Electronic Supplementary Information for

Facile synthesis of iron phosphide nanorods for efficient and durable electrochemical oxygen evolution

Dehua Xiong,[a] Xiaoguang Wang,[a] Wei Li[a] and Lifeng Liu[a,*]

[a] *International Iberian Nanotechnology Laboratory (INL), Av. Mestre Jose Veiga, 4715-330 Braga, Portugal*

* Corresponding author. E-mail: lifeng.liu@inl.int

Experimental details:

Hydrothermal synthesis of FeOOH precursor nanorods (NRs)

All chemicals used in this work are analytical grade and were purchased from Sigma-Aldrich. The FeOOH precursor NRs were synthesized through a hydrothermal approach modified according to a previous report.[S1] Typically, 0.15 M $FeCl_3 \cdot 6H_2O$ and 1 M $NaNO_3$ were dissolved into 35 ml deionized (DI) water with continuous magnetic stirring. After 20 min, the mixed solution was transferred into a Teflon-lined steel autoclave reactor. The reactor was sealed, heated up to 100 °C, and maintained at this temperature for 24 h. Subsequently, the reactor was cooled down to room temperature. The obtained yellow precipitates (i.e., FeOOH NRs) were then washed with DI water and ethanol for several times, and collected by centrifugation.

Fabrication of carbon fiber paper@FeOOH (CP@FeOOH) and carbon fiber paper@FeP (CP@FeP) electrodes

A piece of carbon fiber paper (CP, 3 cm × 5 cm) was successively washed using DI water and ethanol to remove surface impurities, followed by drying in a nitrogen (N_2) flow prior to use as a current collector for preparing CP@FeOOH electrodes. To make FeOOH slurries, the dried FeOOH NRs were re-dispersed in absolute ethanol at a concentration of 1 mg mL^{-1}, and the dispersion was sonicated for 10 minutes to form a uniform suspension. Subsequently, the resulting FeOOH NR suspension was cast onto the CP via the doctor blade method. Thus-prepared CP@FeOOH samples were then dried in a vacuum oven at 60 °C overnight.

The CP@FeP electrodes were obtained by phosphorizing the CP@FeOOH electrodes in phosphorus vapor at elevated temperature. In a typical experiment, phosphorus red (1.0 g) and the CP@FeOOH electrode were loaded in two porcelain boats separated with a distance of 0.5 cm, with phosphorus red at the upstream side and CP@FeOOH at the downstream side in a tube furnace (Carbolite). The phosphorization treatment was performed at 500 °C for 30 minutes using high purity N_2 (99.999%) as the carrier gas. Finally, the furnace was naturally cooled down to room temperature. The resultant CP@FeP samples were then washed successively with DI water and ethanol, and dried in a N_2 flow. The loading mass of CP@FeOOH and CP@FeP were determined to be 0.7 mg cm^{-2} using a high precision microbalance (Sartorius MCM36).

Structural characterization

The morphology, microstructure and chemical composition of samples were examined by filed-emission scanning electron microscopy (FESEM, FEI Quanta 650) and transmission electron microscopy (FEI Titan ChemiSTEM operating at 200 kV). The crystalline structure of samples was studied by X-ray diffractometry (XRD, PANalytical X'Pert PRO) using Cu K_α radiation (λ = 1.540598 Å) and a PIXcel detector. The surface chemical status was analyzed by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000).

Electrochemical measurements

The OER performance was evaluated using linear scan voltammetry (LSV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) in a three-electrode configuration in 1.0 M KOH (pH = 13.5) with a Biologic VMP-3 potentiostat/galvanostat. A platinum sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The as-fabricated CP@FeOOH and CP@FeP were directly used as the working electrode. LSV curves were recorded at a scan rate of 5 mV s^{-1}.

All current density values are normalized with respect to the geometrical surface area of the working electrode. For comparison, the electrocatalytic performance of a bare CP was also measured. All LSV curves measured are *iR*-corrected. The correction was done according to the following equation:

$$E_c = E_m - iR_s \qquad (1)$$

where E_c is the *iR*-corrected potential, E_m experimentally measured potential, and R_s the equivalent series resistance extracted from the EIS measurements. Unless otherwise specified, all potentials are reported versus reversible hydrogen electrode (RHE) by converting the potentials measured vs. SCE according to the following formula:

$$E\ (\mathrm{RHE}) = E\ (\mathrm{SCE}) + 0.241 + 0.059\ \mathrm{pH} \qquad (2)$$

The EIS measurements were performed in the frequency range of 20 mHz – 200 kHz with a sinusoidal perturbation of 10 mV. The evolution of O_2 gas was probed with a home-made graded H-cell. The quantity of O_2 gas produced was determined by converting its volume to mole using the ideal gas law. The Faradaic efficiency was calculated by dividing the total amount of O_2 produced by the total amount of charges passed through the cell, assuming that four electrons are needed to produce one O_2 molecule.

Supplementary Figures

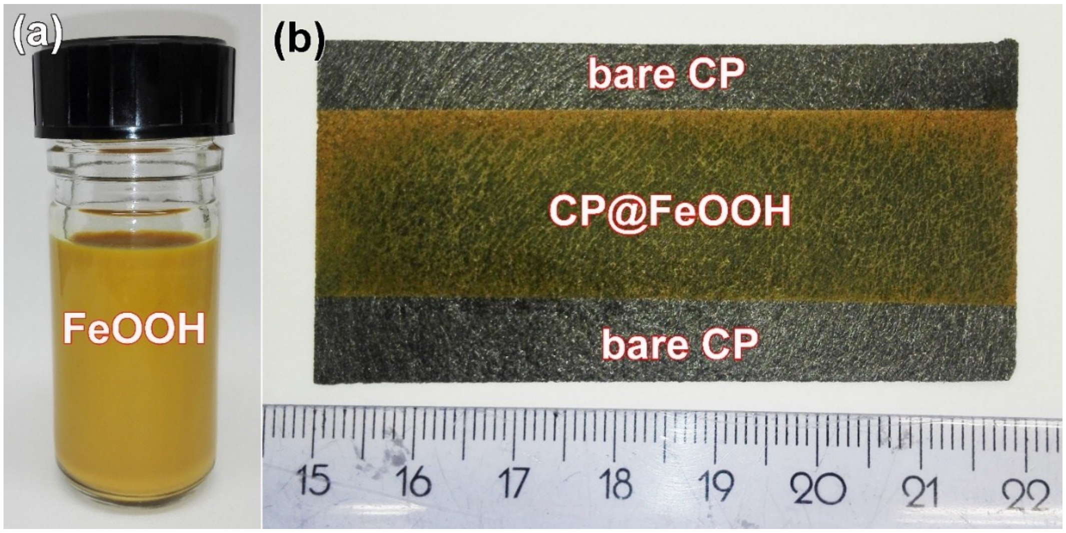

Fig. S1 (a) FeOOH nanorod slurries; (b) A digital photograph showing the appearance of CP@FeP electrodes.

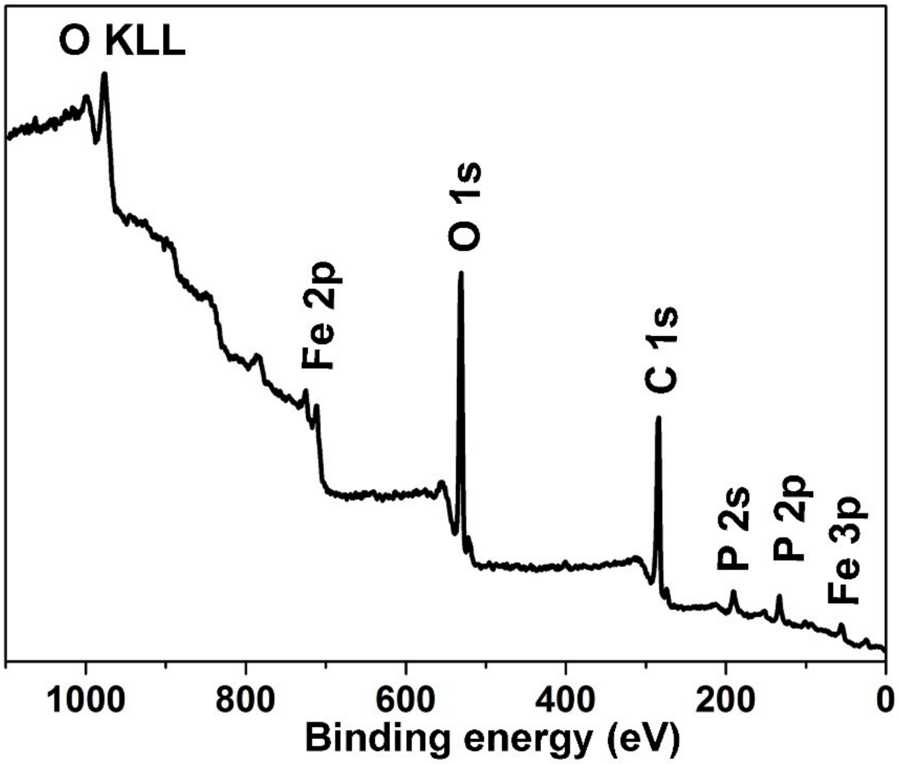

Fig. S2 XPS survey spectrum of the freshly prepared CP@FeP.

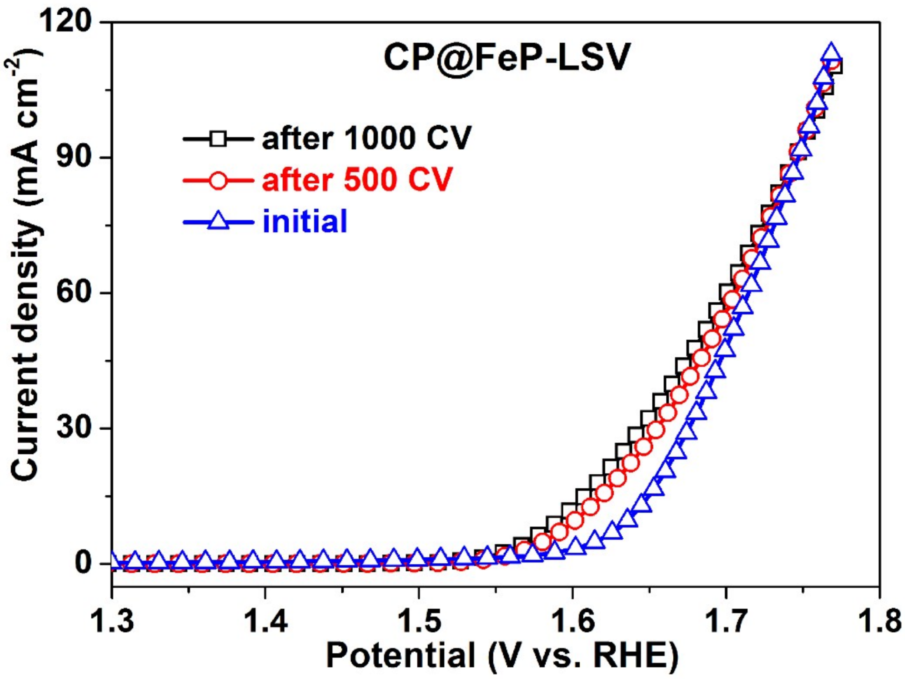

Fig. S3 *iR*-corrected polarization curves of the CP@FeP electrode after different CV scans between 1.0 and 1.6 V vs. RHE at a scan rate of 50 mV s^{-1}. The LSV curves measured after 500 and 1000 cycles virtually overlap, indicating that a steady state has been reached.

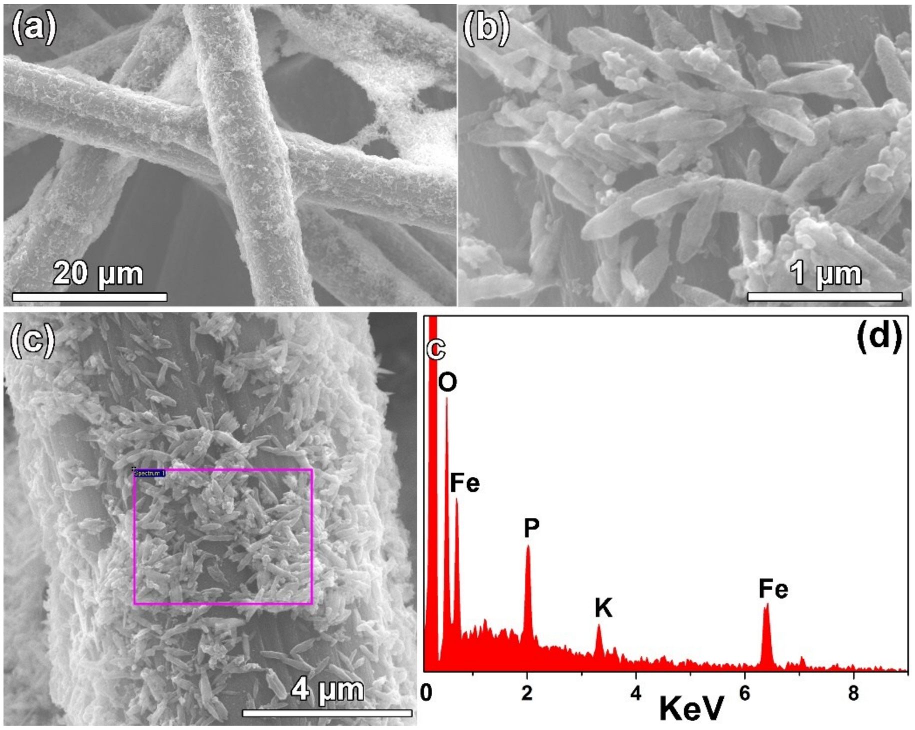

Fig. S4 (a, b, c) SEM images and (d) EDX spectrum of the CP@FeP after 1000 CV scans between 1.0 and 1.6 V vs. RHE at 50 mV s^{-1} in 1 M KOH solution.

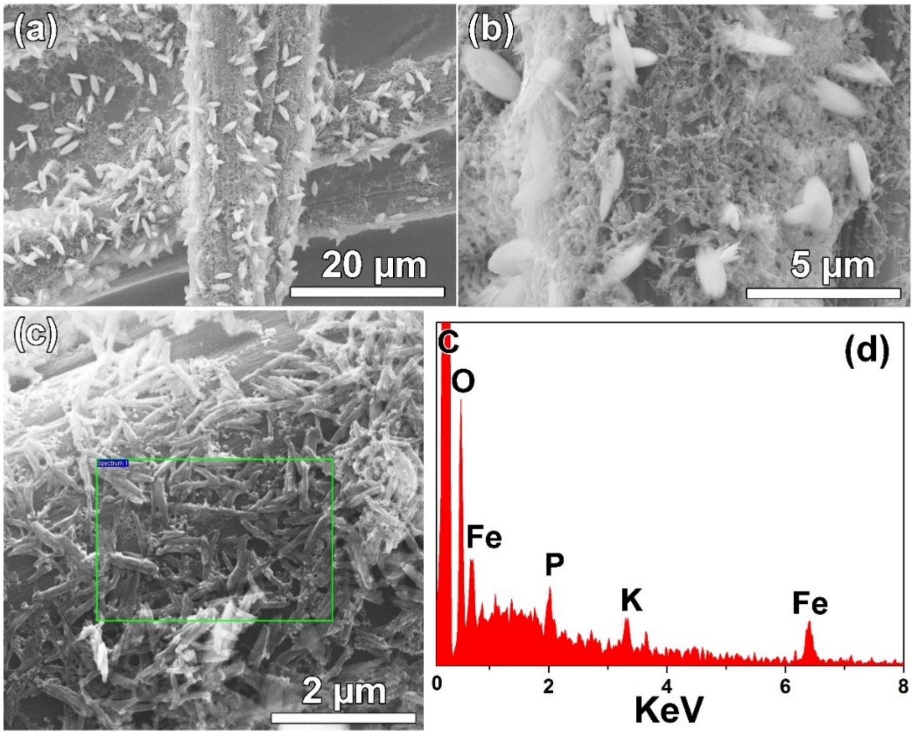

Fig. S5 (a, b, c) SEM images and (d) EDX spectrum of the CP@FeP after the extended durability test at 15 mA cm^{-2} for 48 h in 1 M NaOH solution.

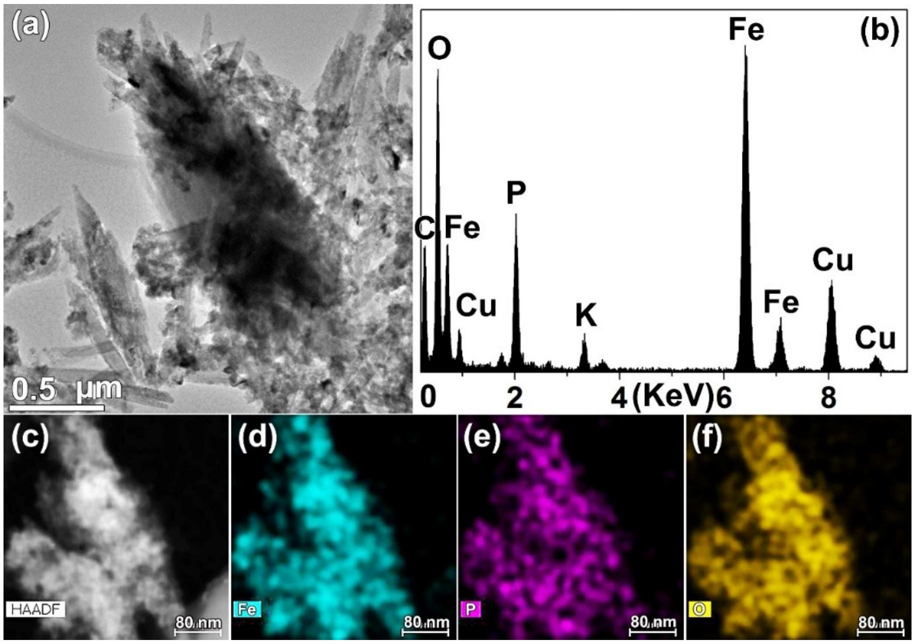

Fig. S6 (a) Bright-field TEM image of FeP NRs after the extended durability test at 15 mA cm^{-2} for 48 h in 1 M NaOH solution. (b) EDX spectrum. (c) HAADF-STEM image. Elemental maps of (d) Fe, (e) P and (f) O.

Supplementary Tables

Table S1. Comparison of the OER activity of the CP@FeP to that of other transition metal based OER catalysts reported in the literature.

Catalysts	Electrolyte	Loading mass (mg cm^{-2})	Onset potential (mV@1 mA cm^{-2})	Tafel slope (mV dec^{-1})	J_{geo} (current density in mA cm^{-2} @overpotential in mV)	Reference
FeP NRs on CP	1.0 M KOH	0.7	290	63.6	10@η=350	This work
FeP nanotubes	1.0 M KOH	1.6	250	43	10@η=288	Chem. Eur. J., 2015, 21(50): 18062-18067.
Co-P film	1.0 M KOH	-	>270	47	10@η=345	Angew. Chem. Int. Ed., 2015, 54(21): 6251-6254.
Ni-P film	1.0 M KOH	-	> 270	49	10@η=344	ChemCatChem 2016, 8, 106-112.
Ni_2P nanowires	1.0 M KOH	0.1	310	60	10@η=400	Chem. Commun., 2015, 51(58): 11626-11629.
Graphene/FeOOH nanoparticles	0.1 M KOH	0.25	430	60	10@η=482	J. Mater. Chem. A, 2016, 4, 3210-3216.
amorphous FeOOH films	1.0 M Na_2CO_3	-	300	-	1@η>420	J. Am. Chem. Soc. 2014, 136, 2843-2850.
Ni:FeOOH films	0.1 M NaOH	-	-	-	1@η>340 10@η>420	J. Mater. Chem. A, 2014, 2, 14957-14962.
FeO_x films	5.0 M NaOH	-	345	40	1@η=445	J. Electrochem. Soc. 2013 160(2): H142-H154.
$NiFeO_x$ film	1.0 M NaOH	-	-	-	10@η>350	J. Am. Chem. Soc. 2013, 135(45): 16977-16987.
Fe-Ni oxides	1.0 M KOH	1	-	51	10@η>375	Acs Catalysis, 2012, 2(8): 1793-1801.

Table S2. Fitting parameters for the Nyquist plots of CP@FeOOH and CP@FeP electrodes.

Samples	R_s(Ω)	R_1(Ω)	CPE1 (μF cm^{-2} S^{m-1})	R_{ct} (Ω)	CPE2 (μF cm^{-2} S^{m-1})
CP@FeOOH	2.74	0.24	1961.0	215.0	621.7
CP@FeP	3.08	2.22	373.7	87.9	1467.0

References

S1. Fu Z, Jiang T, Liu Z, et al. Highly photoactive Ti-doped α-Fe_2O_3 nanorod arrays photoanode prepared by a hydrothermal method for photoelectrochemical water splitting[J]. Electrochimica Acta, 2014, 129: 358-363.