Supporting Information

Hierarchical Porous NiFe-P@NC as Efficient Electrocatalyst for Alkaline Hydrogen Production and Seawater Electrolysis at Large-Current-density

Zhi Chen¹, Qichang Li¹, Huimin Xiang¹, Yue Wang¹, Pengfei Yang¹, Chunlong Dai³, Huadong Zhang³, Weiping Xiao², Zexing Wu^{1, *}, Lei Wang^{1, *}

1. Key Laboratory of Eco-chemical Engineering, Ministry of Education, International Science and Technology Cooperation Base of Eco-chemical Engineering and Green Manufacturing, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: splswzx@qust.edu.cn; inorchemwl@126.com

2. College of Science, Nanjing Forestry University, Nanjing, 210037, PR China

3. Shandong Long Antai Environmental Protection Technology Co., Ltd., No.9, Gongye 1st

Street , Xiashan High-tech Project Zone, Weifang City, Shandong Province

Experimental Section

1. Sample preparation

Firstly, 2-Aminoterephthalic Acid (5 mmol/L) and NaCl (50 mmol/L) were added to 30 ml of deionized water and stirred well. prepared ferric nickel foam was added to the mixture and stirred at room temperature for 12 h. The resulting ferric nickel foam was rinsed three times with deionized water and dried in a vacuum drying oven for 3 hours. Then 500 mg of sodium hypophosphite monohydrate was placed upstream of the tube furnace and the treated ferric nickel foam was placed downstream of the tube furnace. NiFe-P@NC was obtained on the nickel foam iron by holding it at 350°C for 2 h under Ar atmosphere at a heating rate of 5°C/min.

2. Physical Characterization

Morphological and dimensional analysis of the prepared catalysts was performed by field emission scanning electron microscopy (SEM, S-4800, Hitachi) and transmission electron microscopy (TEM, Tecnai G2-F20). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Phi X-tool XPS spectrometer, and X-ray diffraction (XRD) patterns were obtained with an XRD, Bruker D8-Advance diffractometer. Infrared spectroscopy was carried out using a Nicolet 170SX spectrometer.

3. Electrochemical Measurements

All tests were carried out at room temperature using an electrochemical workstation CHI 760D, Gamry Reference 3000) through a typical three-electrode system. Reversible hydrogen (RHE) was used as the reference electrode, graphite carbon rods as the counter electrode and a synthetic catalyst as the working electrode. Linear scanning voltammetry (LSV) was obtained at a scan rate of 5 mV s⁻¹ and 95% IR correction.



Figure S1 SEM images of NIF (a, b).



Figure S2 TEM images of (a, b) NiFe LDH, (c, d) NiFe MOF.



Figure S3 IR spectrum of prepared NiFe MOF.



Figure S4 XRD patterns of NiFe-P@NC.



Figure S5 XRD patterns of NiFe MOF.



Figure S6 High-resolution XPS images of C 1s.



Figure S7 Contact angles of NIF.



Figure S8 LSVs of NiFe-P@NC with various different contents of 2-Aminoterephthalic Acid.



Figure S9 SEM images of NiFe-P@NC afters stability test.



Figure S10 XPS patterns of NiFe-P@NC before and after stability testing. (a) Full range XPS pattern, High-resolution XPS images of (b) Fe 2p, (c) P 2p, (d) N 1s.



Figure S11 Photographs of (a) oxygen and (b) hydrogen collected at different times.



Figure S12 Stability test of NiFe-P@NC in 1 M KOH + 0.5 M NaCl.



Figure S13 Stability test of NiFe-P@NC in 1 M KOH + 1 M NaCl.



Figure S14 Stability test of NiFe-P@NC in 1 M KOH + Seawater.

Catalysts	Electrolyte	η_{10} / mV	Tafel slope / mV dec ⁻¹	Ref.
Ni _{0.85} Se-MoSe ₂ interfacial structure	1 M KOH	108	77	[1]
$Co_9S_8@MoS_2$ heterostructure	1 M KOH	177	83.6	[2]
R-MoS ₂ @NF	1 M KOH	71	100	[3]
CoP NS/C	1 M KOH	111	70.9	[4]
Ni, Zn dualdoped CoO NRs	1 М КОН	53	79	[5]
CoFeP	1 M KOH	78	94	[6]
Ni(OH) ₂ -Fe ₂ P/TM	1 M KOH	76	105	[7]
NHPBAP	1 M KOH	121	67	[8]
CoFe-PBANS@NF-24	1 M KOH	48	66	[9]
CoSe ₂ /MoSe ₂	1 M KOH	218	76	[10]
CoP/NCNHP	1 M KOH	115	66	[11]
CoFe PBA@CoP/NF	1 M KOH	171	75.7	[12]
NiCoFeP/C	1 M KOH	149	89	[13]
CoFeP/CNT	1 M KOH	178	71	[14]
NCP/G NSs	1 M KOH	119	62.3	[15]
P-S-24	1 M KOH	61	52	[16]
Ni ₂ P/Ni/NF	1 M KOH	98	72	[17]
Ni/Ni ₂ P	1 M KOH	73	76	[18]
NiFe-P@C	1 М КОН	40	58	This Work

Table S1. Comparison of the HER activity of the NiFe-P@NC with other previously

 reported electrocatalysts under 1 M KOH

Catalysts	Electrolyte	η_{10} / V	Ref.	
CoP-InNC@CNT/CC	1 М КОН	1 57	[10]	
CoP-InNC@CNT/CC		1.37	[17]	
FeOOH/Ni ₃ N	1 M KOH	1.58	[20]	
FeOOH/Ni ₃ N				
NCS/NSrGO		1.58	[21]	
NCS/NS-rGO				
NiCoP/SCW		1.59	[22]	
NiCoP/SCW				
NiCoP/NF NiCoP/NF	1 M KOH	1.58	[23]	
NiCo-PBA/NF		1.49	[24]	
NiCo-PBA/NF				
S:CoP@NF	1 M KOH	1.61	[25]	
S:CoP@NF				
NiCo ₂ S ₄ /NF	1 M KOH	1.61	[26]	
NiCo ₂ S ₄ /NF				
CoP/NCNHP	1 М КОН	1 64	[11]	
CoP/NCNHP		1.01	[++]	
Co ₂ P/Co-Foil	1 М КОН	1 71	[27]	
Co ₂ P/Co-Foil		1./1	[~,]	
CP/CTs/Co-S	1 М КОН	1 743	[28]	
CP/CTs/Co-S		1.75		
NiFe-P@C	1 М КОН	1.57	This work	
NiFe LDH				

Table S2. Comparison of some recently reported representative electrocatalysts for overall water splitting under1 M KOH.

1. H. R. Inta, S. Ghosh, A. Mondal, G. Tudu, H. V. S. R. M. Koppisetti and V. Mahalingam, Ni_{0.85}Se/MoSe₂ Interfacial Structure: An Efficient Electrocatalyst for Alkaline Hydrogen Evolution Reaction, *ACS Appl. Energy Mater.*, 2021, **4**, 2828-2837.

2. L. Diao, B. Zhang, Q. Sun, N. Wang, N. Zhao, C. Shi, E. Liu and C. He, An in-plane $Co_9S_8@MoS_2$ heterostructure for the hydrogen evolution reaction in alkaline media, *Nanoscale*, 2019, **11**, 21479-21486.

3. M. A. R. Anjum, H. Y. Jeong, M. H. Lee, H. S. Shin and J. S. Lee, Efficient Hydrogen

Evolution Reaction Catalysis in Alkaline Media by All-in-One MoS₂ with Multifunctional Active Sites, *Adv Mater*, 2018, **30**, 1707105.

4. J. Chang, L. Liang, C. Li, M. Wang, J. Ge, C. Liu and W. Xing, Ultrathin cobalt phosphide nanosheets as efficient bifunctional catalysts for a water electrolysis cell and the origin for cell performance degradation, *Green Chem.*, 2016, **18**, 2287-2295.

5. T. Ling, T. Zhang, B. Ge, L. Han, L. Zheng, F. Lin, Z. Xu, W. B. Hu, X. W. Du, K. Davey and S. Z. Qiao, Well-Dispersed Nickel- and Zinc-Tailored Electronic Structure of a Transition Metal Oxide for Highly Active Alkaline Hydrogen Evolution Reaction, *Adv Mater*, 2019, **31**, 1807771.

6. Y. Tan, H. Wang, P. Liu, Y. Shen, C. Cheng, A. Hirata, T. Fujita, Z. Tang and M. Chen, Versatile nanoporous bimetallic phosphides towards electrochemical water splitting, *Energy Environ. Sci.*, 2016, **9**, 2257-2261.

7. X. Zhang, S. Zhu, L. Xia, C. Si, F. Qu and F. Qu, Ni(OH)₂-Fe₂P hybrid nanoarray for alkaline hydrogen evolution reaction with superior activity, *Chem Commun*, 2018, **54**, 1201-1204.

8. Y. Ge, P. Dong, S. R. Craig, P. M. Ajayan, M. Ye and J. Shen, Transforming Nickel Hydroxide into 3D Prussian Blue Analogue Array to Obtain Ni₂P/Fe₂P for Efficient Hydrogen Evolution Reaction, *Adv. Energy Mater.* 2018, **8**, 1800484.

9. Z. Chen, B. Fei, M. Hou, X. Yan, M. Chen, H. Qing and R. Wu, Ultrathin Prussian blue analogue nanosheet arrays with open bimetal centers for efficient overall water splitting, *Nano Energy*, 2020, **68**, 104371.

10. G. Zhao, P. Li, K. Rui, Y. Chen, S. X. Dou and W. Sun, CoSe₂ /MoSe₂ Heterostructures with Enriched Water Adsorption/Dissociation Sites towards Enhanced Alkaline Hydrogen Evolution Reaction, *Chem-Eur J*, 2018, **24**, 11158-11165.

11. Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W. C. Cheong, Z. Chen, Y. Wang, Y. Li, Y. Liu, D. Wang, Q. Peng, C. Chen and Y. Li, Core-Shell ZIF-8@ZIF-67-Derived CoP Nanoparticle-Embedded N-Doped Carbon Nanotube Hollow Polyhedron for Efficient Overall Water Splitting, *J Am Chem Soc*, 2018, **140**, 2610-2618.

12. L. Quan, S. Li, Z. Zhao, J. Liu, Y. Ran, J. Cui, W. Lin, X. Yu, L. Wang, Y. Zhang and J. Ye, Hierarchically Assembling CoFe Prussian Blue Analogue Nanocubes on CoP Nanosheets as Highly Efficient Electrocatalysts for Overall Water Splitting, *Small Methods*, 2021, **5**, e2100125.

13. X. Wei, Y. Zhang, H. He, L. Peng, S. Xiao, S. Yao and P. Xiao, Carbon-incorporated porous honeycomb NiCoFe phosphide nanospheres derived from a MOF precursor for overall water splitting, *Chem Commun*, 2019, **55**, 10896-10899.

14. Z. Zheng, L. Wu, Y. Han, J. Chen, S. Zhu, Y. Yao, B. Wang and L. Li, Gut Microbiota-Controlled Tryptophan Metabolism Improves D-Gal/LPS-Induced Acute Liver Failure in C57BL/6 Mice, *Engineering*, 2022, **14**, 134-146.

15. J. Tian, J. Chen, J. Liu, Q. Tian and P. Chen, Graphene quantum dot engineered nickel-cobalt phosphide as highly efficient bifunctional catalyst for overall water splitting, *Nano Energy*, 2018, **48**, 284-291.

16. F. Wang, X. Qi, Z. Qin, H. Yang, C. Liu and T. Liang, Construction of hierarchical Prussian Blue Analogue phosphide anchored on Ni₂P@MoO_x nanosheet spheres for efficient overall water splitting, *Int. J. Hydrogen Energy.*, 2020, **45**, 13353-13364.

17. B. You, N. Jiang, M. Sheng, M. W. Bhushan and Y. Sun, Hierarchically Porous Urchin-Like Ni2P Superstructures Supported on Nickel Foam as Efficient Bifunctional Electrocatalysts for Overall Water Splitting, *ACS Catal.*, 2015, **6**, 714-721.

18. Q. Zhou, J. Pu, X. Sun, C. Zhu, J. Li, J. Wang, S. Chang and H. Zhang. In situ surface engineering of nickel inverse opal for enhanced overall electrocatalytic water splitting, *J. Mater. Chem. A*, 2017, **5**, 14873-14880.

19. L. Chai, Z. Hu, X. Wang, Y. Xu, L. Zhang, T. T. Li, Y. Hu, J. Qian and S. Huang, Stringing Bimetallic Metal-Organic Framework-Derived Cobalt Phosphide Composite for High-Efficiency Overall Water Splitting, *Adv Sci*, 2020, **7**, 1903195.

20. J. Guan, C. Li, J. Zhao, Y. Yang, W. Zhou, Y. Wang and G.-R. Li, FeOOH-enhanced bifunctionality in Ni3N nanotube arrays for water splitting, Appl.Catal.B-Environm, 2020, **269**, 118600.

H. Li, L. Chen, P. Jin, Y. Li, J. Pang, J. Hou, S. Peng, G. Wang and Y. Shi, NiCo₂S₄ microspheres grown on N, S co-doped reduced graphene oxide as an efficient bifunctional electrocatalyst for overall water splitting in alkaline and neutral pH, *Nano Res.*, 2021, **15**, 950-958.
 V. R. Jothi, R. Bose, H. Rajan, C. Jung and S. C. Yi, Harvesting Electronic Waste for the Development of Highly Efficient Eco-Design Electrodes for Electrocatalytic Water Splitting, *Adv. Energy Mater.*, 2018, **8**. 1802615.

23. H. Liang, A. N. Gandi, D. H. Anjum, X. Wang, U. Schwingenschlogl and H. N. Alshareef, Plasma-Assisted Synthesis of NiCoP for Efficient Overall Water Splitting, *Nano Lett*, 2016, **16**, 7718-7725.

24. L. Ma, B. Zhou, L. Tang, J. Guo, Q. Liu and X. Zhang, Template confined synthesis of NiCo Prussian blue analogue bricks constructed nanowalls as efficient bifunctional electrocatalyst for splitting water, *Electrochim. Acta.*, 2019, **318**, 333-341.

25. M. A. R. Anjum, M. S. Okyay, M. Kim, M. H. Lee, N. Park and J. S. Lee, Bifunctional sulfurdoped cobalt phosphide electrocatalyst outperforms all-noble-metal electrocatalysts in alkaline electrolyzer for overall water splitting, *Nano Energy*, 2018, **53**, 286-295.

26. 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.

27. C.-Z. Yuan, S.-L. Zhong, Y.-F. Jiang, Z. K. Yang, Z.-W. Zhao, S.-J. Zhao, N. Jiang and A.-W. Xu, Direct growth of cobalt-rich cobalt phosphide catalysts on cobalt foil: an efficient and self-supported bifunctional electrode for overall water splitting in alkaline media, *J. Mater. Chem. A*, 2017, **5**, 10561-10566.

28. J. Wang, H. X. Zhong, Z. L. Wang, F. L. Meng and X. B. Zhang, Integrated Three-Dimensional Carbon Paper/Carbon Tubes/Cobalt-Sulfide Sheets as an Efficient Electrode for Overall Water Splitting, *ACS Nano*, 2016, **10**, 2342-2348.