**Electronic Supplementary Information** 

# Advanced Oxygen Evolution Catalysis by Bimetallic Ni-Fe Phosphides Nanoparticles Encapsulated in Nitrogen, Phosphorus, and Sulphur Tri-Doped Porous Carbon

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#### Materials and reagents.

The following chemicals were used as received without any further purification: FeCl<sub>3</sub>·6H<sub>2</sub>O (99%, Sigma–Aldrich), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99%, Sigma–Aldrich), terephthalic acid (H<sub>2</sub>BDC, 98%, Sigma–Aldrich), *N,N*-dimethylformamide (DMF, 99.99%, Fisher), NaOH (97%, Sigma–Aldrich), triethylamine (99%, Sigma–Aldrich), hexachlorocyclophosphazene (HCCP, 99%, Sigma–Aldrich), 4,4'-sulfonyldiphenol (BPS, 98%, Sigma–Aldrich), triethylamine (TEA, 99+%, Acros Organics), sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>, >98%, Sigma–Aldrich), methanol (99.99%, Fisher), and ethanol (99.99%, Fisher). Deionized water was generated by Elga Micromeg Purified Water system.

#### Preparation of NiFeP<sub>x</sub>@NPS-C nanocomposite.

Firstly, NiFe<sub>2</sub>-MIL-88B was prepared according to a previous report with minor modification.<sup>1</sup> In a typical synthesis, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.33 mmol), FeCl<sub>3</sub>·6H<sub>2</sub>O (0.67 mmol) and H<sub>2</sub>BDC (1 mmol) were dissolved in DMF (10 mL). Then 0.4 M NaOH (2 mL) was added into the above solution under stirring. The mixture was transferred into a Teflon-lined autoclave and heated at 100 °C for 15 h. The as-obtained precipitate (NiFe<sub>2</sub>-MIL-88B) was centrifuged, rinsed with ethanol for three times, and dried in an electric oven at 60 °C for 12 h. In the second step, the as-obtained NiFe<sub>2</sub>-MIL-88B was dispersed into methanol (40 mL) to obtain a homogeneous suspension. 15 mL of methanol containing 150 mg of HCCP and 350 mg of BPS was added into the above suspension. Then triethylamine (1 mL) was added to initialize the polymerization and the mixture was stirred continuously for another 10 h. The precipitate (NiFe<sub>2</sub>-MIL-88B@PZS) was collected, washed with ethanol for three times, and dried in the oven at 60 °C for 12 h. Finally, the NiFe<sub>2</sub>-MIL-88B@PZS was pyrolyzed in an electric tubular furnace at 850 °C for 2 h under N<sub>2</sub> atmosphere with a heating rate of 2 °C/min, followed by a treatment in 2 M HCl to remove impurities and/or unstable species; the sample was then washed with deionized water/ethanol and dried at 60 °C for

12 h. The final product from this process is named as  $NiFeP_x@NPS-C$  nanocomposite in the main text.

#### Preparation of the control samples.

 $Fe_2O_3$  nanospindles. Firstly, Fe-MIL-88B nanospindles were fabricated with the similar preparation procedure of NiFe<sub>2</sub>-MIL-88B while without adding the Ni salt. Typically, FeCl<sub>3</sub>·6H<sub>2</sub>O (1 mmol) and H<sub>2</sub>BDC (1 mmol) were dissolved in DMF (10 mL). Then 0.4 M NaOH (0.75 mL) was added into the above solution under stirring. The mixture was transferred into a Teflon-lined autoclave and heated in the oven at 100 °C for 15 h. The precipitate was centrifuged, rinsed with ethanol for three times, and dried in an electric oven at 60 °C for 12 h. Fe<sub>2</sub>O<sub>3</sub> nanospindles were prepared by calcining the above Fe-MIL-88B nanospindles in an electric furnace at 400 °C for 2 h under the laboratory air with a heating rate of 2 °C/min.

 $NiFe_2O_4$  nanospindles. NiFe\_2O\_4 nanospindles were prepared by calcining NiFe\_2-MIL-88B nanospindles in the electric furnace at 400 °C for 2 h under the laboratory air with a heating rate of 2 °C/min.

*FeP<sub>x</sub> nanospindles.* FeP<sub>x</sub> nanospindles were prepared by using a low-temperature phosphidation method. In a typical synthesis, Fe<sub>2</sub>O<sub>3</sub> nanospindles and NaH<sub>2</sub>PO<sub>2</sub> were placed at two separate positions in a porcelain boat and charged into a tube furnace with NaH<sub>2</sub>PO<sub>2</sub> at the upstream side of the furnace. The molar ratio of metal-to-phosphorus is 1:20. Subsequently, the samples were heated in the tube furnace at 400 °C for 2 h with a ramping speed of 2 °C/min under a N<sub>2</sub> flow (20 mL/min), and then naturally cooled to ambient temperature.

*NiFeP<sub>x</sub> nanospindles.* NiFeP<sub>x</sub> nanospindles were prepared by using the similar preparation procedure of  $FeP_x$  nanospindles while using NiFe<sub>2</sub>O<sub>4</sub> nanospindles as the precursor.

*S-doped carbon (S-C).* S-C was prepared by direct carbonization of BPS under  $N_2$  atmosphere in the tubular electric furnace at 850 °C for 2 h with a heating rate of 2 °C/min and then naturally cooled to ambient temperature.

*N*,*P*,*S*-*tri-doped carbon (NPS-C)*. NPS-C was prepared by carbonization of pure PZS polymer. In a typical process, pure PZS polymer was firstly prepared by using the similar preparation procedure of NiFeP<sub>x</sub>@NPS-C nanocomposite while without addition of the MOF core material. Specifically, 150 mg of HCCP and 350 mg of BPS was dissolved in 55 mL of methanol to obtain a clear solution. Then triethylamine (1 mL) was added to initialize the polymerization reaction and the mixture was stirred continuously for another 10 h. The precipitate was collected, washed with ethanol for three times, and dried in the electric oven at 60 °C for 12 h. In the second step, the PZS polymer was pyrolyzed in the tube furnace under N<sub>2</sub> atmosphere at 850 °C for 2 h with a heating rate of 2 °C/min and then naturally cooled to ambient temperature.

### **Electrochemical measurements.**

The electrochemical measurements were carried out using a computer-controlled electrochemical workstation (Autolab, PGSTAT 302N) with a standard three-electrode system, in which a catalyst-modified glassy carbon electrode (GCE, 3 mm in diameter) was used as the working electrode, a Pt plate as the counter electrode, and Ag/AgCl (filled with 3.0 M KCl solution) electrode as the reference electrode. The preparation for the working electrode was as follows: solid catalyst (3 mg) was dispersed in 488.8 µL of water, 122.2 µL of ethanol and 25.46 µL of 5 wt% Nafion solution. Then the homogeneous catalyst ink was obtained by ultrasonicating the mixture for about 30 min. Next, 3 µL of catalyst ink was loaded onto the GCE (loading amount for all the samples: about 0.2 mg cm<sup>-2</sup>). Finally, the electrode was dried at room temperature overnight. Prior to all experiments, the electrolyte solution (1.0 M KOH) was purged with O<sub>2</sub> for 30 min. Before the electrochemical catalytic measurements, all the working

electrodes were conducted by a continuous cyclic voltammetry (CV) for several times at a scan rate of 50 mV s<sup>-1</sup> until the signals were relatively stabilized. Linear sweep voltammetry (LSV) was recorded with a scan rate of 5 mV s<sup>-1</sup> to obtain the polarization curves. All the polarization curves were corrected with iR-compensation. The long-term stability test was performed by chronopotentiometric (CP) measurement in 1.0 M KOH electrolyte with the current density at 10 mA cm<sup>-2</sup>.

In this work, the electrochemical measurements were carried out at least on three working electrodes to check the reproducibility and their average was taken into account. The working electrode was continuously rotated at 1600 rpm to get rid of the oxygen bubbles. All the current densities were normalized to the geometrical area of the GCE, and all the measured potentials vs. Ag/AgCl (3.0 M KCl) were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation: E (RHE) = E (Ag/AgCl) + 0.210 + 0.0591 × pH.

### Materials characterization.

Microscopic features of the above prepared samples were characterised by scanning electron microscopy (SEM, JEOL-6700F) equipped with an energy-dispersive X-ray (EDX) analyser (Oxford INCA), transmission electron microscopy (TEM, JEOL JEM-2010, 200 kV), and high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, 200 kV). The elemental mapping was done by energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments, model 7426). The wide-angle X-ray (Cu  $K_{\alpha}$  radiation) diffraction patterns were taken using Bruker D8 Advance system. Nitrogen adsorption–desorption isotherms were obtained on Quantachrome NOVA-3000 system at 77 K. Prior to the measurement, the samples were degassed at 200 °C for 15 h with a gas flow of N<sub>2</sub>. The surface area of the materials was measured by the Brunauer–Emmet–Teller (BET) method. The pore size distribution curve was obtained using the NLDFT method from the desorption data and the pore volume was calculated at  $P/P_0 = 0.9754$ . The surface composition and oxidation state of the samples

were further investigated by X-ray photoelectron spectroscopy (XPS, AXIS-HSi, Kratos Analytical) with a monochromated Al  $K_{\alpha}$  X-ray source (hv = 1486.71 eV), and all binding energies were referred to the C 1s peak (284.5 eV) arising from the C–C bonds.



Figure S1. (a, b) SEM and (c) TEM images of NiFe<sub>2</sub>-MIL-88B.



Figure S2. (a, b) SEM and (c) TEM images of NiFe<sub>2</sub>-MIL-88B@PZS.



**Figure S3.** (a, b) SEM, (c-e) TEM, and (f) HRTEM images of the NiFeP<sub>x</sub>@NPS-C nanocomposite.



Figure S4. The NLDFT pore size distribution curve of NiFeP<sub>x</sub>@NPS-C nanocomposite from the desorption data of  $N_2$  adsorption–desorption isotherm.



**Figure S5.** XPS spectra of NiFeP<sub>x</sub>@NPS-C: (a) survey spectrum, (b) Ni 2*p*, (c) Fe 2*p*, (d) P 1*s*, (e) N 2*p*, and (f) S 2*p*.

**Notes:** Based on the XPS results ((Figure S5), the quantitative estimations of the metal phosphide species and the oxidised metal species on the surface of the sample are performed. From the Ni 2*p* spectrum (Figure S5b), the Ni–P species accounts for 59.2%, and the oxidised Ni species accounts for 40.8%. From Fe 2*p* spectrum (Figure S5c), the Fe–P species accounts for 23.7%, and the oxidised Fe species accounts for 76.3%.



Figure S6. (a) SEM image, (b, c) TEM images and (d) EDX spectrum of S-C sample.



Figure S7. (a) SEM and (b, c) TEM images of NPS-C sample.



**Figure S8.** XPS investigation of the NPS-C sample: (a) survey spectrum, (b) N 1*s*, (c) P 2*p*, and (d) S 2*p* spectra.

**Notes:** X-ray photoelectron spectroscopy (XPS) analysis is carried out to identify elemental states of NPS-C sample. The survey spectrum (Figure S7a) confirms the presence of N, P, S elements in the carbon. The N 1*s* spectrum (Figure S7b) can be deconvoluted into four peaks at 398.3, 400.3, 401.5, and 405.0 eV, which correspond to the pyridinic N, pyrrolic N, graphitic N, and pyridinic N<sup>+</sup>-O<sup>-</sup> species, respectively.<sup>2</sup> In the P 2*p* spectrum (Figure S7c), the peaks at 132.6 and 134.5 eV are assigned to P-C and P-O, respectively.<sup>2-4</sup> The S 2*p* spectrum (Figure S7d) displays three peaks at 163.8, 165.1, and 168.2 eV, which are ascribed to -C-S-C- and oxidised S species, respectively.<sup>5</sup>



Figure S9. (a, b) SEM images of Fe-MIL-88B nanospindles at different magnifications.



Figure S10. XRD pattern of Fe-MIL-88B nanospindles.



Figure S11. (a, b) TEM images of Fe<sub>2</sub>O<sub>3</sub> nanospindles at different magnifications.



**Figure S12.** XRD pattern of  $Fe_2O_3$  nanospindles (in black) in comparison with the standard pattern of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (in red colour).



Figure S13. (a, b) TEM images of  $FeP_x$  nanospindles at different magnifications.



**Figure S14.** XRD pattern of  $\text{FeP}_x$  nanospindles (in black) in comparison with the standard pattern of FeP (in red colour).

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Figure S15. (a, b) TEM images of NiFe<sub>2</sub>O<sub>4</sub> nanospindles at different magnifications.



**Figure S16.** XRD pattern of NiFe<sub>2</sub>O<sub>4</sub> nanospindles (in black) in comparison with the standard pattern of NiFe<sub>2</sub>O<sub>4</sub> (in red colour).



Figure S17. (a, b) TEM images of NiFeP<sub>x</sub> nanospindles at different magnifications.

![](_page_14_Figure_2.jpeg)

**Figure S18.** XRD pattern of NiFeP<sub>x</sub> nanospindles (in black) in comparison with the standard patterns of NiP<sub>2</sub> (in blue colour) and FeP (in red colour).

![](_page_15_Figure_0.jpeg)

**Figure S19.** (a) The polarization curve and (b) the Tafel plot of the commercial  $RuO_2$  in 1.0 M KOH.

![](_page_15_Picture_2.jpeg)

**Figure S20.** (a, b) SEM images of the second acid-etched NiFeP<sub>x</sub>@NPS-C nanocomposite at different magnifications.

![](_page_16_Figure_0.jpeg)

**Figure S21.** (a-c) TEM images of the second acid-etched NiFeP<sub>x</sub>@NPS-C nanocomposite at different magnifications.

![](_page_16_Figure_2.jpeg)

**Figure S22.** The EDX elemental mappings of the spent NiFeP<sub>x</sub>@NPS-C after 20 h of water electrolysis.

**Table S1.** Comparison of the OER catalytic performance of our NiFeP $_x$ @NPS-Cnanocomposite to other recently reported high-performance OER electrocatalysts indifferent alkaline solutions.

Catalyst	Mass loading (mg cm <sup>-2</sup> )	Electrolyte	$\eta @10 \text{ mA} \ \text{cm}^{-2} (\text{mV})$	Tafel slope (mV dec <sup>-1</sup> )	Ref.
NiFeP <sub>x</sub> @NPS-C	0.2	1.0 M KOH	265	43	this work
FeP nanorods	0.7	1.0 M KOH	350	63.6	6
FeP nanotubes	1.6	1.0 M KOH	288	43	7
Ni-P film	N.A.	1.0 M KOH	344	49	8
Ni-P nanoplates	0.2	1.0 M KOH	300	64	9
Ni <sub>2</sub> P nanoparticles	0.14	1.0 M KOH	290	59	10
Ni <sub>2</sub> P nanowires	0.14	1.0 M KOH	330	47	10
CoP nanorods/C	0.71	1.0 M KOH	320	71	11
Co-P film	N.A.	1.0 M KOH	345	47	12
CoMnP NPs	0.28	1.0 M KOH	330	61	13
Nanoporous (Co <sub>0.52</sub> Fe <sub>0.48</sub> ) <sub>2</sub> P	N.A.	1.0 M KOH	270	30	14
sea-urchin-like (Co <sub>0.54</sub> Fe <sub>0.46</sub> ) <sub>2</sub> P	0.2	0.1 M KOH	370	N.A.	15
NiFeO <sub>x</sub> film	N.A.	1.0 M NaOH	> 350	N.A.	16
Ni-Fe oxides	1.0	1.0 M NaOH	> 375	51	17
Ni <sub>0.9</sub> Fe <sub>0.1</sub> /N-C	0.2	1.0 M KOH	330	45	18
Co <sub>3</sub> O <sub>4</sub> /C nanowire arrays	0.2	1.0 M KOH	220	61	19
Zn <sub>X</sub> Co <sub>3-x</sub> O <sub>4</sub> nanowire arrays	1.0	1.0 M KOH	320	51	20
Ni <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub> nanowire arrays	2.3-2.7	1.0 M NaOH	370	59-64	21
Ni-Co oxide nanosheets	N.A.	1.0 M NaOH	340	51	22
Amorphous NiCo <sub>2.7</sub> (OH) <sub>x</sub> nanocages	0.2	1.0 M KOH	350	65	23

Amorphous Ni-Co binary oxide	N.A.	1.0 M NaOH	325	39	24
Ni–Co mixed oxide cages	N.A.	1.0 M KOH	380	50	25
NiCo LDH nanosheets	0.17	1.0 M KOH	367	40	26
Ultrathin NiCo <sub>2</sub> O <sub>4</sub> nanosheets	0.285	1.0 M KOH	320	30	27
N-doped graphitic carbon	0.2	0.1 M KOH	380	75-80	28
P-doped graphitic C <sub>3</sub> N <sub>4</sub>	0.2	0.1 M KOH	400	61.6	29
Graphitic C <sub>3</sub> N <sub>4</sub> nanosheets/carbon nanotubes	0.2	0.1 M KOH	370	83	30
IrO <sub>x</sub>	N.A.	1.0 M NaOH	320 ± 40 (not stable)	N.A.	16
IrO <sub>x</sub>	N.A.	1.0 M KOH	$427 \pm 5$	$49 \pm 1$	31
IrO <sub>2</sub>	0.21	1.0 M KOH	338	47	32

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