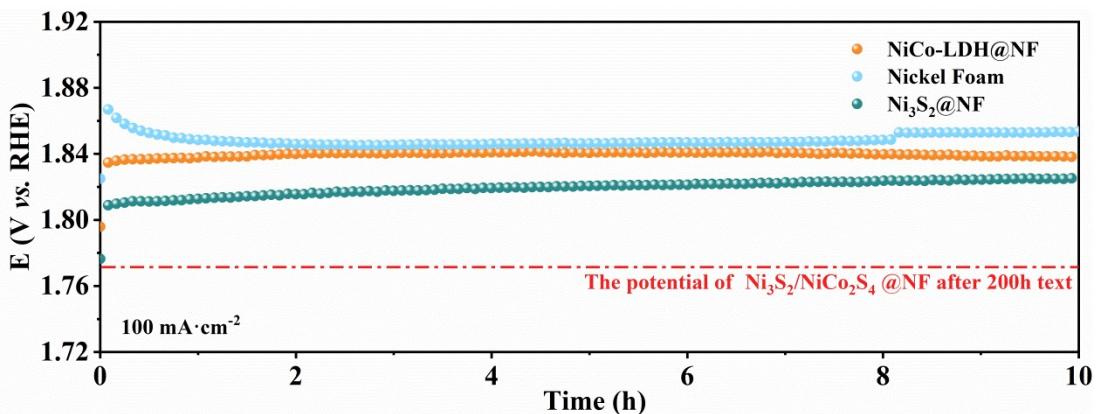


Fig.S7 Chronopotentiometry test of $\text{Ni}_3\text{S}_2@\text{NF}$, $\text{NiCo-LDH}@\text{NF}$, and NF at a constant current density of 100 $\text{mA}\cdot\text{cm}^{-2}$.

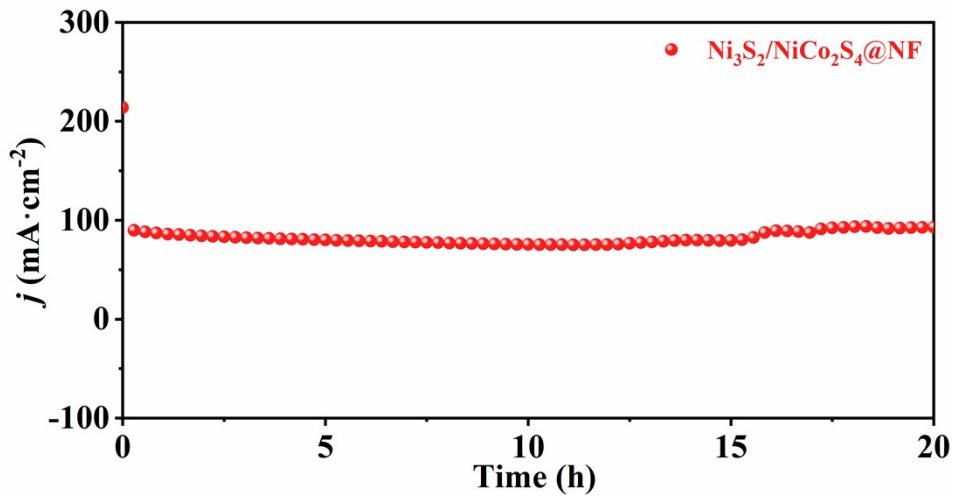


Fig.S8 Chronoamperometry test of $\text{Ni}_3\text{S}_2/\text{NiCo}_2\text{S}_4@\text{NF}$.

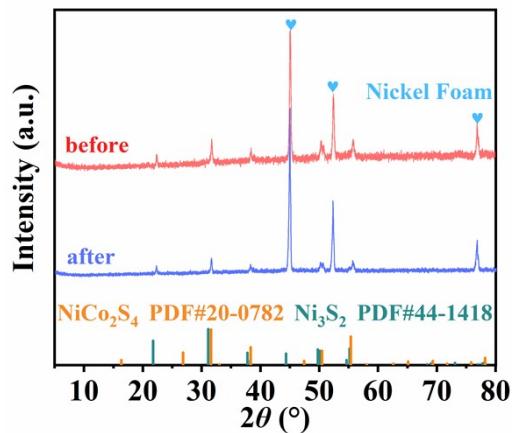


Fig.S9 XRD pattern of $\text{Ni}_3\text{S}_2/\text{NiCo}_2\text{S}_4@\text{NF}$ before and after a continuous 200 h stability test.

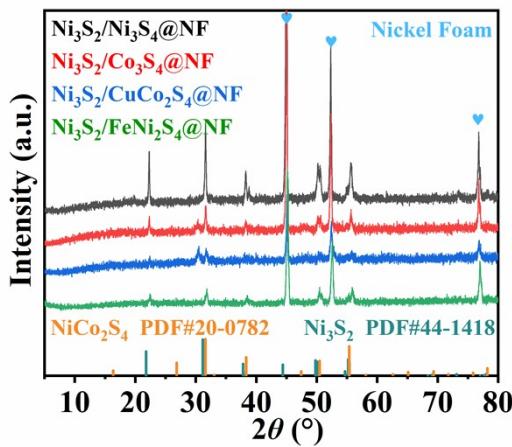


Fig.S10 XRD pattern of $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{S}_4@\text{NF}$, $\text{Ni}_3\text{S}_2/\text{Co}_3\text{S}_4@\text{NF}$, $\text{Ni}_3\text{S}_2/\text{CuCo}_2\text{S}_4@\text{NF}$ and $\text{Ni}_3\text{S}_2/\text{FeNi}_2\text{S}_4@\text{NF}$.

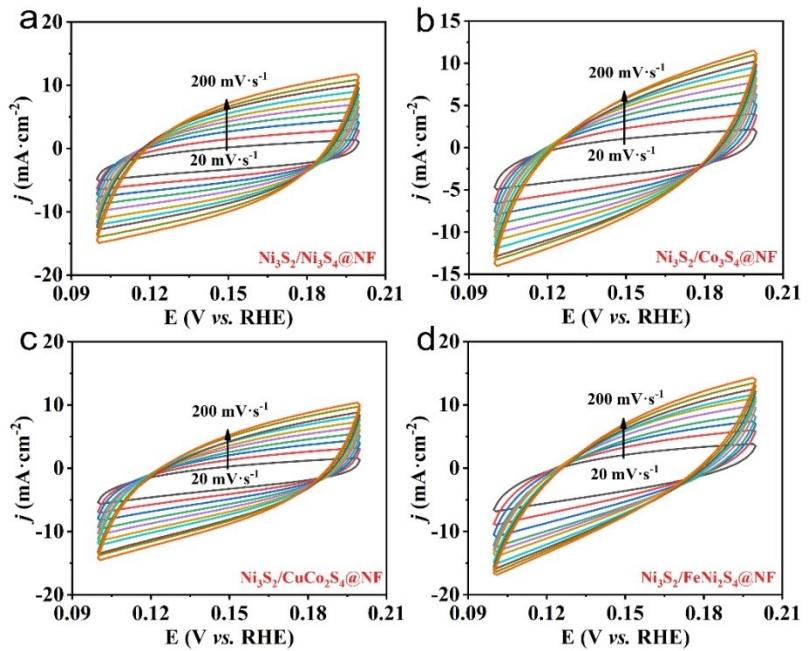


Fig.S11 Cyclic voltammograms in a capacitive current region at a scan rate from 20 to 200 $\text{mV} \cdot \text{s}^{-1}$.
(a) $\text{Ni}_3\text{S}_2/\text{Ni}_3\text{S}_4@\text{NF}$, (b) $\text{Ni}_3\text{S}_2/\text{Co}_3\text{S}_4@\text{NF}$, (c) $\text{Ni}_3\text{S}_2/\text{CuCo}_2\text{S}_4@\text{NF}$ and (d) $\text{Ni}_3\text{S}_2/\text{FeNi}_2\text{S}_4@\text{NF}$.

Table S1 OER activity comparison of different catalysts in alkaline condition.

Catalysts	Electrolyte	Overpotential	Reference
Ni₃S₂/NiCo₂S₄@NF	1.0 M KOH	177 mV at 100 mA·cm⁻²	This Work
NiCo ₂ S ₄ @NiFe-LDH@NF	1.0 M KOH	201 mV at 60 mA·cm ⁻²	1
P-NiCo ₂ S ₄ @NF	1.0 M KOH	300 mV at 50 mA·cm ⁻²	2
Mn-NiCo ₂ S ₄ @NF	1.0 M KOH	220 mV at 10 mA·cm ⁻²	3
NiCo ₂ S ₄ /NiFeP@NF	1.0 M KOH	293 mV at 100 mA·cm ⁻²	4
NiCo ₂ S ₄ @NF	1.0 M KOH	279 mV at 50 mA·cm ⁻²	5
NiCo ₂ S ₄ @N-rGO@NF	1.0 M KOH	230 mV at 10 mA·cm ⁻²	6
MoS ₂ /NiCo ₂ S ₄ @NF	1.0 M KOH	220 mV at 10 mA·cm ⁻²	7
Ru-NiCo ₂ S _{4-x} @NF	1.0 M KOH	330 mV at 100 mA·cm ⁻²	8
CuCo ₂ S ₄ /NiCo ₂ S ₄ @NF	1.0 M KOH	271 mV at 10mA·cm ⁻²	9
NiCo ₂ S ₄ @NF	1.0 M KOH	319 mV at 100 mA·cm ⁻²	10
NiCo ₂ S ₄ @NF	1.0 M KOH	260 mV at 10 mA·cm ⁻²	11

References

1. J. Liu, J. Wang, B. Zhang, Y. Ruan, L. Lv, X. Ji, K. Xu, L. Miao and J. Jiang, Hierarchical NiCo₂S₄@NiFe LDH heterostructures supported on nickel foam for enhanced overall-water-splitting activity, *ACS Appl. Mater. Interfaces*, 2017, 9, 15364-15372.
2. K. Min, R. Yoo, S. Kim, H. Kim, S. E. Shim, D. Lim and S.-H. Baeck, Facile synthesis of P-doped NiCo₂S₄ nanoneedles supported on Ni foam as highly efficient electrocatalysts for alkaline oxygen evolution reaction, *Electrochim. Acta*, 2021, 396, 139236.
3. X. Yu, S. Xu, X. Liu, X. Cheng, Y. Du and Q. Wu, Mn-doped NiCo₂S₄ nanosheet array as an efficient and durable electrocatalyst for oxygen evolution reaction, *J. Alloys Compd.*, 2021, 878, 160388.
4. J. Jiang, F. Li, H. Su, Y. Gao, N. Li and L. Ge, Flower-like NiCo₂S₄/NiFeP/NF composite material as an effective electrocatalyst with high overall water splitting performance, *Chin Chem Lett*, 2021.
5. Y. Gong, J. Wang, Y. Lin, Z. Yang, H. Pan and Z. Xu, Synthesis of 1D to 3D nanostructured NiCo₂S₄ on nickel foam and their application in oxygen evolution reaction, *Appl. Surf. Sci.*, 2019, 476, 600-607.
6. H. S. Lee, J. Pan, G. S. Gund and H. S. Park, Vertically Aligned NiCo₂S₄ Nanosheets Deposited on N-Doped Graphene for Bifunctional and Durable Electrode of Overall Water Splitting, *Adv. Mater. Interfaces*, 2020, 7, 2000138.
7. X. Xu, W. Zhong, L. Zhang, G. Liu, W. Xu, Y. Zhang and Y. Du, NiCo-LDHs derived NiCo₂S₄ nanostructure coated by MoS₂ nanosheets as high-efficiency bifunctional electrocatalysts for overall water splitting, *Surf. Coat. Technol.*, 2020, 397, 126065.
8. H. Su, S. Song, Y. Gao, N. Li, Y. Fu, L. Ge, W. Song, J. Liu and T. Ma, In Situ Electronic Redistribution Tuning of NiCo₂S₄ Nanosheets for Enhanced Electrocatalysis, *Adv. Funct. Mater.*, 2021, 2109731.
9. L. Ma, J. Liang, T. Chen, Y. Liu, S. Li and G. Fang, 3D CuCo₂S₄/NiCo₂S₄ core-shell composites as efficient bifunctional electrocatalyst electrodes for overall water

- splitting, *Electrochim. Acta*, 2019, 326, 135002.
10. J. Yu, C. Lv, L. Zhao, L. Zhang, Z. Wang and Q. Liu, Reverse Microemulsion-Assisted Synthesis of NiCo₂S₄ Nanoflakes Supported on Nickel Foam for Electrochemical Overall Water Splitting, *Adv. Mater. Interfaces*, 2018, 5, 1701396.
11. A. Sivanantham, P. Ganesan and S. Shanmugam, Hierarchical NiCo₂S₄ nanowire arrays supported on Ni foam: an efficient and durable bifunctional electrocatalyst for oxygen and hydrogen evolution reactions, *Adv. Funct. Mater.*, 2016, 26, 4661-4672.