

Electronic Supplementary Information

Controlled Synthesis of FeP Nanorod Arrays as Highly Efficient Hydrogen Evolution Cathode

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Experimental section

Materials

Sodium hypophosphite (NaH_2PO_2) was purchased from Aladdin Ltd. (Shanghai, China). Ti foil, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Na_2SO_4 , ethanol and hydrochloric acid were obtained from Beijing Chemical Corporation. All chemical reagents were used without further purification. Pt/C (20 wt% Pt on Vulcan XC-72) and Nafion (5 wt%) were purchased

from Sigma-Aldrich. The water used throughout all experiments was purified through a Millipore system.

Preparation of HCl-treated Ti foil, α -FeO(OH) NAs/Ti and FeP NAs/Ti

For the fabrication of HCl-treated Ti foil, the Ti foil was degreased with ethanol, rinsed with deionized. Then pre-treated Ti foil was immersed into 250 mL of 37 wt% HCl at 60 °C for about 10 min. The obtained HCl-treated Ti foil was washed with deionized water and dried for further use. To synthesize α -FeO(OH) NAs/Ti, 0.40 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.24 g Na_2SO_4 were dissolved in 35 ml of deionized water, respectively. After thorough magnetic stirring for 10 min, the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave. Afterwards, the as-prepared 2 cm \times 4 cm HCl-treated Ti foil was placed against the wall and hydrothermally treated at 120 °C for 6 h.¹⁶ To prepare the FeP NAs/Ti, the α -FeO(OH) NAs/Ti was annealed at 300 °C for 2 h in a crucible with a moderate amount of NaH_2PO_2 in Ar flow. The load weight of the FeP NAs was about 0.6 mg cm⁻².

Characterizations

XRD data were recorded on a RigakuD/MAX 2550 diffractometer. SEM measurements were made on a XL30 ESEM FEG microscope. TEM measurements were made on a HITACHI H-8100 microscopy (Tokyo, Japan). XPS data were collected on an ESCALAB MK II X-ray photoelectron spectrometer using Mg as the exciting source.

Determination of Faradaic efficiency (FE)

The generated gas was confirmed by gas chromatography (GC) analysis and measured quantitatively using a calibrated pressure sensor to monitor the pressure change in the cathode compartment of a H-type electrolytic cell. The FE was calculated by comparing the amount of measured hydrogen generated by potentiostatic cathodic electrolysis with calculated hydrogen (assuming 100% FE). The rough agreement of both values suggests nearly 100% FE for hydrogen evolution. GC analysis was carried out on GC-2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

Active sites calculation

The absolute components of voltammetric charges (cathodic and anodic) can be obtained from the CV of Fig. S5A. Assuming one electron redox process, this absolute charge was divided by two. When the number of voltammetric charges (Q) is obtained after deduction of the blank value, n (mol) can be calculated with the following equation:

$$n = Q / 2F$$

Turnover frequency (TOF) calculation^{S1}

The TOF (s⁻¹) is calculated with the following equation:

$$\text{TOF} = I / (2Fn)$$

I : Current (in A) during the LSV measurement.

F : Faraday constant (C mol⁻¹)

n : Number of active sites (mol).

Turnover number (TON) calculation^{S2}

$$\text{TON} = Q \times \text{FE} / (F \times n_{\text{ele}} \times n_{\text{cat}}) \text{ mol H}_2 \text{ per mol catalyst}$$

Q = charge from catalyst solution during CPE (C) - charge from solution without catalyst during CPE (C)

FE = Faradaic efficiency

$$F = 96485 \text{ (C mol}^{-1}\text{)}$$

n_{ele} = mol of electrons required to generate a mol of H₂ = 2

n_{cat} = total mol of catalyst = 0.15 mg / Mr (FeP)

Electrochemical Measurements

Electrochemical measurements are performed with a CHI614D electrochemical analyzer (CH Instruments, Inc., Shanghai). A three-electrode cell is used, including the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a carbon plate as the counter electrode. In all measurements, SCE was used as the reference, and all the potentials reported in our work were vs. RHE. The potential, measured against a SCE electrode, was converted to the potential versus RHE according to $E \text{ (RHE)} = E \text{ (SCE)} + 0.281 \text{ V}$.^{S3}

Reference

S1. Y. Yan, X. Ge, Z. Liu, J.Y. Wang, J.M. Lee and X. Wang, *Nanoscale*, 2013, **5**, 7768-7771.

S2. L. Chen, M. Wang, K. Han, P. Zhang, F. Gloaguen and L. Sun, *Energy Environ. Sci.*, 2014, **7**, 329-334.

S3. Y. F. Xu, M. R. Gao, Y. R. Zheng, J. Jiang, and S. H. Yu, *Angew. Chem. Int. Ed.*, 2013, **52**, 8546.

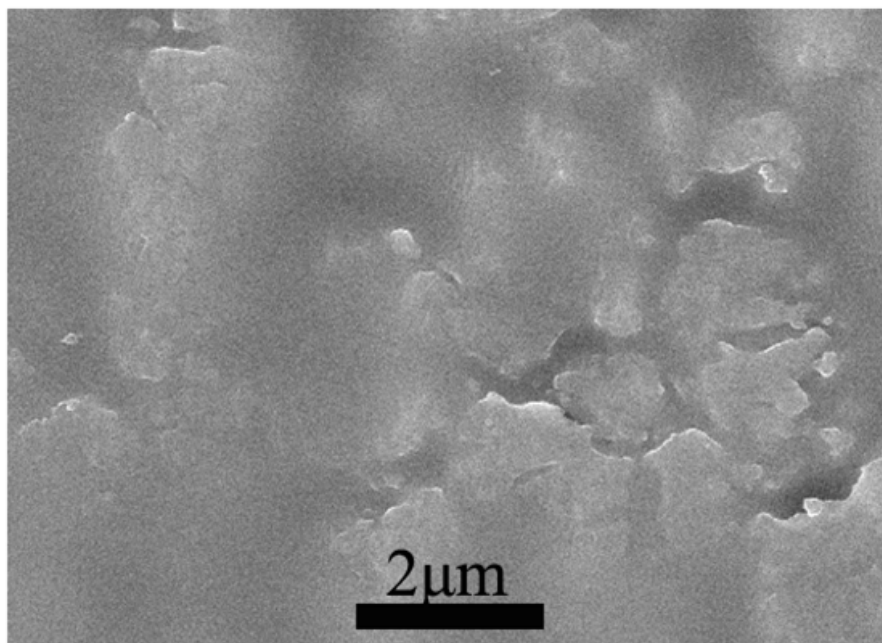


Fig. S1 SEM image of Ti foil.

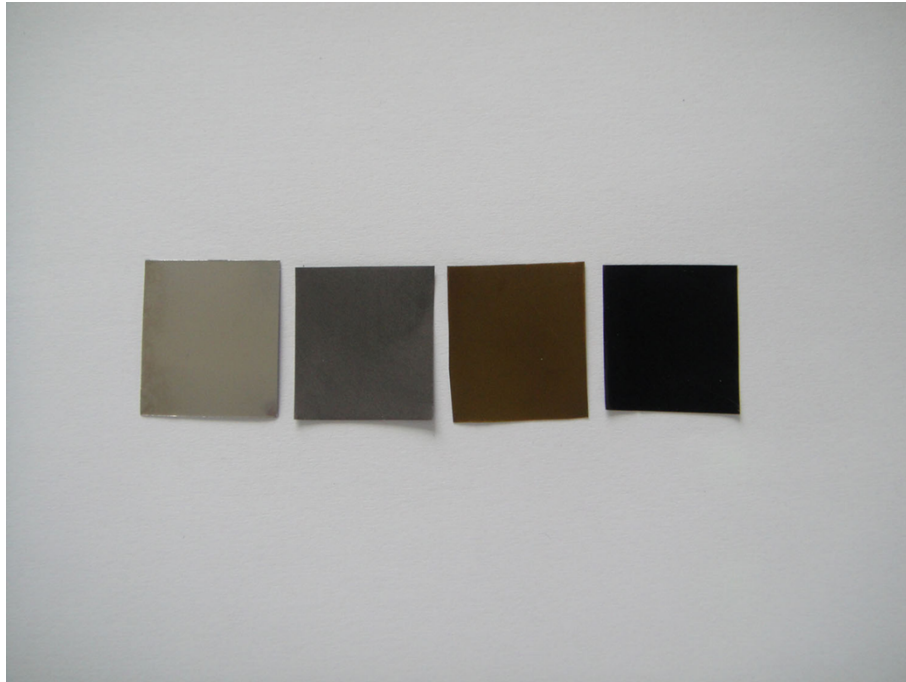


Fig. S2 Optical photograph of the Ti foil, HCl-treated Ti foil, α -FeO(OH) NAs/Ti and FeP NAs/Ti.

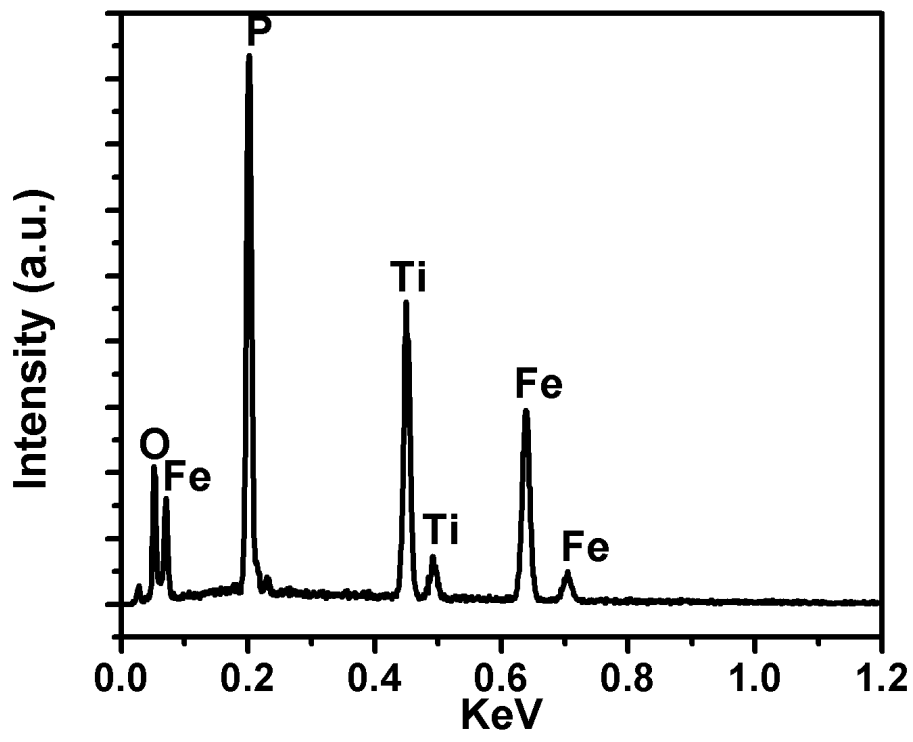


Fig. S3 EDX spectrum for FeP NAs/Ti.

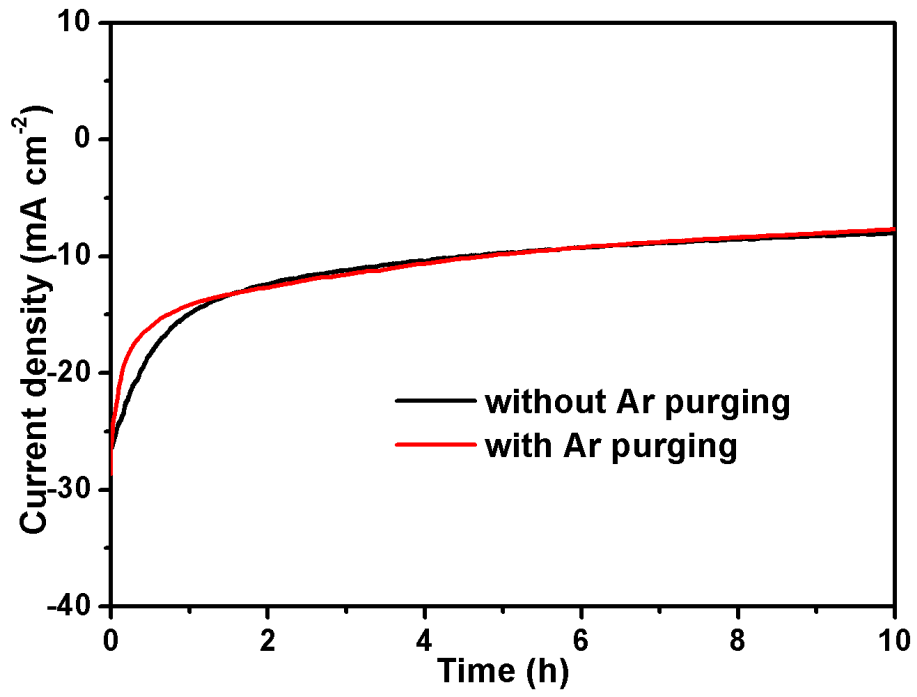


Fig. S4 Time-dependent curves of FeP NAs/Ti with and without Ar purging in 0.5 M H₂SO₄.

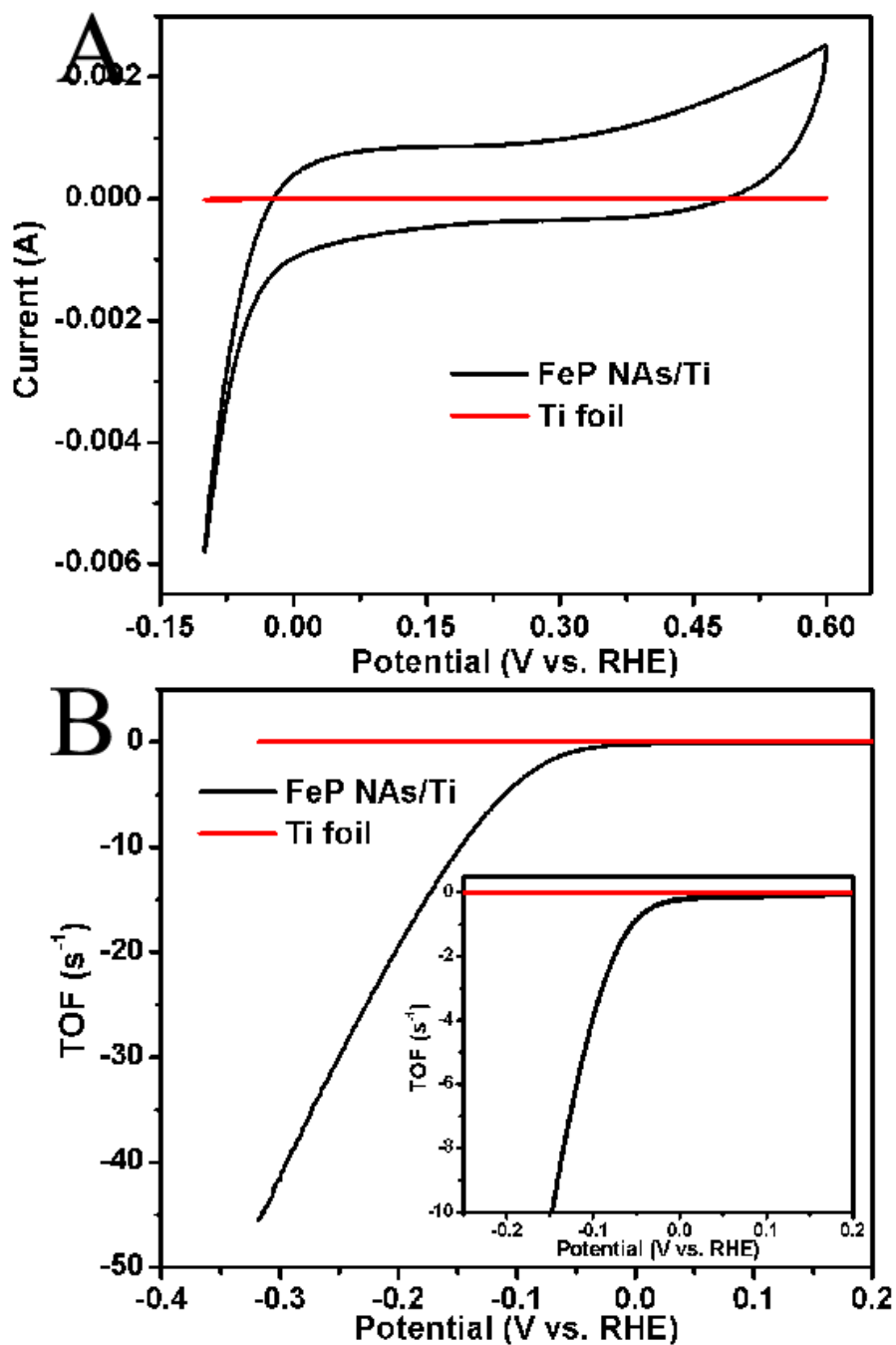


Fig. S5 (A) Cyclic voltammograms of the FeP NAs/Ti and Ti foil recorded in 0.5 M H₂SO₄ between -0.1 V and 0.6 V vs. RHE with a scan rate of 0.05 V s⁻¹. (B) Calculated TOFs for FeP NAs/Ti and Ti foil in 0.5 M H₂SO₄.

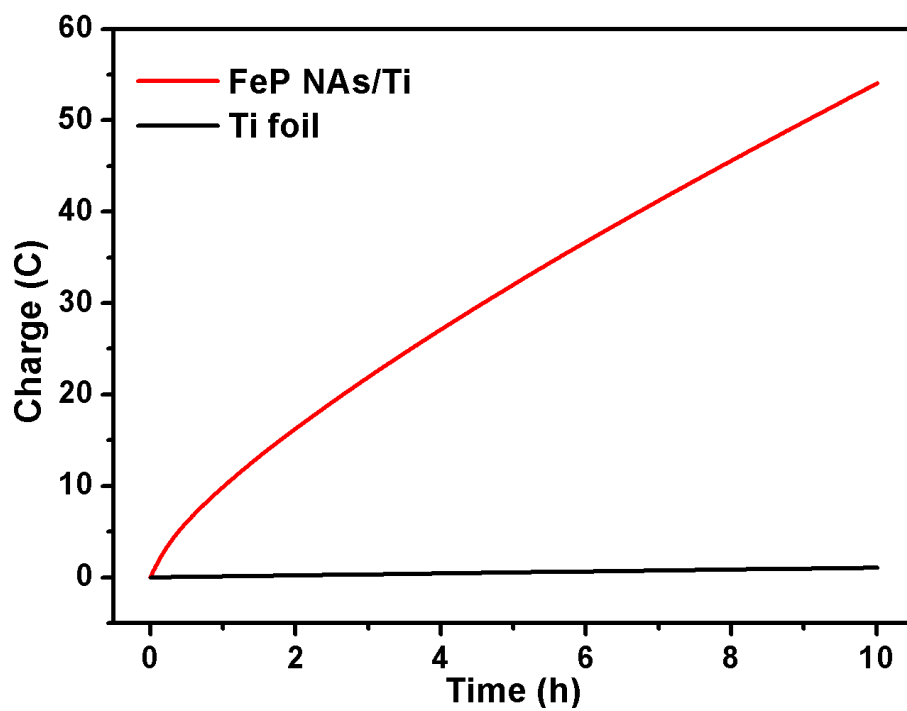


Fig. S6 Controlled potential electrolysis (CPE) voltamogram at -85 mV vs. RHE in 0.5 M H₂SO₄

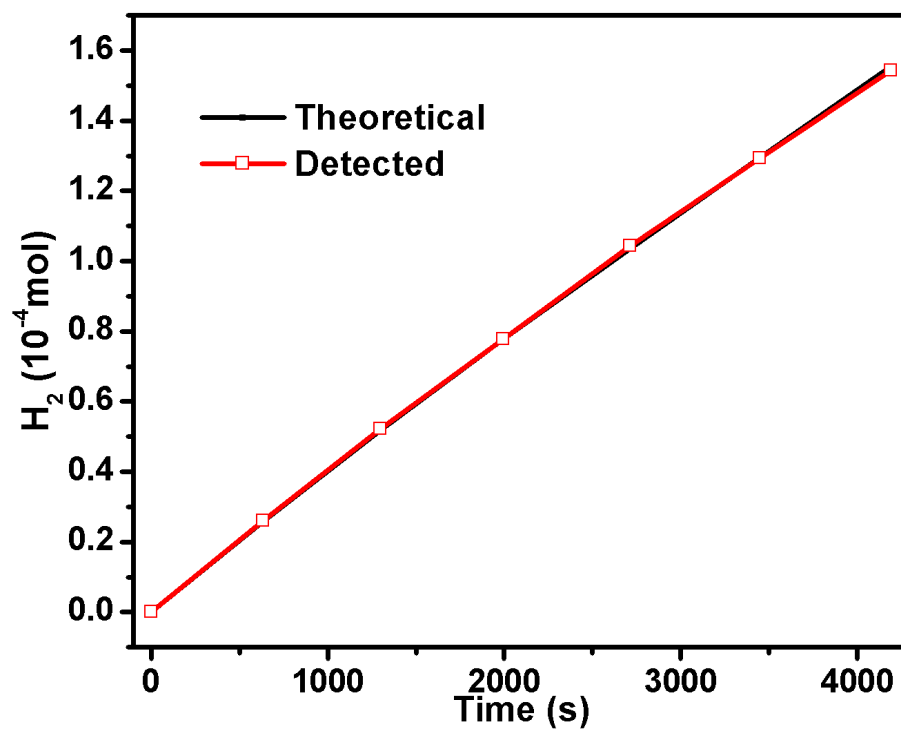


Fig. S7 The theoretical (solid) and detected (square) values represent the expected and observed amount of H₂ produced versus time for FeP NAs/Ti.

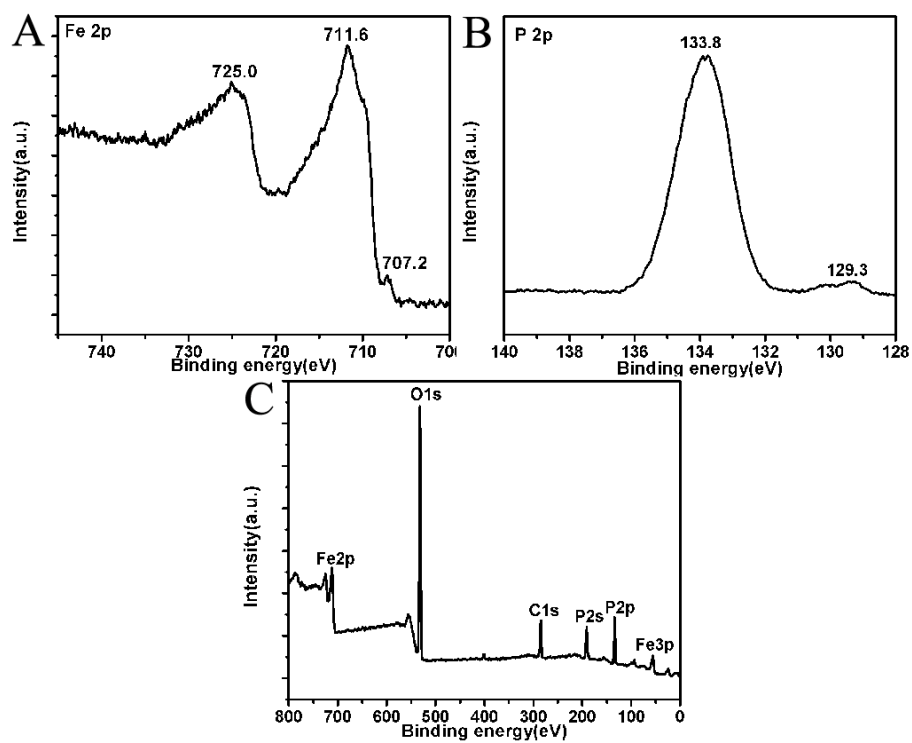


Fig. S8 XPS spectra in the (A) Fe(2p) and (B) P(2p) regions and (C) the survey spectrum for FeP.

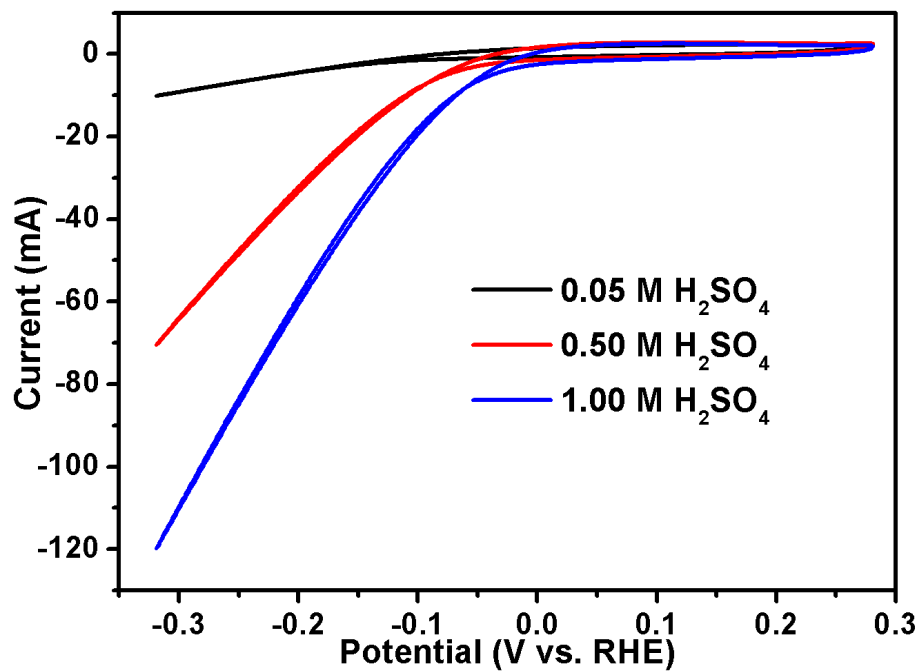


Fig. S9 Polarization curves for FeP NAs/Ti in different pH mediums with a scan rate of 0.05 V s⁻¹.

Table S1 Comparison of HER performance in acid media for FeP NAs/Ti with other HER electrocatalysts (^a catalysts directly grown on current collectors).

Catalyst	Onset η (mV)	Tafel slope (mV dec ⁻¹)	Current density (j , mA cm ⁻²)	η at the corresponding j (mV)	Ref.
CoSe ₂ nanoparticles on carbon fiber paper ^a	-	42.1	10	139	<i>J. Am. Chem. Soc.</i> 2014 , 136, 4897
			100	184	
MoO ₃ -MoS ₂ /FTO ^a	150-200	50-60	10	310	<i>Nano Lett.</i> 2011 , 11, 4168
nanoporous Mo ₂ C nanowire	70	53	60	200	<i>Energy Environ. Sci.</i> 2014 , 7, 387
NiMoN _x /C	78	35.9	5	220	<i>Angew. Chem. Int. Ed.</i> 2012 , 51, 6131
Ni ₂ P/Ti ^a	-	46	10	116	<i>Am. Chem. Soc.</i> 2013 , 135, 9267
			100	180	
FeP nanosheets	100	67	10	~240	<i>Chem. Commun.</i> 2013 , 49, 6656
CoP/Ti ^a	-	50	20	95	<i>Angew. Chem. Int. Ed.</i> 2014 , 53, 5427
Bulk MoB	-	55	20	~240	<i>Angew. Chem. Int. Ed.</i> 2012 , 51, 12703
CoP/CNT	-	54	10	122	<i>Angew. Chem. Int. Ed.</i> 2014 , 53, 6710
MoS ₂ nanoflower/rGO paper ^a	190	95	~43	~400	<i>Nanoscale</i> 2014 , 6, 5624
MoS ₂ nanostructured electrode ^a	~150	~51	~45	~300	<i>Adv. Mater.</i> , 2014 , 26, 2683
Li-MoS ₂ ^a	-	62	200	200	<i>ACS Nano</i> , 2014, 8, 4940
3D porous MoS _x electrodes ^a	-	185	72	200	<i>Small</i> , 2013 , 10, 895.
MoS ₂ /graphene/Ni foam ^a	-	42.8	10	141	<i>Adv. Mater.</i> , 2013 , 25, 756
			100	263	
FeP NAs/Ti ^a	65	60	10	85	<i>This work</i>
			240	183	