Supplementary Information

Facile Synthesis of Nanoporous Ni-Fe-P Bifunctional Catalysts with High performance for Overall Water Splitting

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Experimental Section

The synthesis of Ni-Fe-P/NF₀ electrode material: The chemicals used in the synthesis process are all analytical grades and added without further treatment. A batch of nickel foam was cut to the size of 1×3 cm², then soaked in acetone for a certain time, and washed with deionized water. The nickel foam was soaked in 3 M HCl for 30 min to remove the oxide layer, and then washed with deionized water and anhydrous ethanol for a period of time. The nickel foam was dried in a vacuum oven to avoid further oxidation. The electroless deposition of Ni-Fe-P/NF₀ alloy is carried out in an alkaline solution containing 7.5 g L⁻¹ nickel sulfate, 17.5 g L⁻¹ ammonium ferrous sulfate, 40 g L⁻¹ sodium hypophosphite monohydrate as a reducing agent, 10g L⁻¹ ammonium fluoride as a buffering agent and 20 g L⁻¹ trisodium citrate as a complexing agent. The pH of the electroless plating solution was adjusted and controlled to 9 with ammonia water. The temperature of the electroless plating solution was raised to 90 °C and the deposition time was controlled to be 1 h. After the electroless plating, the Ni-Fe-P/NF₀ electrode material was rinsed with deionized water for later use.

The synthesis of Ni-Fe-P/NFx electrode material: The prepared Ni-Fe-P/NF₀ electrode material was immersed in 1.5 M HCl for x seconds with a copper wire suspension to obtain a Ni-Fe-P/NFx electrode material. The Ni-Fe-P/NFx electrode material was then ultrasonically cleaned several times with deionized water. Then, it was placed in a drying oven set at 60 $^{\circ}$ C for 8 h.

Structural Characterization: The morphologies and microstructure of the catalysts were characterized using field-emission scanning electron microscopy (FE-SEM, JEOL, and JSM-6700F). The crystal structure of the Ni-Fe-P/NF₃₀ is characterized by a X-ray diffraction (XRD, Rigaku D-max-A with Cu k radiation, λ =1.54178 Å) from 10° to 90°. The atomic ratio of Ni, Fe, and P in the coatings was analyzed by energy dispersive X-ray spectroscopy (EDS). The surface chemical states of the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) using Perkin-Elmer PHI 550 spectrometer, with Al Ka (1486.6 eV) as an X-ray source.

Electrochemical tests: All electrochemical tests were carried out at room temperature. The OER and HER electrochemical activities were tested in a three-electrode configuration on a cs multichannel electrochemical workstation (CorrTest, Wuhan, China), and the overall water splitting was investigated in a two-electrode system. An Hg/HgO electrode was used as a reference electrode and a Pt electrode was used as a counter electrode. All potentials were calibrated to a reversible hydrogen electrode (RHE) in 1 M KOH according to the Nernst equation. The obtained Ni-Fe-P/NF₃₀ electrode was custom-made to 1 cm x 1 cm and used directly as a

working electrode for electrochemical testing. Linear-sweep voltammetry, which corrected regarding iR compensation, was carried out at a scan rate of 1 mV s⁻¹. The linear sweep voltammetry (LSV) curves of each sample was measured five times, and the final sweep was always used for analysis. A series cyclic voltammetry (CV) measurement were performed at various scan rates (0.010, 0.012, 0.014, 0.016, 0.018 V s⁻¹). Electrochemical impedance spectra (EIS) were measured in the frequency range of 0.01 HZ to 105 HZ by applying an AC voltage of 5 mV. Long-term durability test of HER and OER was determined by chronoamperometry and chronopotentiometry, respectively.



Figure S1. Energy-dispersive X-ray spectrum (EDS) of a) Ni-Fe-P/NF₀ and b) Ni-Fe-P/NF₃₀.



Figure S2. Chronopotentiometric curve of HER at 20 mA cm⁻² for Ni-Fe-P/NF₃₀.



Figure S3. CV curves of a) Ni-Fe-P/NF₀, b) Ni-Fe-P/NF₃₀,

and c) Ni-Fe-P/NF45 at different scan rate.

Sample	Ni (atm %)	Fe (atm %)	P (atm %)	O (atm %)	Fe/Ni ratio
Ni-Fe-P/NF ₀	61.02	7.95	11.56	19.46	1/7
Ni-Fe-P/NF ₃₀	45.65	2.48	15.33	36.55	1/14

Table S1. The Fe/Ni atom ratio of Ni-Fe-P/NF₀ and Ni-Fe-P/NF₃₀.

Table S2. Summary of various electrocatalysts for OER.

Catalyst	Electrolyte	Overpotential at 10 mA cm ⁻² (mV)	Reference
Ni-Fe-P/NF ₃₀	1 M KOH	229	This work
np-(Ni $_{0.67}$ Fe $_{0.33}$) $_4$ P $_5$	1 M KOH	245	Ref. S1
Co5Mo1.0O NSs@NF	1 M KOH	270	Ref. S2
NiCoP	1 M KOH	280	Ref. S3
Co-Ni-B@NF	1 M KOH	313	Ref. S4
CoS-Co(OH) 2	1 M KOH	380	Ref S5
$@aMoS_{2+x}$	1 WI KOII	500	Re 1. 55
CoFePi	1 M KOH	277	Ref. S6
Co-Ni(1:1)/PI-CNT	1 M KOH	365	Ref. S7
NiCoFe-LDH/CFC	1 M KOH	280	Ref. S8
Co-MoS ₂ /BCCF-21	1 M KOH	260	Ref. S9

Catalyst	Electrolyte	Water splitting Voltage at 10 mA cm ⁻² (V)	Reference
Ni-Fe-P/NF ₃₀	1 M KOH	1.58	This work
np-(Ni 0.67 Fe 0.33) 4 P 5	1 M KOH	1.62	Ref. S1
Co5Mo1.0ONSs@NF//	1 М КОН	1.68	Pof S7
Co5Mo1.0P NSs@NF	I M KOII	1.00	Kci. 52
Co-Ni-B@NF	1 M KOH	1.72	Ref. S4
CuCoO-NWs	1 M KOH	1.61	Ref. S10
Ni 5 Fe LDH@NF	1 M KOH	1.59	Ref. S11
Se-(NiCo)S/OH	1 M KOH	1.60	Ref. S12

Table S3. Summary of various electrocatalysts for overall water splitting.

References

- 1 W. Xu, S. Zhu, Y. Liang, Z. Cui, X. Yang and A. Inoue, *Journal of Materials Chemistry A*, 2018, **6**, 5574–5579.
- 2 H. Xu, J. Wei, C. Liu, Y. Zhang, L. Tian, C. Wang and Y. Du, *Journal of Colloid and Interface Science*, 2018, **530**, 146–153.
- 3 H. Liang, A. N. Gandi, D. H. Anjum, X. Wang, U. Schwingenschlögl and H. N. Alshareef, *Nano Letters*, 2016, **16**, 7718–7725.
- 4 Y. Z. Zhu, Y. S. Keum, L. Yang, H. Lee, H. Park and J. H. Kim, *Journal of Agricultural and Food Chemistry*, 2010, **58**, 12379–12384.
- 5 T. Yoon and K. S. Kim, Advanced Functional Materials, 2016, 26, 7386–7393.
- 6 Y. Zhou and H. C. Zeng, Small, , DOI:10.1002/smll.201704403.
- 7 X. Li, T. Wang and C. Wang, Journal of Alloys and Compounds, 2017, **729**, 19–26.
- 8 T. Wang, W. Xu and H. Wang, *Electrochimica Acta*, 2017, **257**, 118–127.
- 9 Q. Xiong, Y. Wang, P. F. Liu, L. R. Zheng, G. Wang, H. G. Yang, P. K. Wong, H. Zhang and H. Zhao, *Advanced Materials*, 2018, **30**, 1–7.
- 10 M. Kuang, P. Han, Q. Wang, J. Li and G. Zheng, Advanced Functional Materials, 2016, 26, 8555-8561.
- 11 Y. Zhang, Q. Shao, Y. Pi, J. Guo and X. Huang, Small, 2017, 13, 1–7.
- 12 C. Hu, L. Zhang, Z. J. Zhao, A. Li, X. Chang and J. Gong, Advanced Materials, 2018, 30, 1–8.