

Double-Shelled Hollow Bimetallic Phosphide Nanospheres Anchored on Nitrogen-Doped Graphene for Boosting Water Electrolysis

Dongxu Yang^{#a}, Zhe Su^{#a}, Yuanfu Chen^{a,b*}, Yingjiong Lu^a, Bo Yu^a, Katam Srinivas^a, Bin Wang^a,
Wanli Zhang^a

^a School of Electronic Science and Engineering, and State Key Laboratory of Electronic Thin Films
and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054,
PR China

^b School of Science, and Institute of Oxygen Supply, Tibet University, Lhasa 850000, PR China

[#] D. Yang and Z. Su contribute equally in this work.

* Corresponding author.

Email addresses: yfchen@uestc.edu.cn (Y.F. Chen)

Supporting Information

Experimental Section

Catalyst Synthesis

NiFe-MIL-88@GNS: As a starting material, graphene oxide (GO) was synthesized using a modified Hummer's method as presented in previously report.^{1,2} In a typical synthesis of NiFe-MIL-88@GNS, GO (60 mg) was dispersed in dimethylacetamide (DMA, 30 mL) and dispersed by ultra-sonicating for at least 30 min to obtain homogeneous solution. Next, Ni(ac)₂·4H₂O (180 mg) and FeCl₃·6H₂O (135 mg) were added into the prepared GO dispersion with stirring to obtain solution A. Then, 1, 4-BDC (83.0 mg) was added into DMA (30 mL) under stirring for 10 min to obtain transparent solution B. Subsequently, the solution A was injected into solution B and stirred several minutes, followed by adding 2 mL acetonitrile. After continuously stirring for 15 min, the mixture was transferred into a Teflon vessel (100 mL) to heat at 150 °C for 3 h before naturally cooling to room temperature. The resulting saffron precipitate was obtained through centrifugation (8500 rpm) and washed with ethanol/DMA for three times. The collected powder was dried at 60 °C overnight. In the case of mono-metallic samples, only Ni(ac)₂·4H₂O or FeCl₃·6H₂O was added.

NiFe-P@GNS: The as-synthesized NiFe-MIL-88@GNS were transferred into tube furnace and heated to 600 °C under N₂ flow (100 sccm). The heating rate was 5 °C min⁻¹ and the temperature maintains at 600°C for 2 hours. The obtained black powder was transferred into a ceramic vial, which was then placed into a Teflon vessel with 10 mL hydrazine hydrate (130 °C) for 2 hours for GO reduction and nitrogen doping to obtain NiFe-C@GNS. Then 100 mg of the pre-treated powder was placed at downstream of 500 mg NaH₂PO₂ in a quartz boat and was heated to 300 °C for another 2 h under N₂ flow (50 sccm).

NiFe-P: The reference NiFe-P sample was synthesized using same conditions as for the NiFe-P@GNS, but without adding GO. In the case of reference samples with different Ni:Fe ratios, the feeding amount of Ni(ac)₂·4H₂O and FeCl₃·6H₂O was adjusted accordingly.

Electrochemical measurements

HER and OER evaluations were carried out using a three-electrode configuration, where a Hg/HgO electrode was used as reference electrode and a graphite rod was used as counter electrode. To prepare the working electrode, catalyst powders (4 mg) were dispersed in a 3:1 mixture of deionized water and ethanol (total 1 mL) added with 50 μL of 5 wt % Nafion solution. 5 μL of the dispersed ink was dropped and dried onto the 3 mm glassy carbon electrode

to give a loading amount of 0.27 mg cm^{-2} . To activate the catalyst materials, CV cycling was performed on the work electrodes for more than 30 cycles before measurements. During the linear sweep voltammetry (LSV), scan rate of 5 mV s^{-1} was used. For the electrochemical impedance spectroscopy (EIS) test, AC frequency range was set from 10^5 to 10^{-1} Hz . The reference electrode was calibrated to reversible hydrogen electrode (RHE) via a CV method, as shown in Fig. S1.³ The potentials of reference electrodes were calibrated to be $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.927 \text{ V}$. All the electrochemical data was presented without i - R correction.

References

- 1 D. Li, M.B. Muller, S. Gilje, R.B. Kaner and G.G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101-105.
- 2 D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu and J.M. Tour, *ACS Nano*, 2010, **4**, 4806-4814.
- 3 C. Wei, R.R. Rao, J. Peng, B. Huang, I.E.L. Stephens, M. Risch, Z.J. Xu and Y. Shao-Horn, *Adv. Mater.*, 2019, **31**, 1806296.

Figures

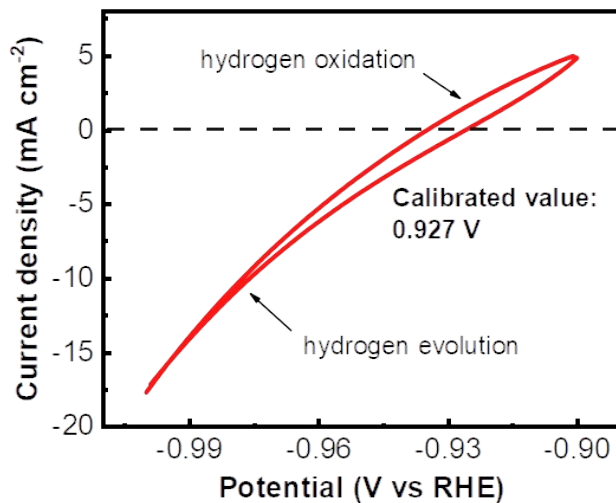


Fig. S1. Voltammograms of two platinum wire electrodes as both working and counter electrodes at a scan rate of 10 mV s^{-1} in 1.0 M KOH

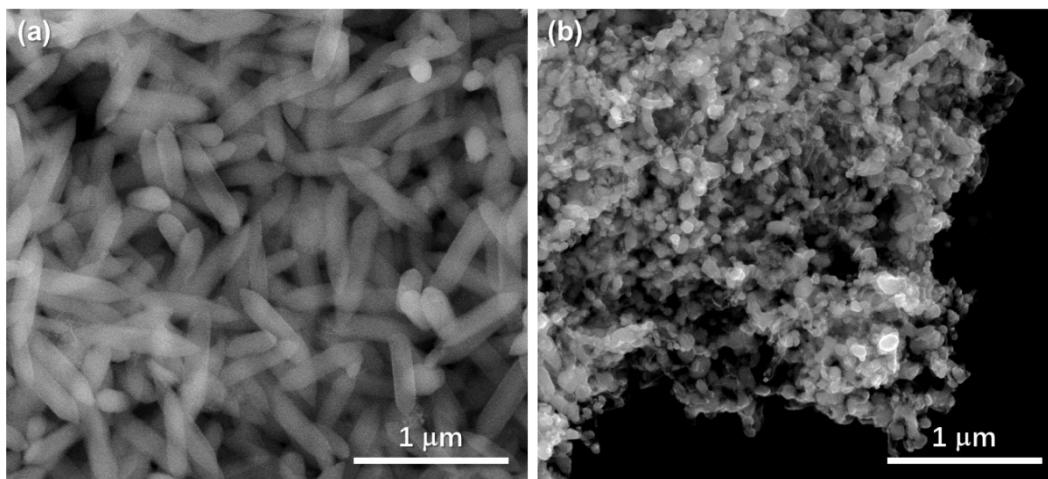


Fig. S2. SEM images of (a) MOF precursor NiFe-MIL-88 without GO and (b) NiFe-P after thermal treatments

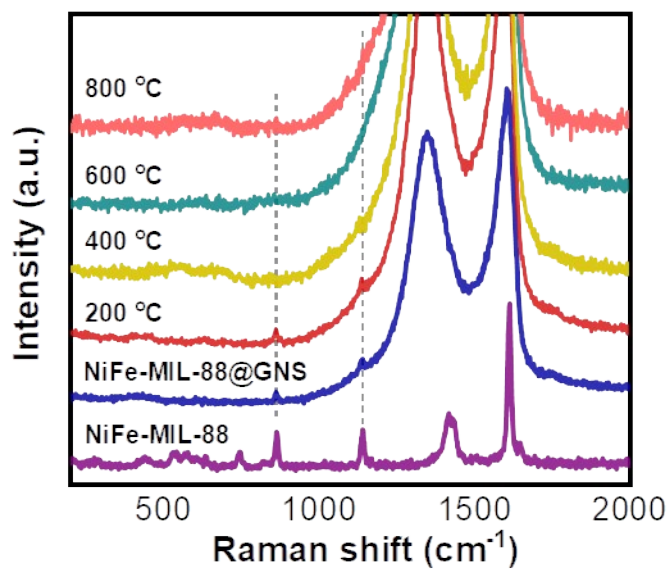


Fig. S3. Raman spectra of the pristine MOF and NiFe-C@GNS samples with various pyrolysis temperatures

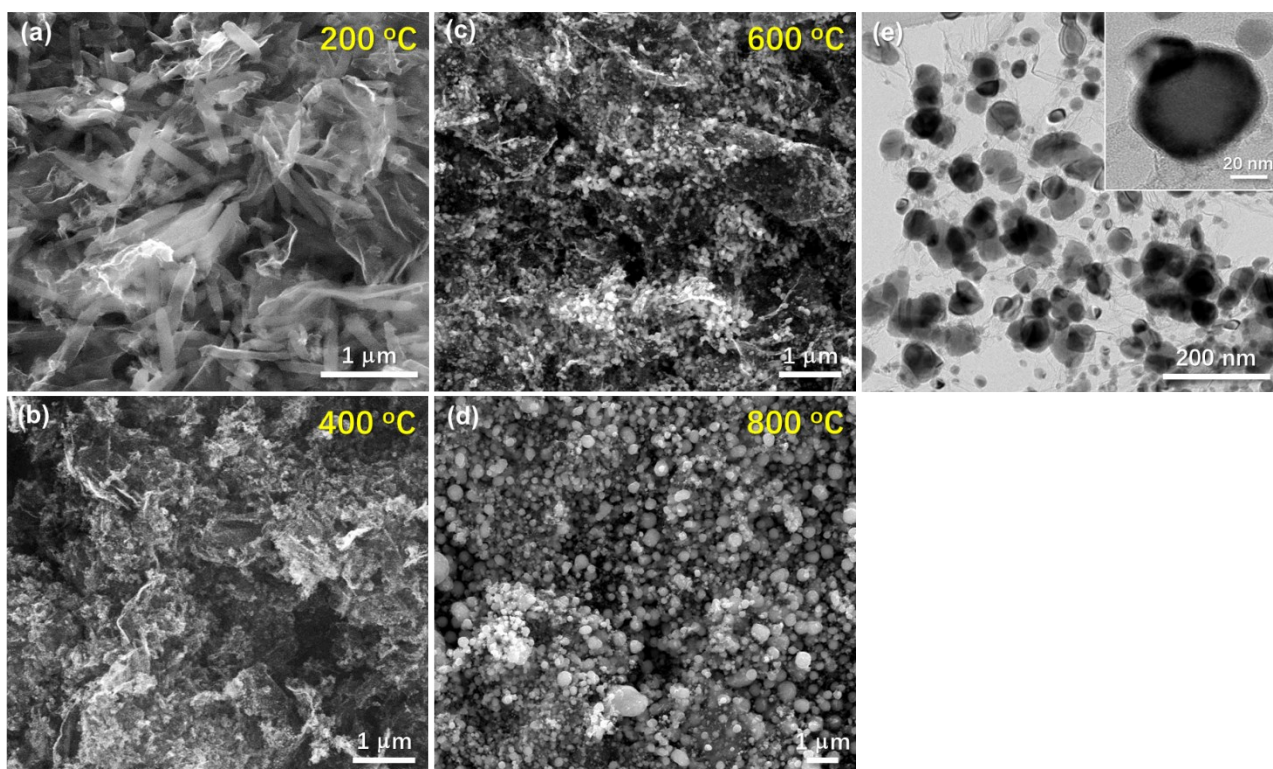


Fig. S4. (a-d) SEM images of the NiFe-C@GNS samples with various pyrolysis temperatures, and (e) TEM image of NiFe-C@GNS under 600 °C pyrolysis

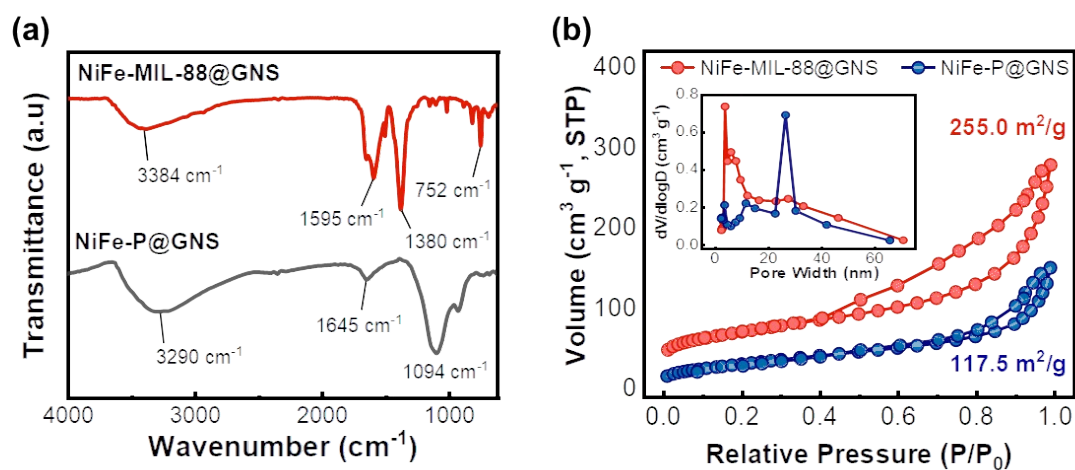


Fig. S5. (a) FT-IR spectra of NiFe-MIL-88@GNS and NiFe-P@GNS; (b) nitrogen adsorption-desorption isotherm and corresponding pore-size distribution plots (inset) of NiFe-MIL-88@GNS and NiFe-P@GNS

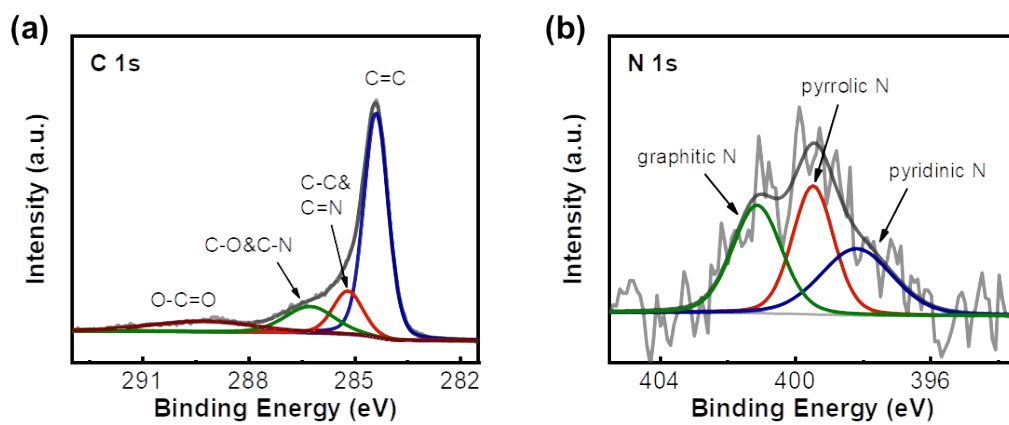


Fig. S6. XPS spectra of NiFe-P@GNS at (a) C 1s and (b) N 1s regions

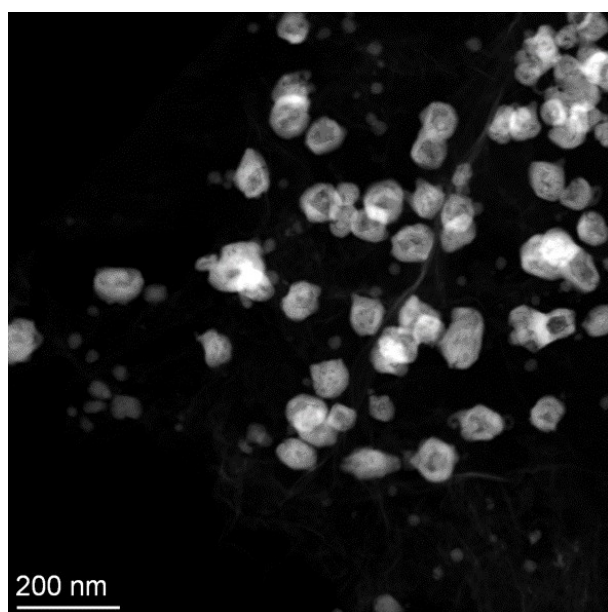


Fig. S7. TEM HAADF image of NiFe-P@GNS, showing a hollow nanosphere structure

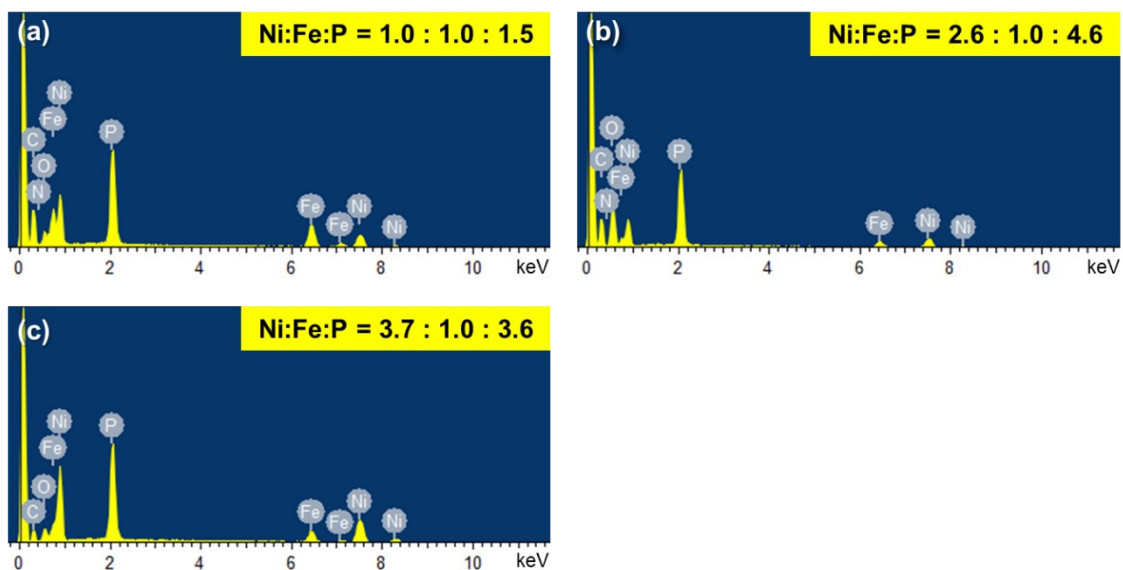


Fig. S8. EDX spectra of (a) Ni_{1.0}Fe_{1.0}-P, (b) Ni_{1.5}Fe_{1.0}-P, and (c) Ni_{2.0}Fe_{1.0}-P

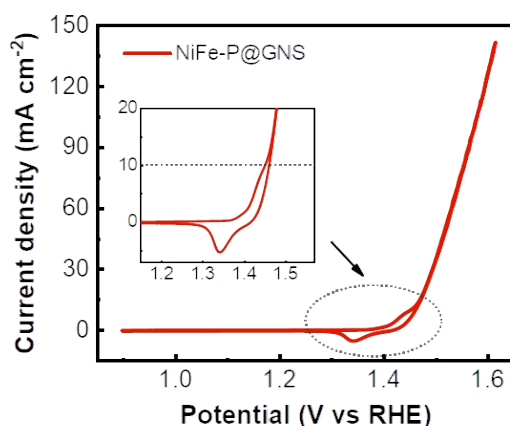


Fig. S9. CV plot of NiFe-P@GNS at scan rate of 5 mV s⁻¹

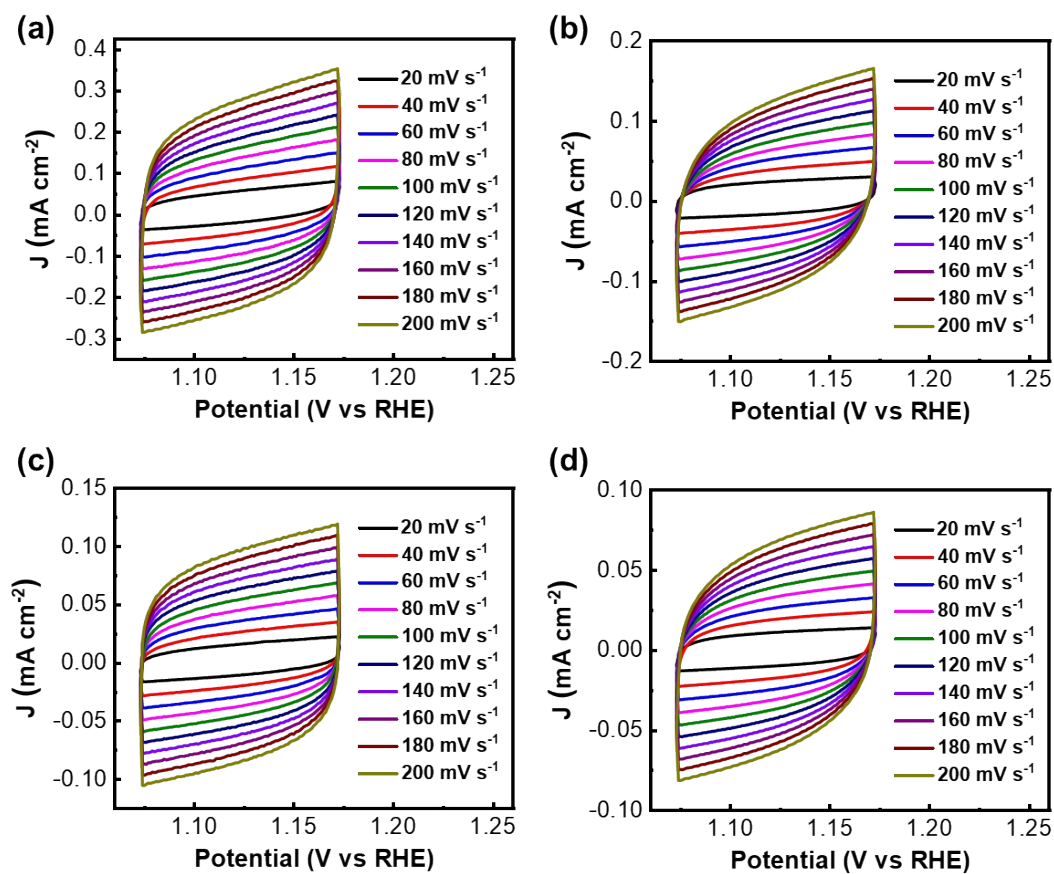


Fig. S10. CV scan curves at different scan rates for (a) NiFe-P@GNS, (b) Ni-P@GNS, (c) Fe-P@GNS and (d) NiFe-P

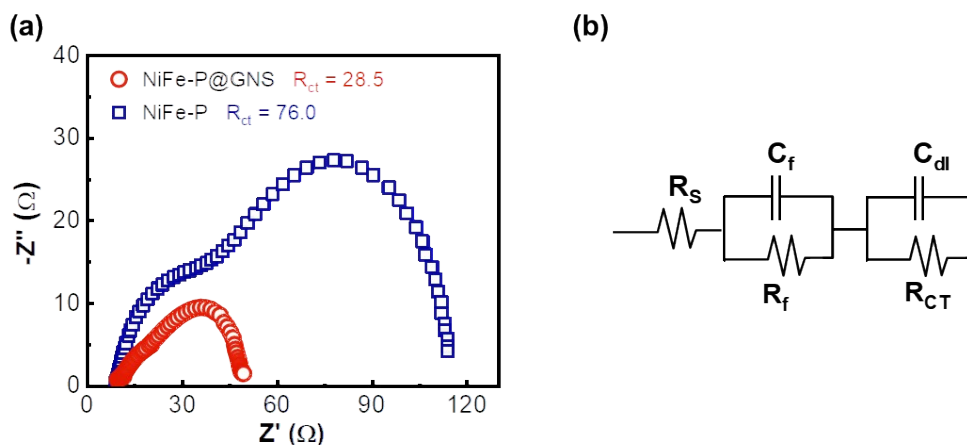


Fig. S11. (a) Nyquist plots (0.1 Hz-10 MHz) at overpotential of 300 mV in and (b) the equivalent circuits used for Nyquist plot fitting, in which R_s is the resistance of the electrolyte. R_f is the resistance of the catalyst layer and C_f is the capacitance. C_{dl} is the double layer capacitance and R_{ct} is the charge transfer resistance. In the high frequency region, the resistance is related to the uncompensated solution resistance, which is comparable for all catalysts.

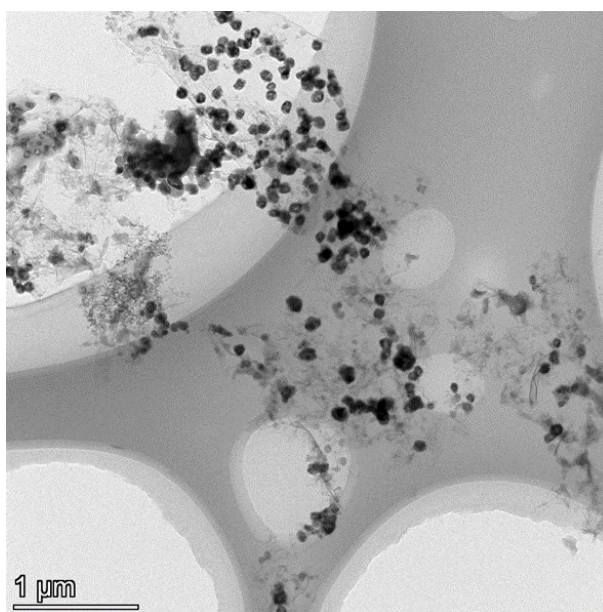


Fig. S12. TEM image of NiFe-P@GNS after 1000 CV cycles in OER

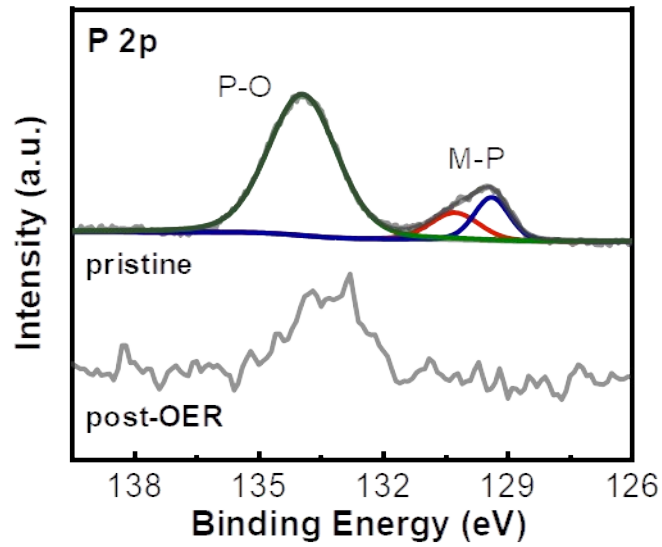


Fig. S13. XPS P 2p spectrum of NiFe-P@GNS before and after OER cycling test

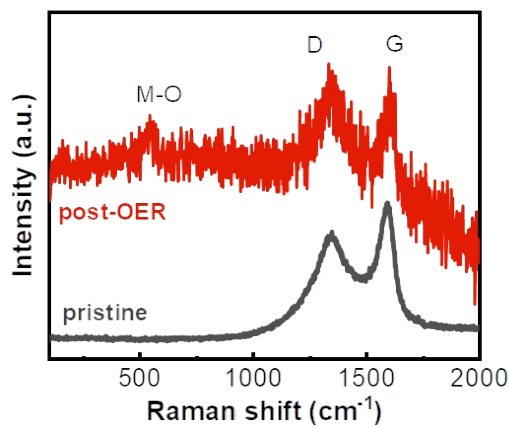


Fig. S14. Raman spectra of NiFe-P@GNS before and after 1000 CV cycles in OER

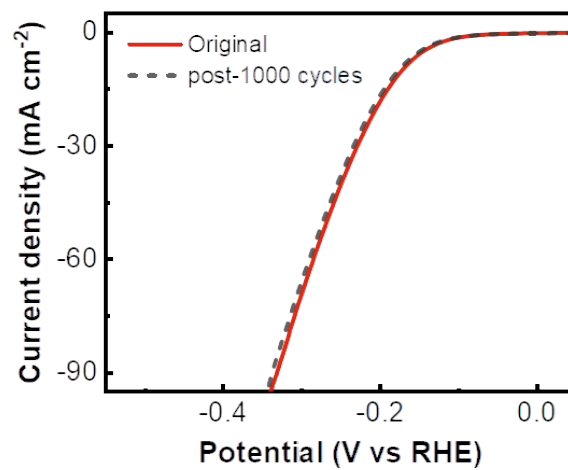


Fig. S15. HER LSV curves of NiFe-P@GNS before and after 1000 CV cycling test



Fig. S16. Digital photographs of the setup of the water decomposition hydrogen production system

Samples	Potential (V) @10mA cm ⁻²	References
NiFe-P@GNS	1.578	This work
Co ₂ P/Ni ₂ P-2%Mo	1.57	Appl. Catal. B-Environ., 269(2020)118951
Co _{0.6} Fe _{0.4} P-1.125	1.57	Chem. Sci.10 (2019) 464
FCP@NG	1.63	Nanoscale 11 (2019) 12837
CoP/NCNHP	1.64	J. Am. Chem. Soc. 140 (2018) 2610
NiS/NiS ₂	1.62	J. Mater. Chem. A 6 (2018) 8233
Co ₄ Ni ₁ P NTs	1.59	Adv. Funct. Mater., 27(2017) 1703455
NiCoP/rGO	1.59	Adv. Funct. Mater., 26(2016) 6785
N-NiMoO ₄ /NiS ₂	1.60	Adv. Funct. Mater., 29(2019) 1805298
NiS/NiS ₂	1.62	J. Mater. Chem. A, 6(2018) 8233
MoS ₂ -NiS ₂ /NGF	1.64	Appl. Catal. B-Environ.,254 (2019) 15
Ni@NC-800	1.60	Adv. Mater., 29(2017) 1605957
CoN _x @GDY NS/NF	1.48	Nano Energy 59 (2019) 591

Table S1. Summary of overall water-splitting performance of recently reported catalysts