Supporting Information

Self-supporting, hierarchically structured hollow NiFe-PBA electrocatalyst for efficient alkaline seawater oxidation

Kaiyan Zhang, Mingze Xu, Jianying Wang*, and Zuofeng Chen*

Shanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical

Science and Engineering, Tongji University, Shanghai 200092, China

*Corresponding Authors: wang_jianying@tongji.edu.cn (J. Y. Wang), zfchen@tongji.edu.cn (Z. F. Chen).

Experimental Section

Chemicals. Ethanol (C₂H₃OH, \geq 99.7%, Sinopharm), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98%, Sigma-Aldrich), 2,5-thiophenedicarboxylic acid (CH₄O₄S, 98%, Aladdin), sodium hydroxide (NaOH, Sinopharm), potassium ferricyanide (K₃Fe(CN)₆, 98%, Sigma-Aldrich), potassium hydroxide (KOH, 98%, Macklin), sodium chloride (NaCl, 98%, Macklin), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 98%, Sigma-Aldrich), and Ni foam was utilized as received (thickness: 1.6 mm, porosity: ~95%). The seawater was purchased from Taobao and sourced from the Huanghai Sea in Qingdao, China. All other reagents were directly used in experiments without any treatment or further purification. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.3 MΩ cm.

Synthesis of Ni-MOF. The Ni-MOF was synthesized by using a hydrothermal

reaction method. First, the Ni foam was cut into a size of 2.5×3.5 cm² and rinsed with ethanol, 1 M HCl, and DI water sequentially. A total of 2 mmol Ni(NO₃)₂·6H₂O, 2 mmol 2,5-thiophenedicarboxylic acid, 2.4 mmol NaOH, 24 mL DI water, and a piece of Ni foam were added to a 100 mL Teflon-lined autoclave and heated at 200 °C for 6 h. After being cooled down to room temperature, the synthesized material was rinsed with DI water and ethanol several times and dried at 60 °C overnight.

Synthesis of NiFe-PBA. The NiFe-PBA was synthesized using the as-prepared Ni-MOF as the precursor electrode. A total of 300 mg $K_3Fe(CN)_6$ was dissolved in 30 mL DI water in a 100 mL Teflon-lined autoclave with a piece of Ni-MOF and heated at 150 °C for 2, 4, and 6 h, respectively. After being cooled down to room temperature, the as-obtained NiFe-PBA was rinsed with DI water and ethanol several times and dried at 60 °C overnight. The self-supporting NiFe-PBA catalysts were collected and directly used as OER electrodes. The synthesized samples were labeled as NiFe-PBA (2 h), NiFe-PBA (4 h), and NiFe-PBA (6 h), respectively.

Preparation of IrO₂ catalyst. To prepare the IrO_2 electrode for comparison, 40 mg IrO_2 and 60 μ L Nafion were dissolved in 0.40 mL DI water and 0.54 mL ethanol in a tiny sealed tube. The mixture was ultrasonicated for 30 minutes, after which the dispersion was coated onto a Ni foam substrate and the electrode was dried in air overnight.¹

Synthesis of NiMoN. First, we fabricated the NiMoO₄ on Ni Foam with a hydrothermal reaction method. A total of 2 mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 0.5 mmol $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in 50 mL DI water in a 100 mL Teflon-lined

autoclave with a piece of cleaned Ni foam and heated at 150 °C for 6 h. After being cooled down to room temperature, the sample was rinsed with DI water and ethanol several times, and finally fully dried at 60 °C overnight. Following the synthesis of the NiMoO₄ on Ni foam, a one-step thermal nitridation was used to prepare the NiMoN catalyst. One piece of the as-prepared NiMoO₄ was placed in the middle of a tube furnace and thermal nitridation was performed at 500 °C for 1 h under a flow of 120 standard cubic centimeters NH₃ and 30 standard cubic centimeters Ar per minute at a heating rate of 5 °C/min. After the reaction, the furnace was naturally cooled down to room temperature under Ar atmosphere, and the NiMoN catalyst was collected for further use.²

Characterization. The surface morphology structure of the prepared catalysts was measured by using scanning electron microscopy (SEM, Hitachi S4800) equipped with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM, JEM-2100; JEOL). Atomic force microscopy (AFM) characterization was performed using a Shimadzu SPM-9700. The phase structure was characterized by Xray diffraction (XRD) using a Bruker D8 Focus instrument with Cu K α radiation. Xray photoelectron spectroscopy (XPS) was conducted on a Thermo ESCALAB 250Xi instrument with Al K α radiation, and the C 1s peak was rectified to 284.80 eV. Fouriertransform infrared spectroscopy (FTIR) was measured using a Nicolet iS50 spectrometer. The molar ratio of Ni and Fe in the sample was determined by conducting an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) test on an Agilent Technologies 730 Series instrument. The contact angle measurements were conducted using a contact angle meter (Attention Theta Flex, Biolin, Sweden).

Electrochemical Tests. Electrochemical tests were performed at room temperature using an electrochemical working station (CHI660E) with a standard threeelectrode setup. The prepared samples served as the working electrode, a carbon rod acted as the counter electrode, and a standard Hg/HgO electrode served as the reference electrode. Four different electrolytes with a pH of ~ 14, namely 1 M KOH, 1 M KOH + 0.5 M NaCl, 1 M KOH + 1 M NaCl, and 1 M KOH + seawater, were used in the experiments. The seawater used was collected from the Huanghai Sea in Qingdao, China. OER polarization curves were obtained at a scan rate of 1 mV s⁻¹, and all linear sweep voltammetry (LSV) curves were obtained with 60% iR compensation, which was automatically conducted on the electrochemical workstation. Stability tests were performed under a constant current density with iR compensation. To determine the double-layer capacitance (C_{dl}) values, the cyclic voltammetry (CV) tests were conducted at different scan rates ranging from 40 mV s⁻¹ to 90 mV s⁻¹ with an interval of 10 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were performed from 100 kHz to 0.1 Hz with an amplitude of 5 mV. All measured potentials vs. Hg/HgO were converted to the reversible hydrogen electrode (RHE) using the Nernst equation ($E_{RHE} = E_{Hg/HgO} + 0.0591 \times pH + 0.098$).

In situ Raman measurements. In situ electrochemical Raman spectroscopic measurements were carried out using a confocal Raman microscope (Invia Reflex, Renishaw, UK) and an electrochemical working station (CHI660E). The Raman spectra were collected with an *in-situ* Raman spectra-electrochemical cell, where the NiFe-

PBA functioned as the working electrode, an Hg/HgO electrode served as the reference electrode, and a Pt wire served as the counter electrode. The Raman spectrometer was calibrated at a wavenumber of 520 cm⁻¹ using a silicon wafer and the spectra were recorded in 1 M KOH electrolyte under an applied potential range of 1.23-1.50 V (vs. RHE) for 120 s.

Supplementary Figures



Fig. S1 The molar ratio of Fe: Ni in NiFe-PBA catalysts prepared under reaction times

of 2, 4, and 6 hours.



Fig. S2 Photographs of NiFe-PBA catalysts prepared under reaction times of 2, 4, and 6 hours.



Fig. S3 Photograph of NiFe-PBA catalyst prepared under the reaction time of 8 hours.



Fig. S4 Morphology characterization. 3D surface topography of NiFe-PBA.



Fig. S5 Digital images of a droplet placed on the surface of (a) Ni-MOF and (b) NiFe-

PBA to investigate the wettability between the catalyst surface and the electrolyte.



Fig. S6 CV curve of the NiFe-PBA electrode in 1 M KOH electrolyte.



Fig. S7 Equivalent circuit for the EIS Nyquist plots.



Fig. S8 (a) CV curves of Ni foam at the scan rate ranging from 40 to 90 mV s⁻¹ with an interval of 10 mV s⁻¹; (b) Calculation of C_{dl} of Ni foam by plotting the capacitive current density against the scan rate to fit with linear regression.



Fig. S9 (a) CV curves of Ni-MOF at the scan rate ranging from 40 to 90 mV s⁻¹ with an interval of 10 mV s⁻¹; (b) Calculation of C_{dl} of Ni-MOF by plotting the capacitive current density against the scan rate to fit with linear regression.



Fig. S10 (a, c, e) CV curves of NiFe-PBA (2 h, 4 h, 6 h) at the scan rate ranging from 40 to 90 mV s⁻¹ with an interval of 10 mV s⁻¹; (b, d, f) Calculation of C_{dl} of NiFe-PBA (2 h, 4 h, 6 h) by plotting the capacitive current density against the scan rate to fit with linear regression.



Fig. S11 SEM image of NiFe-PBA after the stability test.



Fig. S12 (a) TEM and (b) HRTEM images of NiFe-PBA after the stability test.



Fig. S13 XRD patterns of NiFe-PBA before and after the stability test.



Fig. S14 High-resolution XPS of Ni 2p for NiFe-PBA before and after the stability test.



Fig. S15 *In-situ* Raman spectra of the NiFe-PBA catalyst at various potentials (vs. RHE) for the OER process. The signal peak at 510 cm⁻¹ is ascribed to the NiFe-PBA materials.

			1		
Catalyst	Electrolyte	Current	Overpotential	Tafel slope	Reference
		density	(mV)	(mV dec ⁻¹)	
		(mA cm ⁻			
		²)			
NiFe-PBA	1 M KOH	200	368	40.29	This work
		500	470		
NiFe-PBA	1 M KOH +	200	370	NA	This work
	0.5 M NaCl	500	485		
Ni ₂ P-Fe ₂ P	1 M KOH	100	261	58	3
NiFeRh-	1 M KOH	400	290	29	4
LDH					
B-Co ₂ Fe	1 M KOH	100	246	39.2	5
LDH					
r-NiFe/NF	1 M KOH	240	270	40	6
NiFe LDH	1 M KOH	200	251	32.8	7
Ni ₃ S ₂	1 M KOH	100	470	116	8
NiFe/NiFeB _x	30% KOH +	100	328	47.10	9
	0.5 M NaCl				
NiFe LDH	1 M KOH +	100	386	110.7	10
/NiS	0.5 M NaCl				
FeOOH	1 M KOH +	500	312	105	11
@NiCoOH	0.5 M NaCl				
NiOOH	1 M KOH +	500	401	103	11
@NiCoOH	0.5 M NaCl				
CeO _{2-x}	1 M KOH	100	204	NA	12
@CoFe LDH					
Fe-Ni(OH) ₂	1 M KOH +	100	320	46	13
$/Ni_3S_2$	0.5 M NaCl				

Table S1 Comparison of the OER performance between the NiFe-PBA catalyst and

 some recently reported OER electrocatalysts in alkaline electrolytes.

 Table S2 Comparison of the performance between the NiMoN||NiFe-PBA electrolyzer

 and some recently reported electrolyzers for overall seawater electrolysis.

Electrolyzer	Electrolyte	Current density	Cell voltage	Reference	
		(mA cm ⁻²)	(V)		
NiMoN NiFe-PBA	1 M KOH +	100	1.602	This work	
	seawater				
		500	1.782		
MoS ₂ -NiS ₂ /NGF/NF	1 M KOH	10	1.64	14	
NiMoN S-	1 M KOH +	100	1.661	15	
(Ni,Fe)OOH	seawater	500	1.837		
Ni-MoN SSM	1 M KOH +	100	1.635	16	
	seawater	500	1.783		
NiVRu-LDH NiVIr-	1 M KOH +	100	1.67	17	
LDH	seawater				
CoPx CoPx@FeOOH	1 M KOH +	100	1.710	18	
	seawater	500	1.867		
Ni ₂ P-Fe ₂ P Ni ₂ P-Fe ₂ P	1 M KOH +	100	1.811	3	
	seawater	500	2.004		
S,P-(Ni,Mo,Fe)OOH	1 M KOH +	100	1.741	19	
/NiMoP/wood aerogel	seawater	500	1.861		
	1 M KOH +	100	1.725	20	
CoFe-Ni ₂ P CoFe-	seawater	500	1.840		
Ni ₂ P	6 M KOH +	100	1.690	20	
	seawater	500	1.801		

References

- L. Yu, J. Xiao, C. Huang, J. Zhou, M. Qiu, Y. Yu, Z. Ren, C.-W. Chu and J. C. Yu, *Proceedings of the National Academy of Sciences*, 2022, 119, e2202382119.
- L. Yu, Q. Zhu, S. Song, B. McElhenny, D. Wang, C. Wu, Z. Qin, J. Bao, Y. Yu,
 S. Chen and Z. Ren, *Nature Communications*, 2019, 10, 5106.
- 3. L. Wu, L. Yu, F. Zhang, B. McElhenny, D. Luo, A. Karim, S. Chen and Z. Ren, *Advanced Functional Materials*, 2021, **31**, 2006484.
- H. Sun, W. Zhang, J.-G. Li, Z. Li, X. Ao, K.-H. Xue, K. K. Ostrikov, J. Tang and C. Wang, *Applied Catalysis B: Environmental*, 2021, 284, 119740.
- L. Wu, L. Yu, Q. Zhu, B. McElhenny, F. Zhang, C. Wu, X. Xing, J. Bao, S. Chen and Z. Ren, *Nano Energy*, 2021, 83, 105838.
- M. Asnavandi, Y. Yin, Y. Li, C. Sun and C. Zhao, ACS Energy Letters, 2018, 3, 1515-1520.
- 7. M. Ning, L. Wu, F. Zhang, D. Wang, S. Song, T. Tong, J. Bao, S. Chen, L. Yu and Z. Ren, *Materials Today Physics*, 2021, **19**, 100419.
- 8. C. Wang, M. Zhu, Z. Cao, P. Zhu, Y. Cao, X. Xu, C. Xu and Z. Yin, *Applied Catalysis B: Environmental*, 2021, **291**, 120071.
- J. Li, Y. Liu, H. Chen, Z. Zhang and X. Zou, Advanced Functional Materials, 2021, 31, 2101820.
- Q. Wen, K. Yang, D. Huang, G. Cheng, X. Ai, Y. Liu, J. Fang, H. Li, L. Yu and T. Zhai, *Advanced Energy Materials*, 2021, **11**, 2102353.

- A. R. Jadhav, A. Kumar, J. Lee, T. Yang, S. Na, J. Lee, Y. Luo, X. Liu, Y. Hwang, Y. Liu and H. Lee, *Journal of Materials Chemistry A*, 2020, 8, 24501-24514.
- 12. Y. Hu, W. Liu, K. Jiang, L. Xu, M. Guan, J. Bao, H. Ji and H. Li, *Inorganic Chemistry Frontiers*, 2020, 7, 4461-4468.
- B. Cui, Z. Hu, C. Liu, S. Liu, F. Chen, S. Hu, J. Zhang, W. Zhou, Y. Deng, Z.
 Qin, Z. Wu, Y. Chen, L. Cui and W. Hu, *Nano Research*, 2021, 14, 1149-1155.
- P. Kuang, M. He, H. Zou, J. Yu and K. Fan, *Applied Catalysis B: Environmental*, 2019, **254**, 15-25.
- L. Yu, L. Wu, B. McElhenny, S. Song, D. Luo, F. Zhang, Y. Yu, S. Chen and Z.
 Ren, *Energy & Environmental Science*, 2020, 13, 3439-3446.
- L. Wu, F. Zhang, S. Song, M. Ning, Q. Zhu, J. Zhou, G. Gao, Z. Chen, Q. Zhou,
 X. Xing, T. Tong, Y. Yao, J. Bao, L. Yu, S. Chen and Z. Ren, *Advanced Materials*, 2022, 34, 2201774.
- D. Wang, Q. Li, C. Han, Q. Lu, Z. Xing and X. Yang, *Nature Communications*, 2019, 10, 3899.
- L. Wu, L. Yu, B. McElhenny, X. Xing, D. Luo, F. Zhang, J. Bao, S. Chen and Z.
 Ren, *Applied Catalysis B: Environmental*, 2021, **294**, 120256.
- H. Chen, Y. Zou, J. Li, K. Zhang, Y. Xia, B. Hui and D. Yang, *Applied Catalysis B: Environmental*, 2021, 293, 120215.
- C. Huang, Q. Zhou, L. Yu, D. Duan, T. Cao, S. Qiu, Z. Wang, J. Guo, Y. Xie, L.
 Li and Y. Yu, *Advanced Energy Materials*, 2023, 13, 2301475.