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Supplementary information for

Synthesis of Two-Dimensional Hematite and Iron Phosphide for Hydrogen Evolution

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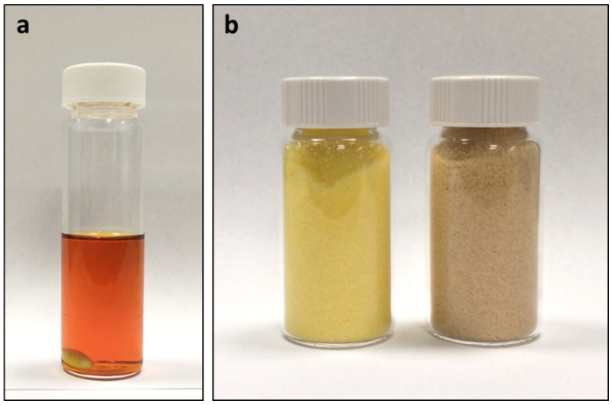

Fig. S1 (a) Iron precursor, and (b) precursor and template mixture (left-immediately after preparation, right – after aging).

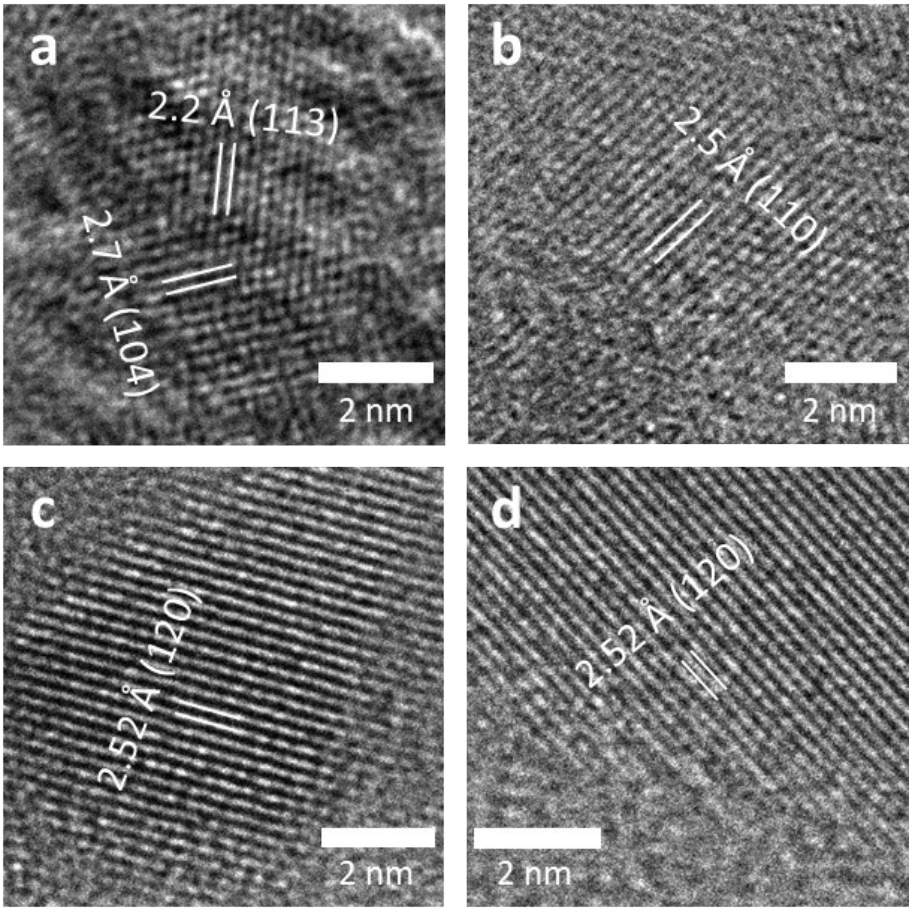

Fig. S2 Additional HR-TEM image of (a) α-Fe_2O_3 nanosheet, (b) α-Fe_2O_3 nanonet, (c) FeP nanosheet, and (d) FeP nanonet.

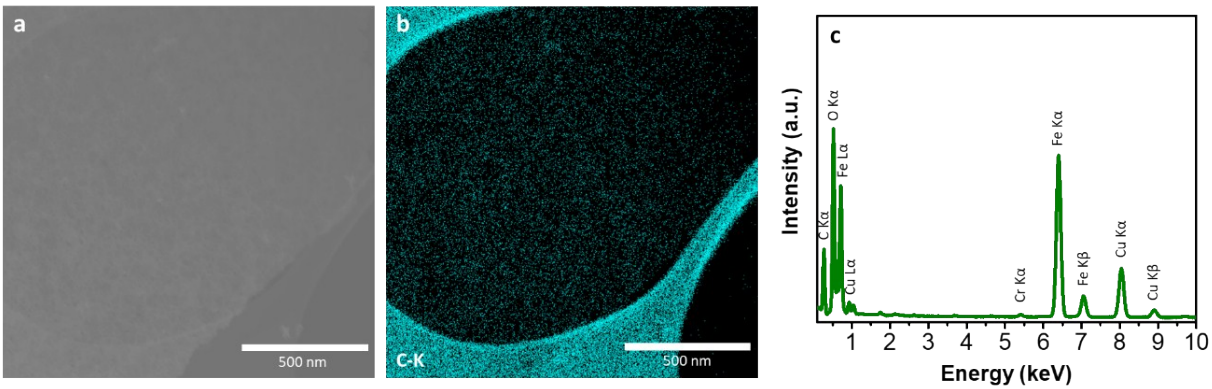

Fig. S3 α-Fe_2O_3 nanosheet (a) STEM image, (b) elemental map of carbon, and (c) STEM EDS spectrum.

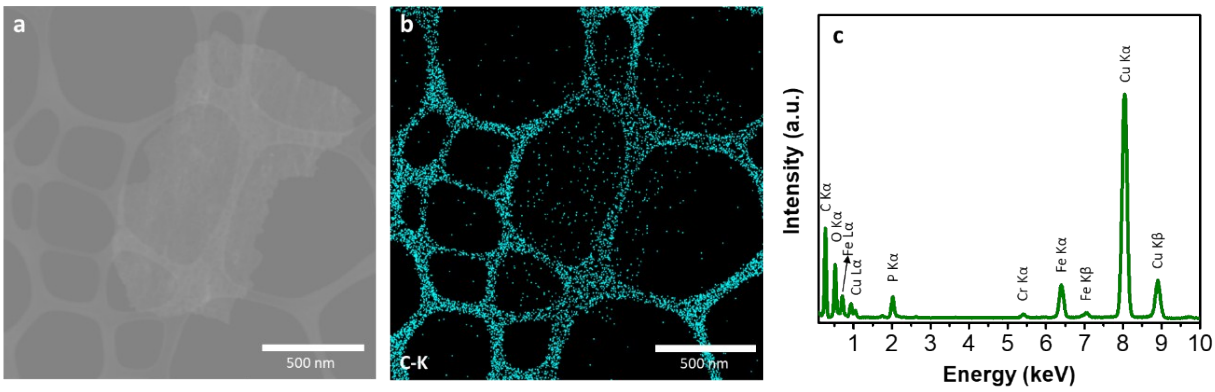

Fig. S4 FeP nanosheet (a) STEM image, (b) elemental map of carbon, and (c) STEM EDS spectrum.

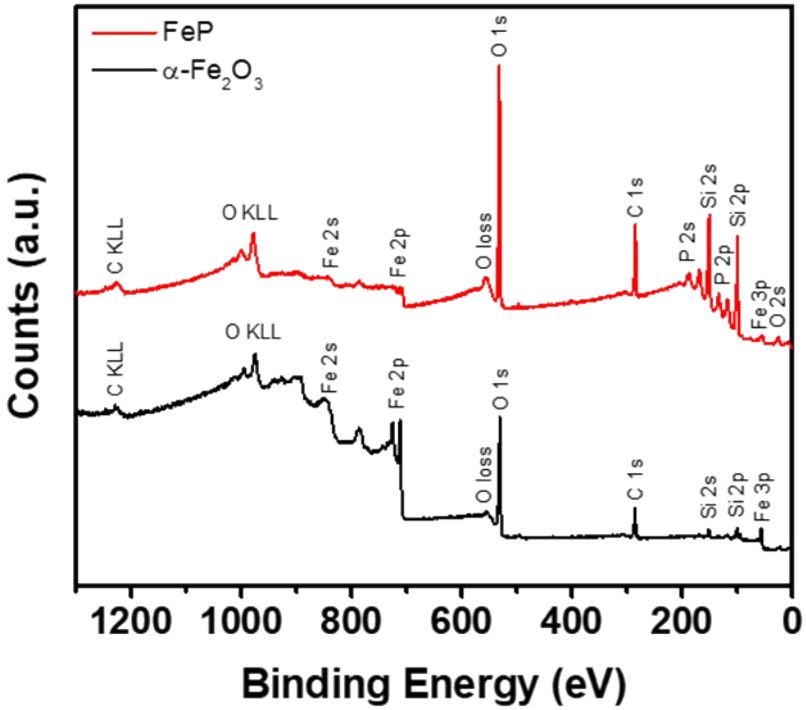

Fig. S5 XPS survey spectrum of FeP and α-Fe_2O_3 performed on Si substrate demonstrates the absence of Na and Cl from the growth template.

Fig. S6 The optical image shows the liquid suspensions of α-Fe_2O_3 (left), and FeP (right).

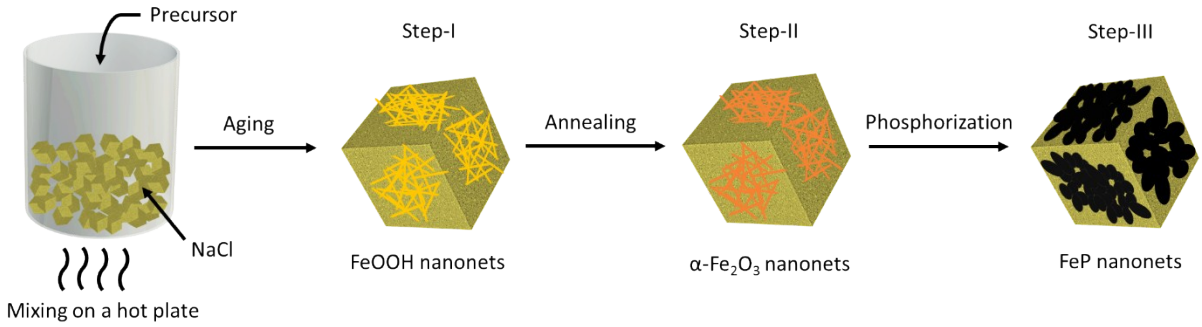

Fig. S7 Schematic of the fabrication procedure of FeOOH, α-Fe_2O_3, and FeP nanonets.

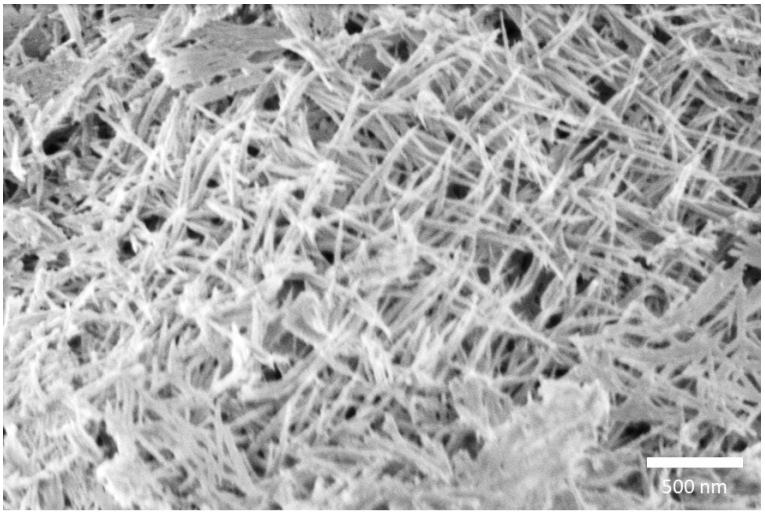

Fig. S8 SEM image of the FeOOH nanonets.

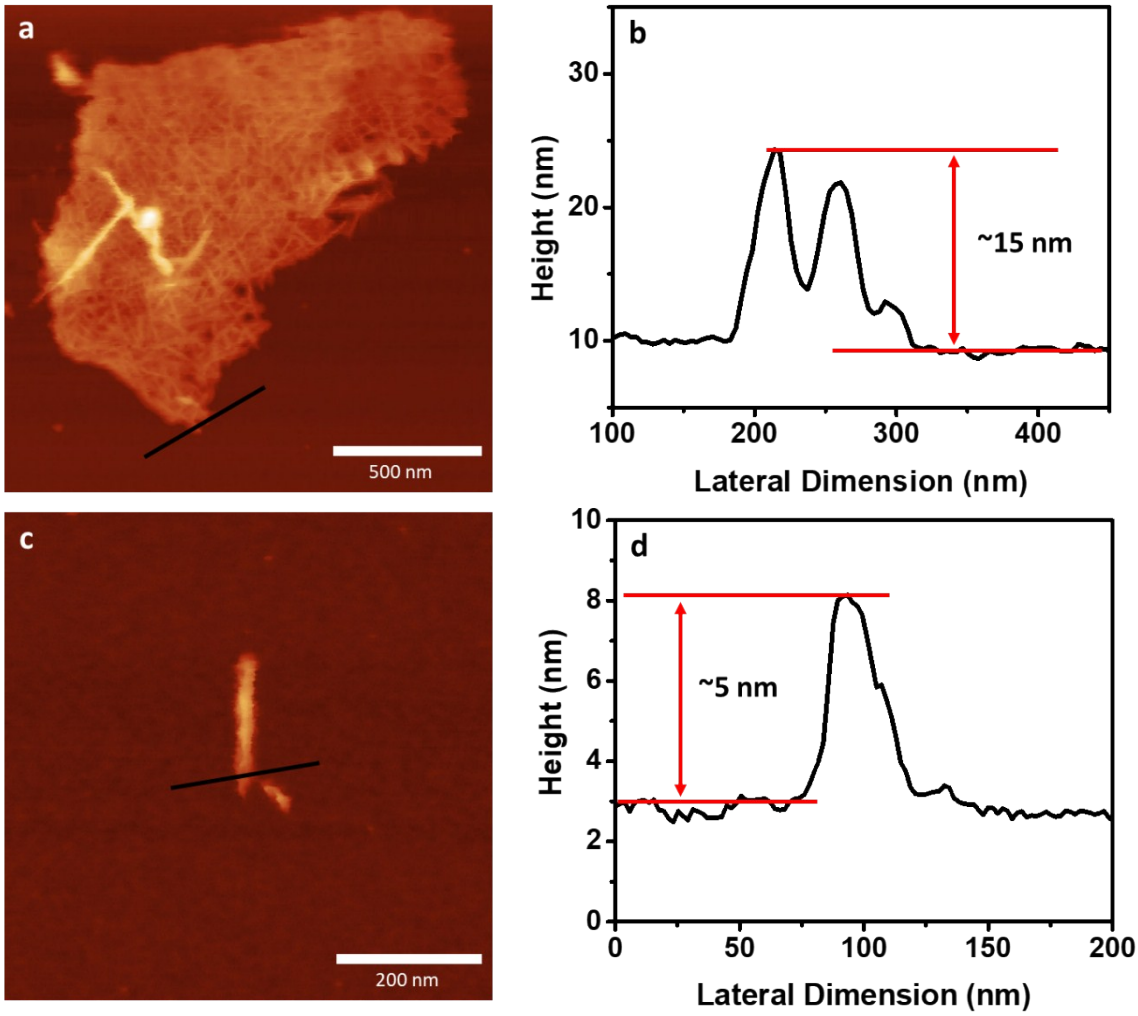

Fig. S9 AFM image of (a) one FeOOH nanonet with (b) thickness profile of the woven edge of nanonet which shows ~15 nm thickness, in addition to nanonet, (c) individual building block nanorod with corresponding (d) thickness profile shows the typical thickness of ~5 nm.

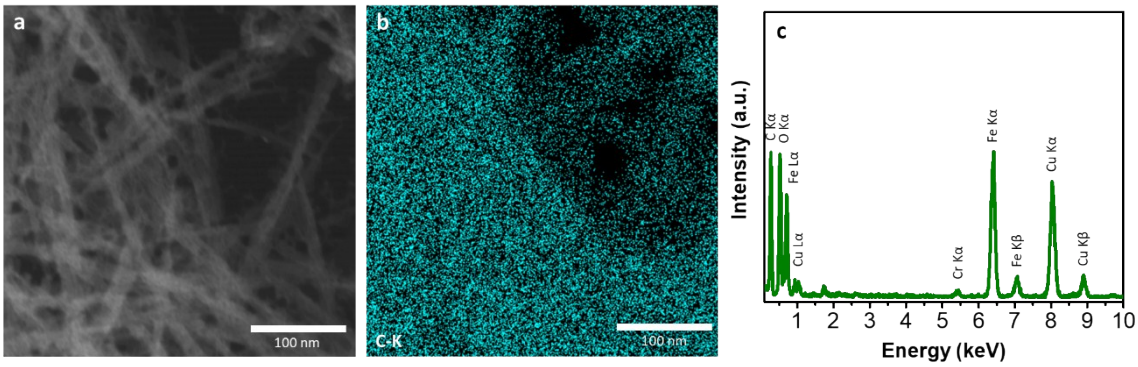

Fig. S10 α-Fe_2O_3 nanonet (a) STEM image, (b) elemental map of carbon, and (c) STEM EDS spectrum.

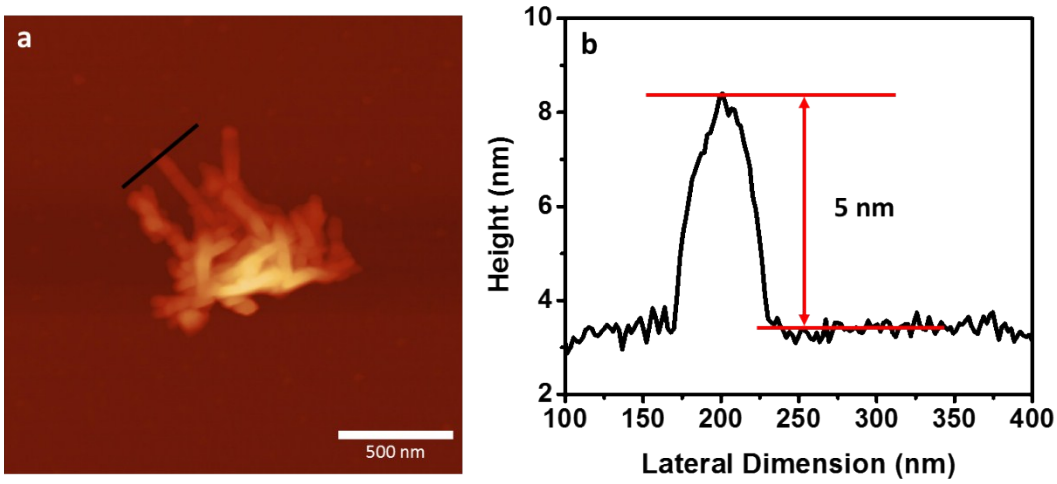

Fig. S11 (a) AFM images of α-Fe_2O_3 nanonet with corresponding (b) thickness profile.

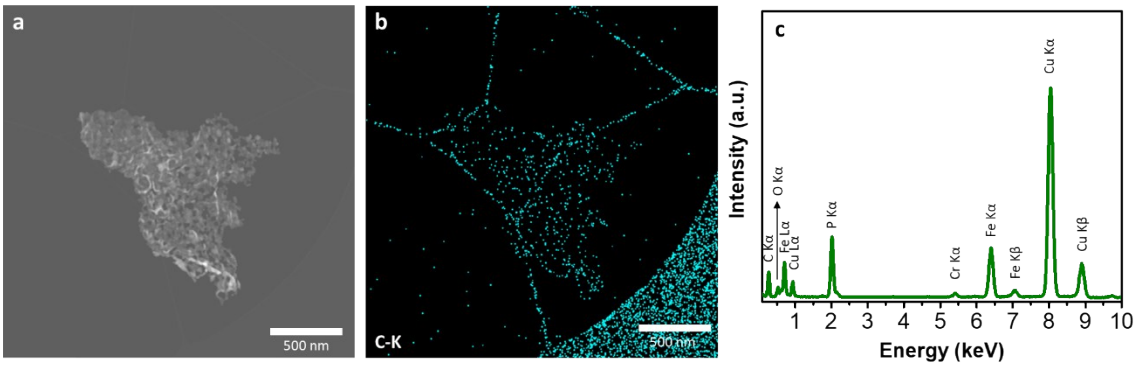

Fig. S12 FeP nanonet (a) STEM image, (b) elemental map of carbon, and (c) STEM EDS spectrum.

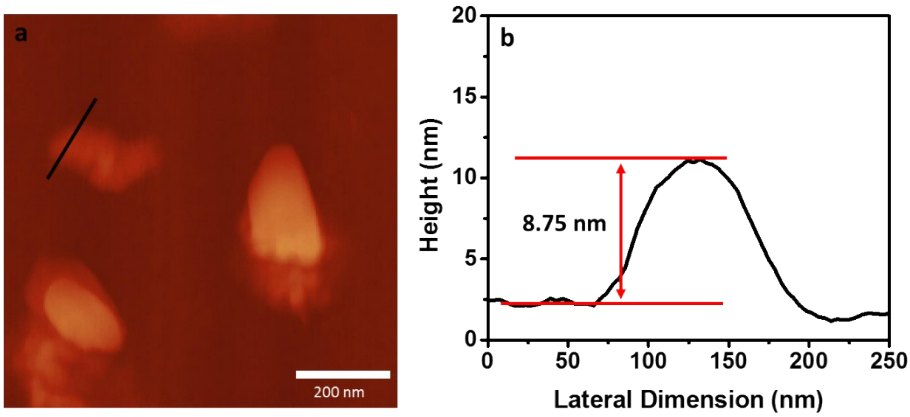

Fig. S13 (a) AFM image of a FeP nanonet with corresponding (b) thickness profile.

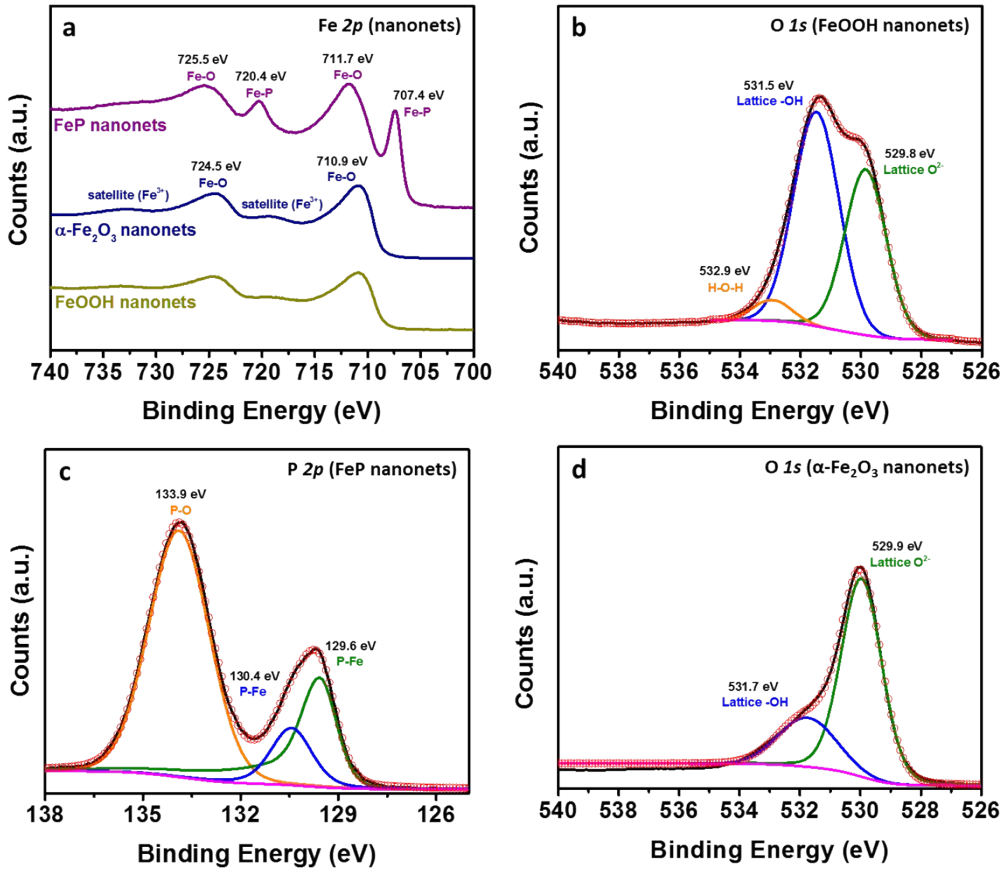

Fig. S14 XPS spectrum of nanonets (a) Fe 2p, (b) O 1s of FeOOH, (c) P 2p of FeP, and (d) O 1s of α-Fe_2O_3.

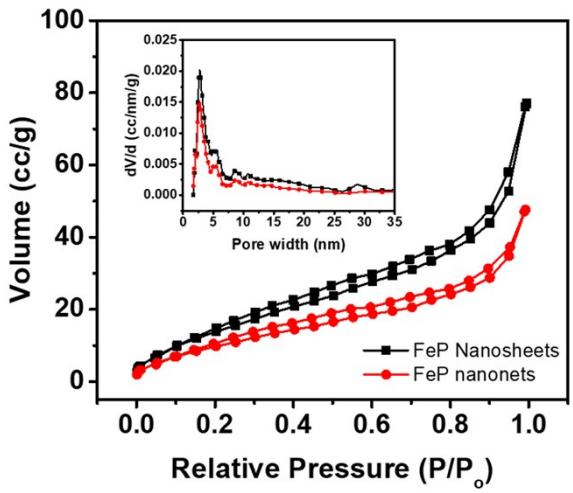

Fig. S15 Nitrogen sorption isotherms and pore size distribution curves (inset) of FeP nanosheets and nanonets.

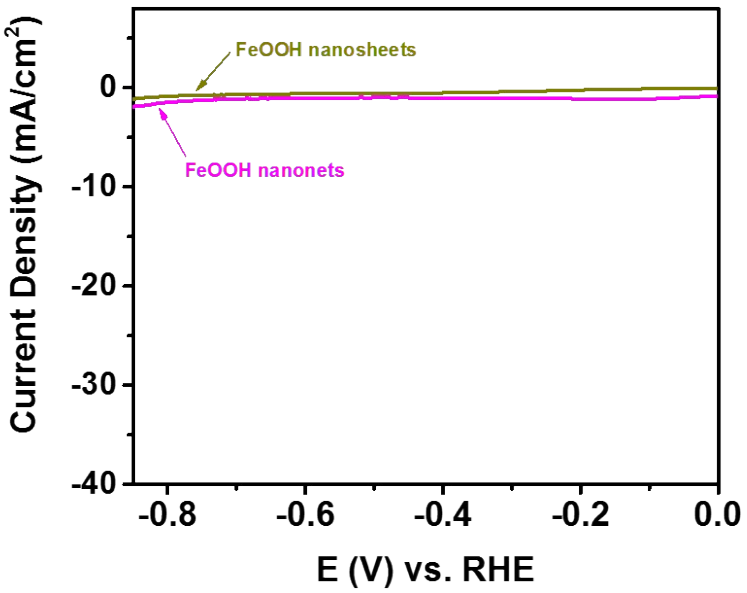

Fig. S16 Polarization curves of FeOOH nanosheets and nanonets.

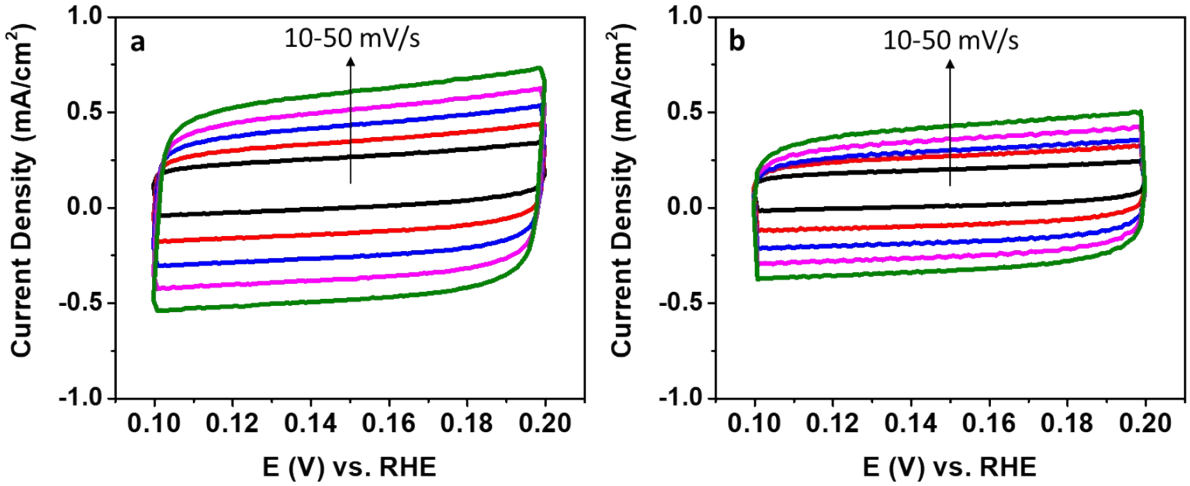

Fig. S17 Cyclic voltammetry (CV) curves in 0.5 M H_2SO_4 for (a) FeP nanosheets, and (b) FeP nanonets in the region of 0.10 - 0.20 V vs. RHE at various scan rates.

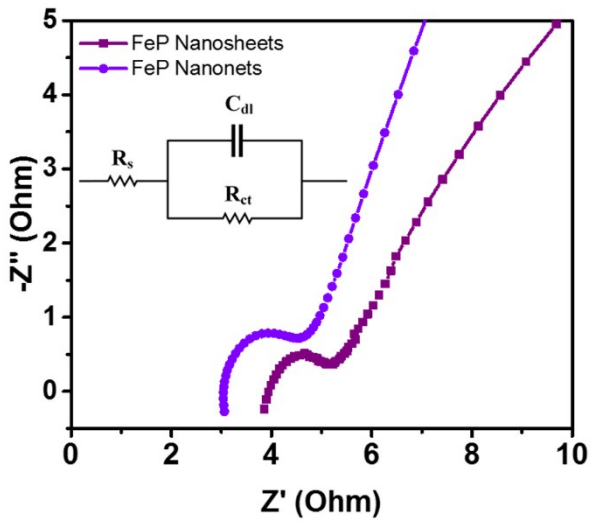

Fig. S18 EIS Nyquist plot, showing charge transfer resistance of FeP nanosheets and nanonets.

Table S1 Impedance components derived by fitting the experimental EIS data shown in Fig. S18 using an equivalent Reddles circuit. The equivalent Reddles circuit comprising of electrolyte resistance (R_s), charge transfer resistance (R_{ct}), and constant phase element (CPE) best fit the semicircle. The CPE element accounts for the capacitance dispersion effect.

Samples	R_s (Ω)	R_{ct} (Ω)	CPE (μF)
FeP nanosheets	~4	1.2	52.3
FeP nanonets	~3	1.6	47.5

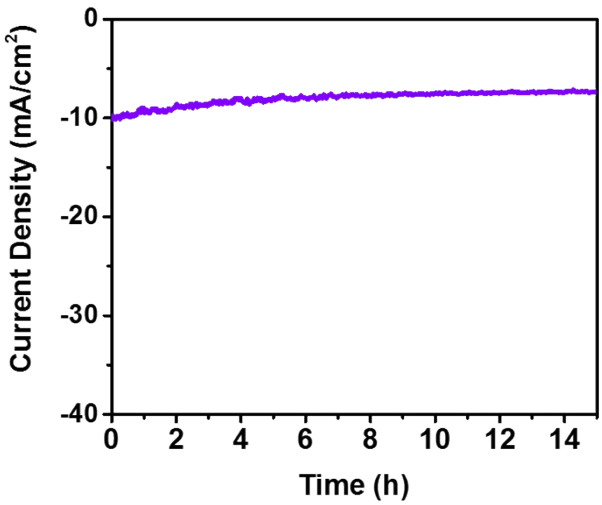

Fig. S19 Time-dependent HER current density of FeP nanonets.

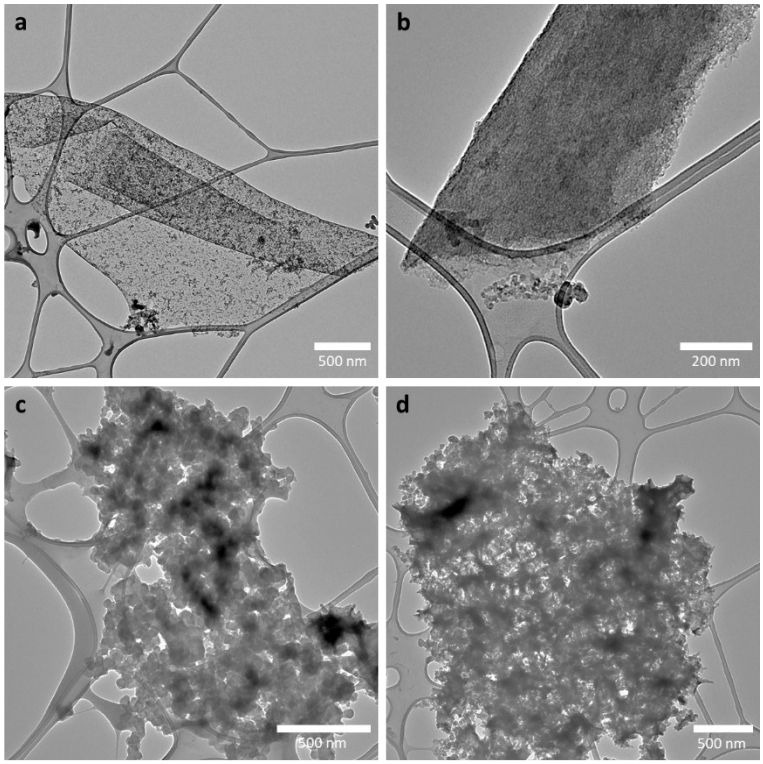

Fig. S20 TEM images of FeP (a, b) nanosheet, and (c, d) nanonet after 15 h stability test in 0.5 M H_2SO_4.

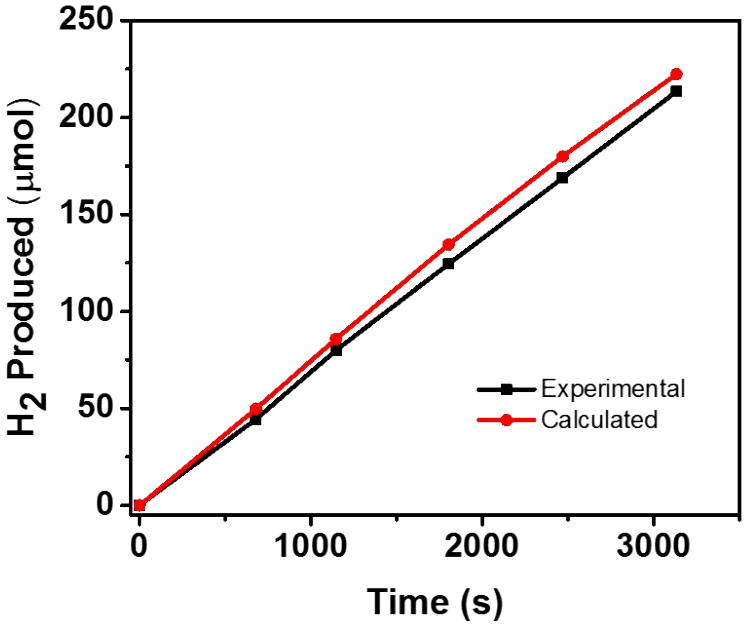

Fig. S21 The calculated and experimentally measured amount of H_2 during hydrogen evolution process using FeP nanosheets.

Table S2 Comparison of the HER activity of free-standing binary transition-metal phosphide based catalysts in acidic media (0.5 M H_2SO_4).

Catalysts	Working electrode	Overpotential (mV@η_{10})	Tafel slope (mV dec^{-1})	Reference
Ultrathin FeP nanosheets	Carbon Paper	117	56	This work
Nanoporous FeP nanosheets	GCE	250	67	1
FeP nanowires	GCE	193	66	2
CoP nanotubes	GCE	129	60	3
Defect-rich MoP	GCE	156	49	4
WP_2 submicroparticles	GCE	161	57	5

1 Y. Xu, R. Wu, J. Zhang, Y. Shi, B. Zhang, *ChemComm,* 2013, **49**, 6656-6658.
2 C. Y. Son, I. H. Kwak, Y. R. Lim, J. Park, *ChemComm,* 2016, **52**, 2819-2822.
3 H. Du, Q. Liu, N. Cheng, A. M. Asiri, X. Sun, C. M. Li, *J. Mater. Chem. A,* 2014, **2**, 14812-14816.
4 X. Zhang, Z. Wu, D. Wang, *Electrochim. Acta*, 2018, **281**, 540-548.
5 Z. Xing, Q. Liu, A. M. Asiri, X. Sun, *ACS Catal.*, 2015, **5**, 145-149.