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Supplementary Information

Potential-driven surface active structure rearrangement over FeP@NC towards efficient electrocatalytic hydrogen evolution

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S1. Calibration of potential vs Ag/AgCl to RHE.[1]

the relation between Ag/AgCl and RHE potential can be calibrated in the high purity H_2 saturated 0.5 M H_2SO_4 electrolyte with a Pt wire as the working electrode. With a scan rate of 1 mV/s, the average potential, where the current density started to came across X axis (becoming zero) in CV curves, was regarded as the thermodynamic potential for the hydrogen electrode reactions (Figure S2).

S2. Calculation of j_{ECSA} and TOF (Figure S9).[2,3]

$$ECSA = \frac{C_{dl}}{C_s} \quad (1);$$

$$j_{ECSA} = \frac{j \times S}{ECSA} \quad (2);$$

$$TOF = \frac{j \times S}{2nF} \quad (3).$$

ECSA is short for electrochemical active surface area;

C_{dl} and C_s is double layer capacitance and specific capacitance of samples, and C_s is assumed to 35 μC/cm^2 according to previous report[3].

j, S, F and n is the current density under given overpotential, the surface area of the electrode, Faraday constant and the mole number of active metal atoms for the electrode.

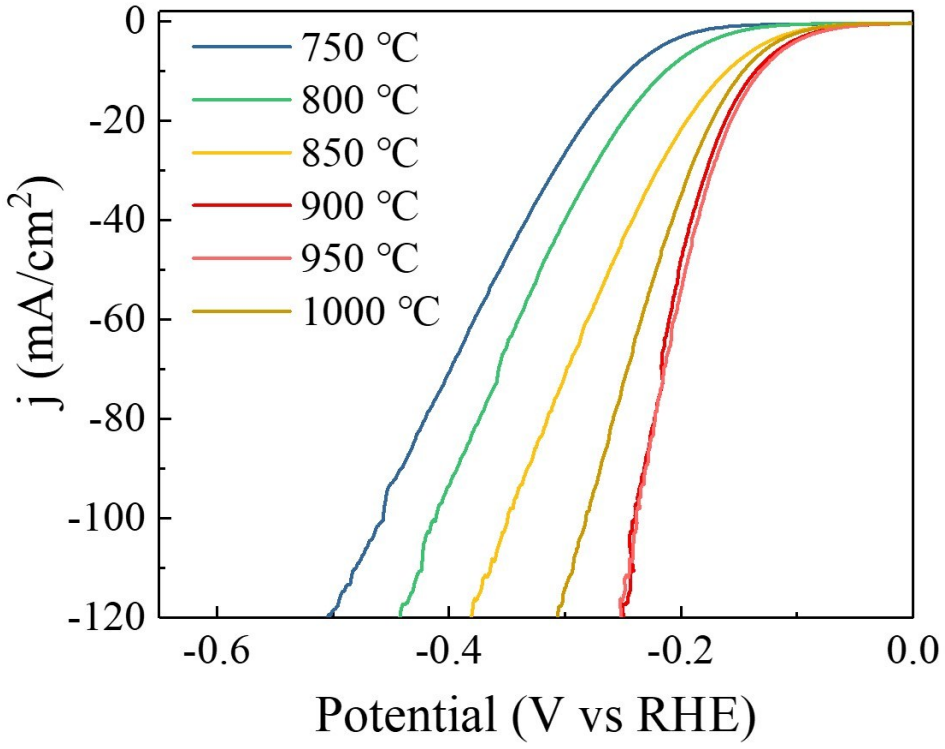

Figure S1. LSV curves in 0.5 M H_2SO_4 for FeP@NC synthesized under different temperatures.

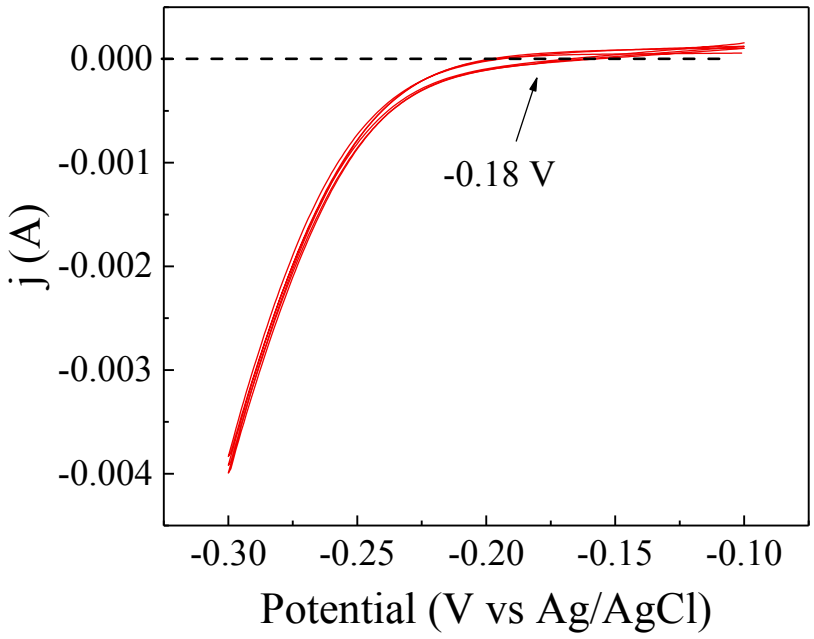

Figure S2. CV curve of Pt wire in 0.5 M H_2SO_4 electrolyte.

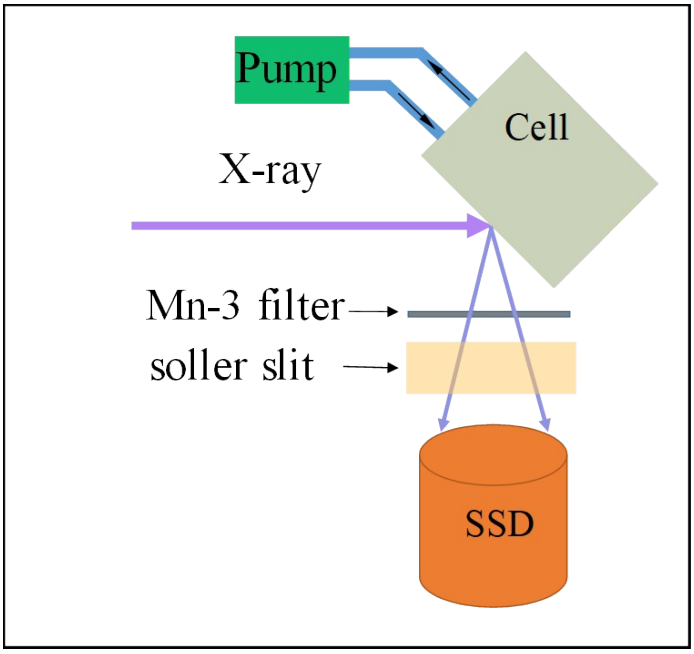

Figure S3. Details of the device in in-situ XAS measurement.

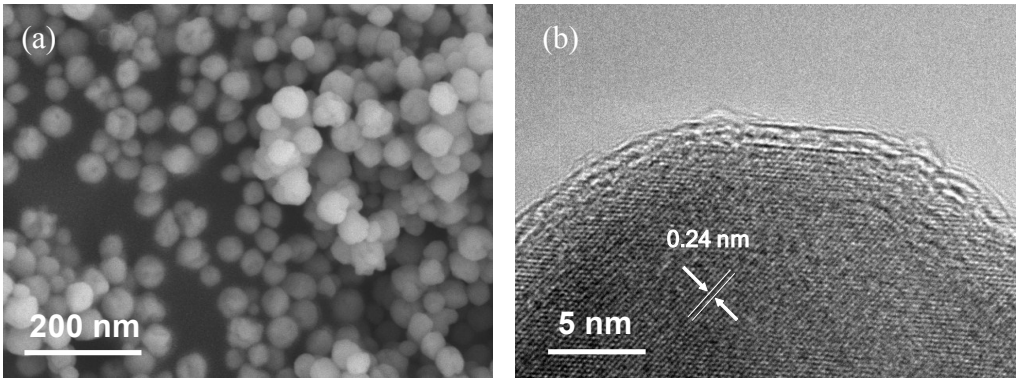

Figure S4. SEM and HRTEM images of FeP particles.

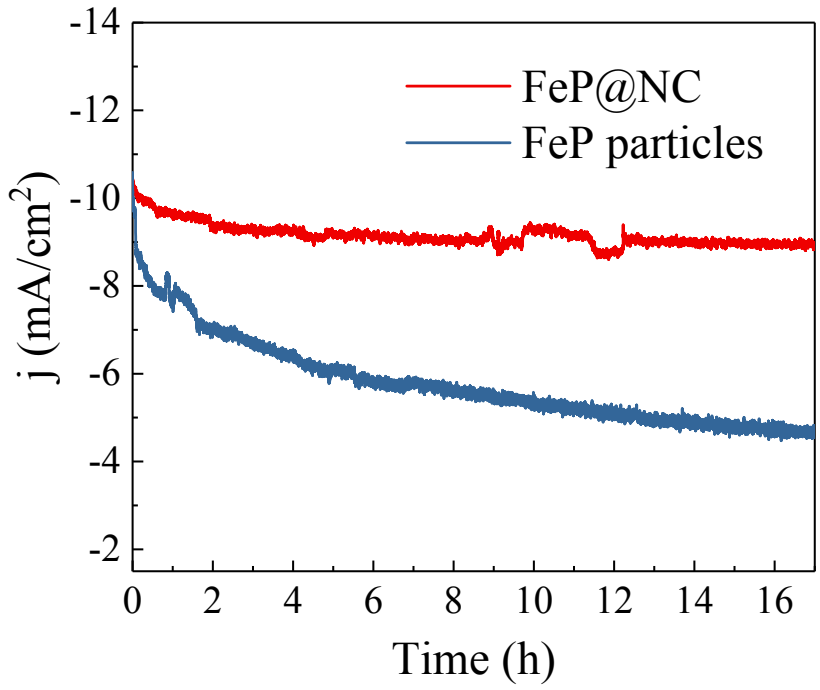

Figure S5. Chronopotentiometric measurements with an initial current density of 10 mA/cm^2 for FeP@NC at -0.135 V_{RHE} and for FeP particles at -0.495 V_{RHE}.

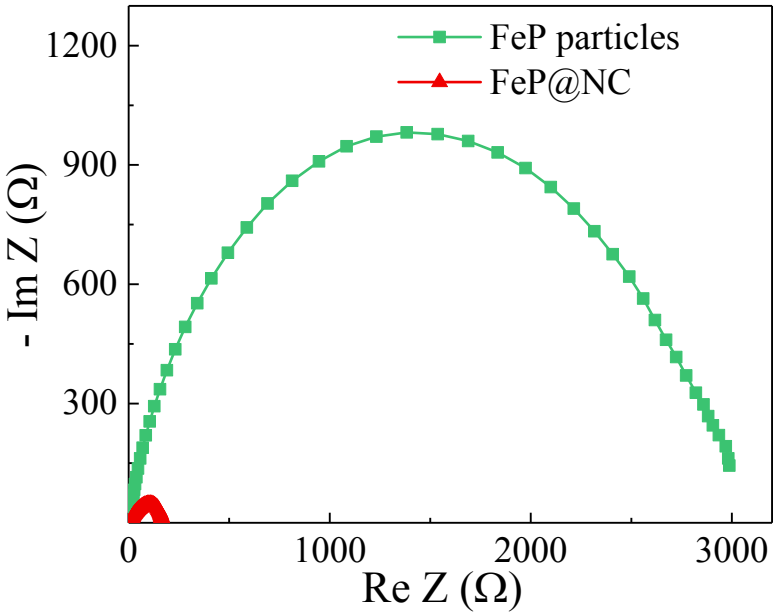

Figure S6. Nyquist plots of FeP particles and FeP@NC at -0.15 V_{RHE} in a large scale.

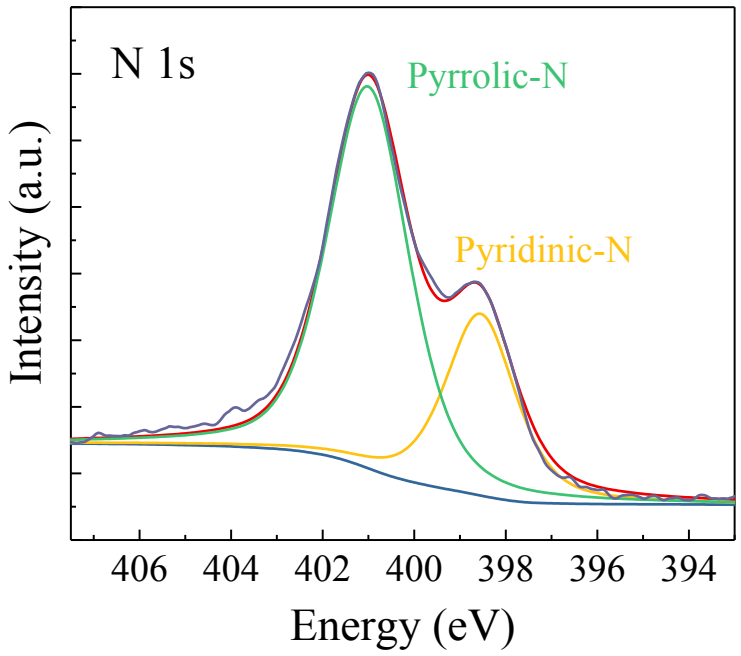

Figure S7. Deconvolution of N 1s XPS spectra for FeP@NC.

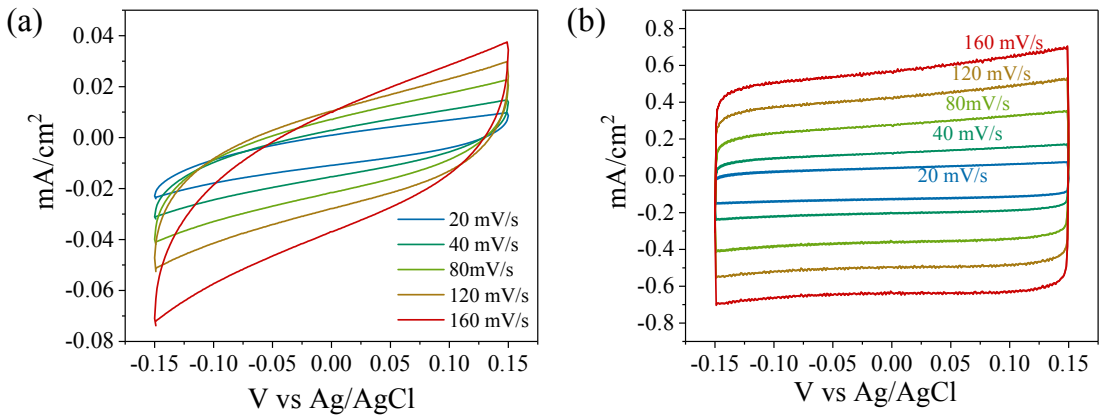

Figure S8. Cyclic voltammetry curves of (a) FeP particles and (b) FeP@NC.

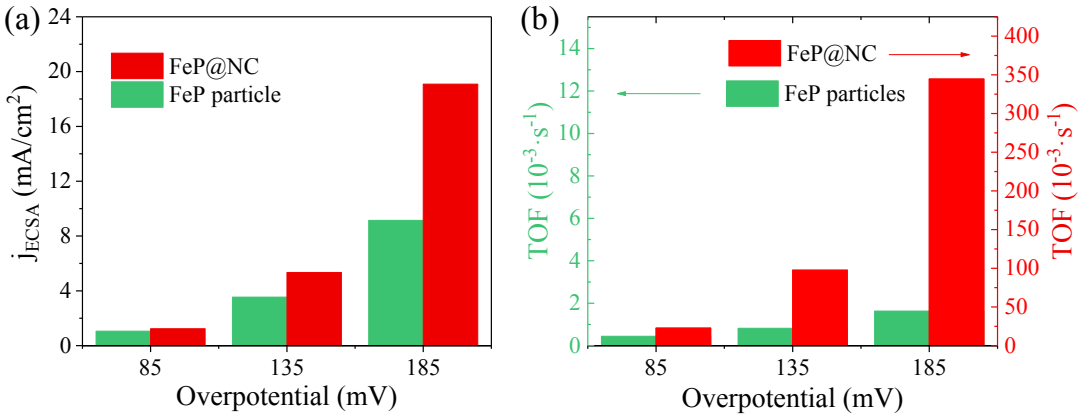

Figure S9. (a) J_{ECSA}, and (b) TOF comparison of FeP@NC and FeP particles under different overpotentials in 0.5 M H_2SO_4.

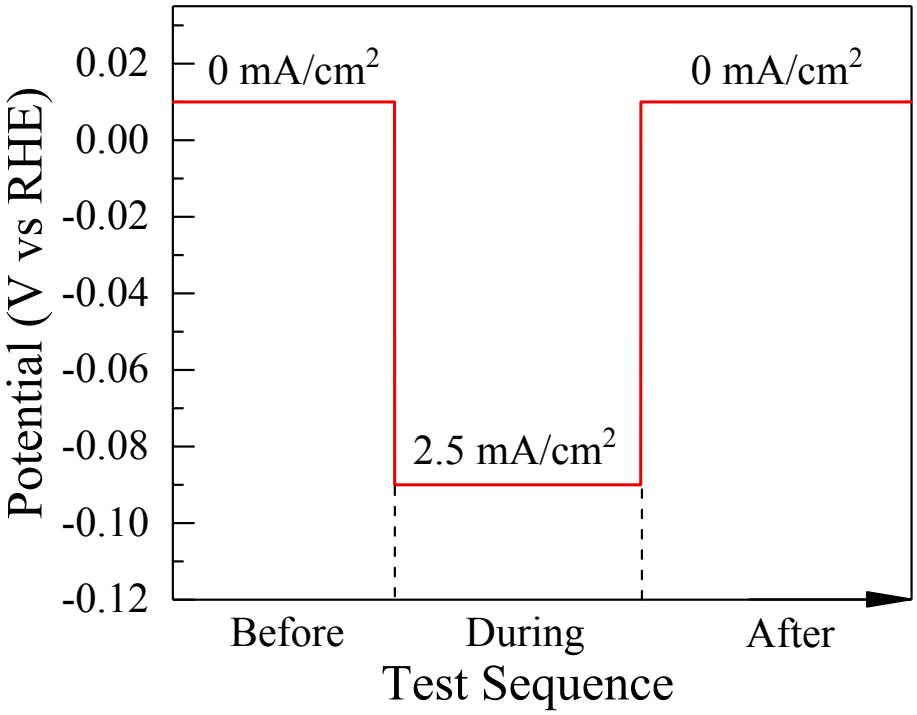

Figure S10. Working condition of work electrode during in-situ XAS measurement.

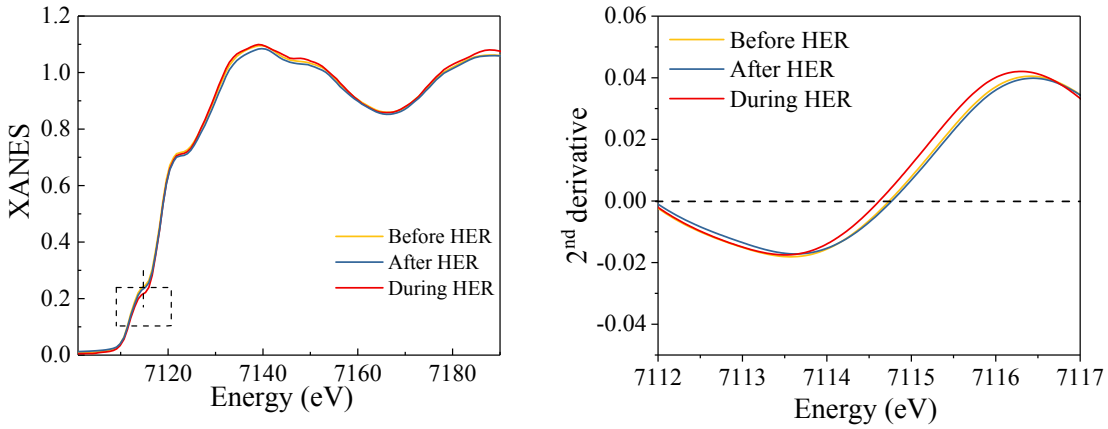

Figure S11. (a) XANES and (b) 2nd derivative curves of pre-edge region.

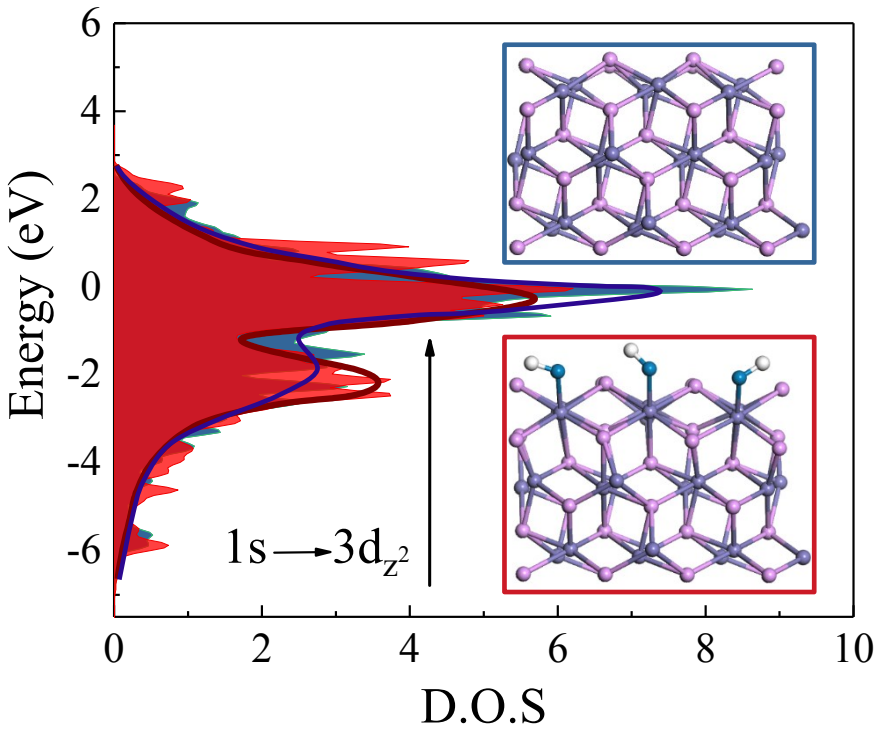

Figure S12. DOS calculation of 3dz^2 orbits in different surface structure.

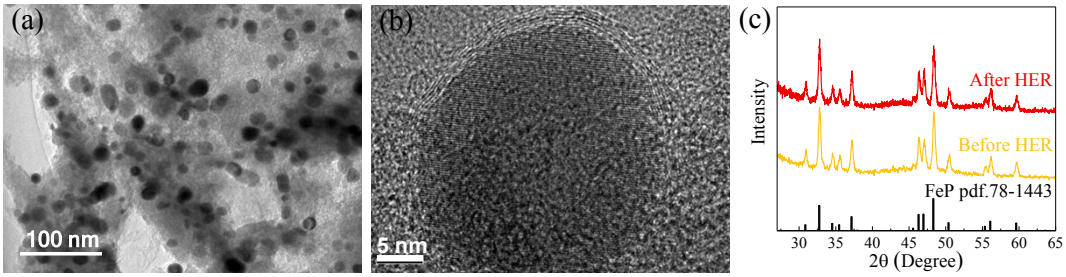

Figure S13. (a) TEM, (b) HRTEM images and XRD patterns of FeP@NC after long-time HER measurement.

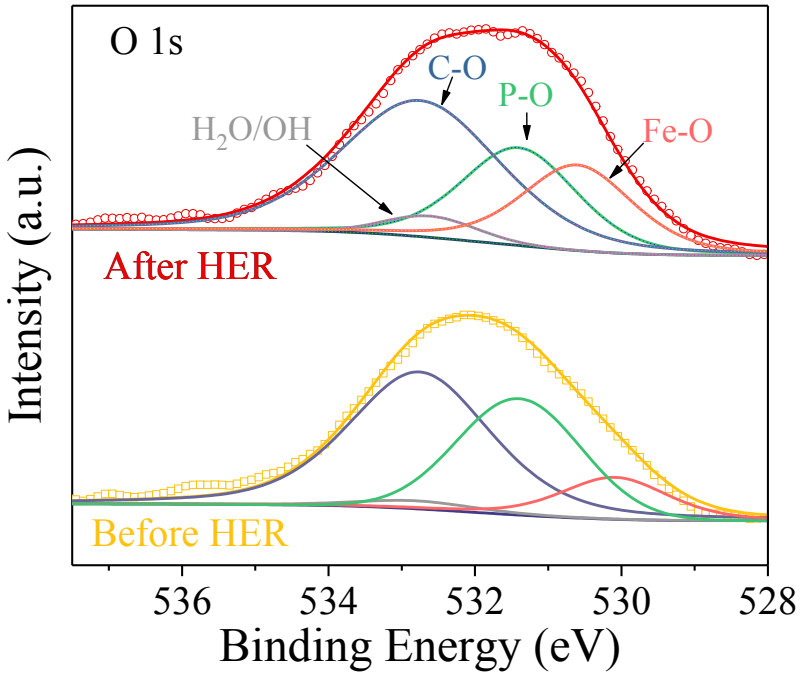

Figure S14. XPS comparison of O 1s for FeP@NC.

Table S1. The EXAFS fitted results for structure parameters around Fe atoms.

	Paths	N	σ^2 (10^{-3})	ΔE(eV)	ΔR(Å)
Before HER	Fe-P	5.6	6.4	-1.84	0.024
	Fe-O	<0.05			
During HER	Fe-P	5.8	5.3	-1.55	0.039
	Fe-O	0.85	5.5	-2.12	-0.04
After HER	Fe-P	5.6	6.3	-1.84	0.024
	Fe-O	0.23	5.0	-3.25	-0.04

Table S2. The ratio of different bonds according to Figure S14.

	Fe-O	**P-O**	**C-O**	**H_2O/OH**
Before HER	12.0 %	32.9 %	52.7 %	2.4 %
After HER	22.1 %	24.9 %	49.7 %	3.3 %

Table S3. Summary of HER performance for recent typical TMP electrocatalysts in 0.5 M H2SO4 electrolyte.
(Stability is defined as the time when current density decays to its' 90 %)

	η@10 mA/cm^2 (mV)	Tafel slope (mV/dec)	Stability	Ref.
FeP@NC	135	78	>15 h	This work
FeP	240	67	-	Chem. Commun., 2013, 49, 6656.
FeP/NCNSs	114	64	-	ACS Sustain. Chem. Eng., 2018, 6, 11587-11594.
FeP nanowires	96	39	< 1 h	Chem. Commun., 2016, 52, 2819–2822.
CoP nanorod bundle arrays/Ti	203	40	~10 h	Electrochem. Commun., 2015, 56, 56–60.
CoP@BCN-1	87	46	< 10 h	Adv. Energy Mater., 2017, 7, 1601671.
Ni-P@Carbon fiber paper	98	58.8	-	Adv. Funct. Mater., 2016, 26, 4067–4077.
Ni_3P porous hollow	85	50	> 11 h	J. Mater. Chem. A, 2016, 4, 10925–10932.
Ni_2P nanoparticles	172	62	< 6 h	RSC Adv., 2015, 10290–10295.
MoP2 nanoparticles/Mo	143	57	-	Nanoscale, 2016, 8, 8500–8504 .
MoP nanosheet array	124	58	< 10 h	Appl. Catal. B: Environ., 2016, 196, 193–198

References

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2. Liu B. et al, *Adv. Mater.*, 2018, **30**, 1803144.

3. McCrory C. C. L., *J. Am. Chem. Soc.*, 2013, **135**, 16977−16987.