Electronic Supplementary Information

3D structured porous CoP_3 nanoneedle arrays as an efficient bifunctional electrocatalyst for the evolution reaction of hydrogen and oxygen

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Experimental Section

Materials: $Co(NO_3)_3 \cdot 6H_2O$, NH_4F, and urea were purchased from Aladdin Ltd. (Shanghai, China). NaH_2PO_4 and Na_2HPO_4 (Chengdu Chemical Corp) were used for preparation of PBS. H_2SO_4 and KOH were purchased from Aladdin Lth. (Shanghai, China). Nafion ethanol solution (5 wt%) and Commercial Pt/C (20 wt%) catalysts were purchased from Alfa Aesar. All other chemical reagents used in this study were analytical grade without further purification. Carbon fiber paper (CFP) is provided by Shanghai Hesen Corp. All aqueous solutions were prepared with ultrapure water (> 18.25 MΩ·cm) obtained from Millipore system.

Preparation of Co(OH)F/CFP and CoP_3/CFP: Co(OH)F/CFP was prepared as follows. In a typical synthesis, $Co(NO_3)_2 \cdot 6H_2O$ (0.582 g), NH_4F (0.186 g) and urea (0.60 g) were dissolved in 40 mL water under vigorous stirring for 30 min. Then the solution was transferred into a Teflon-lined stainless autoclave (50 mL) and a piece of CFP (3 cm × 1.8 cm), which was cleaned by sonication sequentially in acetone, water and ethanol for 10 min each, was immersed into the solution. The autoclave was sealed and maintained at 120 °C for 6 h in an electric oven. After the autoclave cooled down slowly at room temperature, the Co(OH)F/CFP was taken out and washed with water thoroughly before vacuum dried. To prepare CoP_3 NAs/CFP, a piece of the Co(OH)F

NAs/CFP (0.6 cm*1.5 cm) and 30 mg red phosphorus were put into a quartz tube and vacuum-sealed (10^{-5} Pa) and then these sealed quartz tubes were placed in a chamber furnance and heat treated at 750 ^{o}C for 5 hours. The final reaction products were thoroughly washed with deionized water, ethanol and dried under 50 ^{o}C for 10 h.

Preparation of CoP_3 nanoparticles: The CoP_3 nanoparticles were synthesized through a solid-state reaction method. In a typical synthesis, First, Co_3O_4 bulk were prepared by calcining 1.0 g $Co(NO_3)_3 \cdot 6H_2O$ at 300 ^{o}C for 5h with a heating rate of 10 ^{o}C min^{-1} in air. Furthermore, 0.1 g of Co_3O_4 and 0.2 g of red phosphorus (P) were mixed uniformly and vacuum-sealed (10^{-5} Pa) in a quartz tube, and then these sealed quartz tubes were placed in a chamber furnace and heat treated at 750 ^{o}C for 5 hours. The final reaction products were thoroughly washed with deionized water, ethanol and dried under 50 ^{o}C for 10 h.

Characterization: X-ray diffraction analysis (XRD) was conducted by using a PANalytical X'pert diffractometer operating at 40 kV and 50 mA using Cu Kα radiation. Field emission scanning electron microscopy (FE-SEM, TESCAN MARI3) and transmission electron microscopy (TEM, FEI TECNAI G2 F20) coupled with Energy dispersive X-ray spectroscope (EDS), were applied for the morphologies, sizes, compositions and structures of the samples. X-ray photoelectron spectroscopy (XPS) measurement were performed on a Thermo ESCALAB 250Xi with an Al Kα (1486.6 eV) X-ray source on the samples. The energy calibrations were preferenced the C 1s peak at 284.6 eV to eliminate the charging of the sample during analysis. Nitrogen adsorption-desorption isotherms were obtained on a Quantachrome NOVA 1000 system with all samples degassed at 100 ^{o}C prior to measurements. Gas chromatography measurements were conducted on GC–9790 (Fuli Co., China) with thermal conductivity detector.

Electrode preparation and electrochemical measurements: Polarization curves of the HER in 0.5 M H_2SO_4 were performed using an electrochemical workstation (CHI 660E, CH Instruments, Chenhua Co., Shanghai, China) at room temperature. Saturated calomel electrode (SCE) and Pt foil were used as the reference and counter electrodes, respectively. The SCE electrode was calibrated with respect to the reversible hydrogen

electrode (RHE). Catalyst ink was typically made by dispersing 10 mg of catalyst into 2 mL of water/ethanol (V/V=950:1000) solvent. After adding 50 μL of 5 wt% of Nafion solution and sonicated for at least 30 min, 50 μL of this catalyst ink dispersion (containing 0.25 mg of catalyst) was loaded onto a carbon fiber paper (CFP) to achieve the sample loading 1 mg cm^{-2}. Polarization data is collected at the scan rate of 2 $mV \cdot s^{-1}$. The time dependency of catalytic currents during electrolysis for the catalyst was tested in 0.5 M H_2SO_4 at potentiostatic voltage. AC impedance measurements was carried out in a potentiostatic mode in the frequency range of 0.01 Hz to 10^5 Hz.

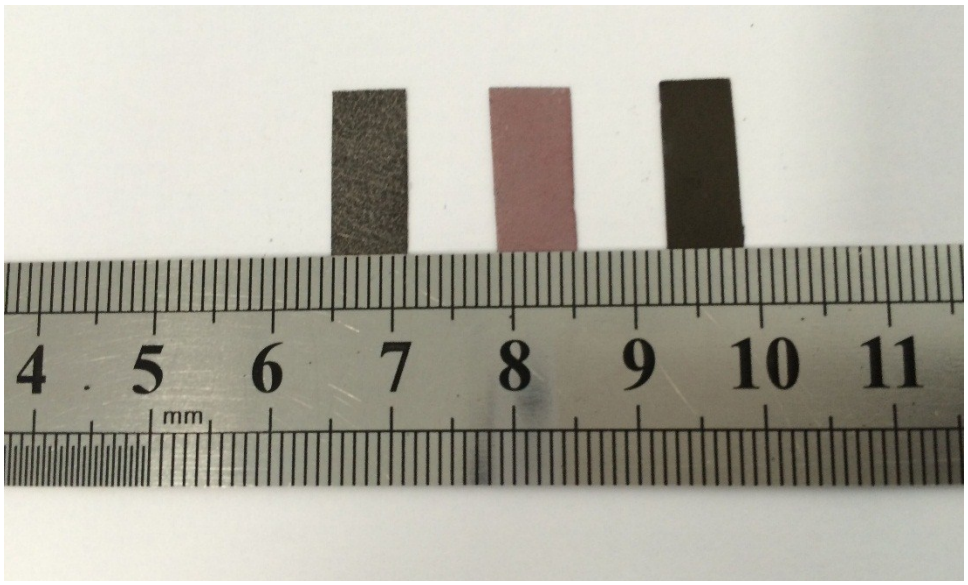


Fig. S1 Optical photograph (from left to right) of blank CFP, Co(OH)F/CFP, and CoP_3 NAs/CFP.

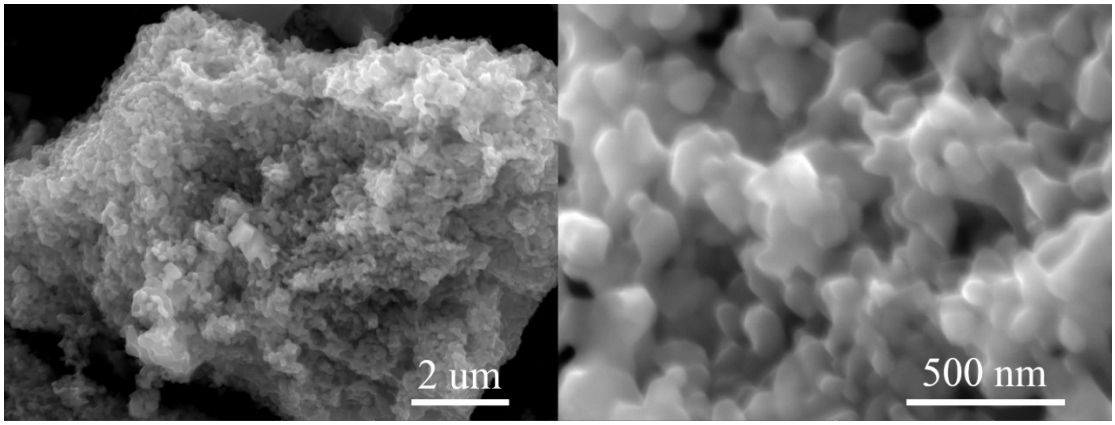


Fig. S2 Low- and high- magnification SEM images of CoP_3 NPs.

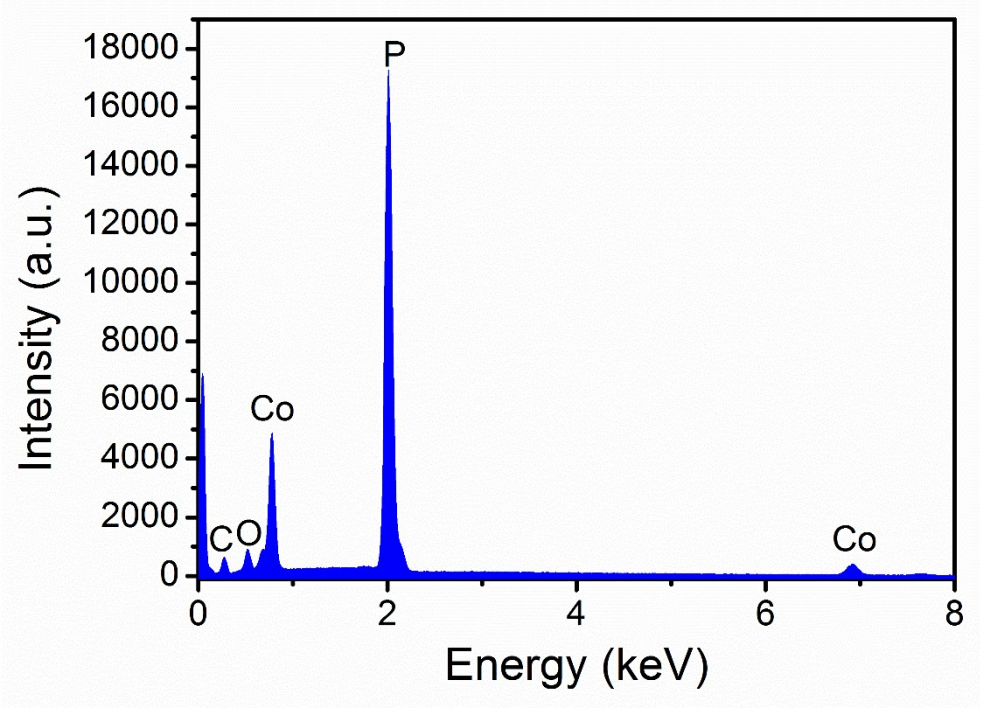


Fig. S3 EDX spectrum of CoP_3 nanoneedles.

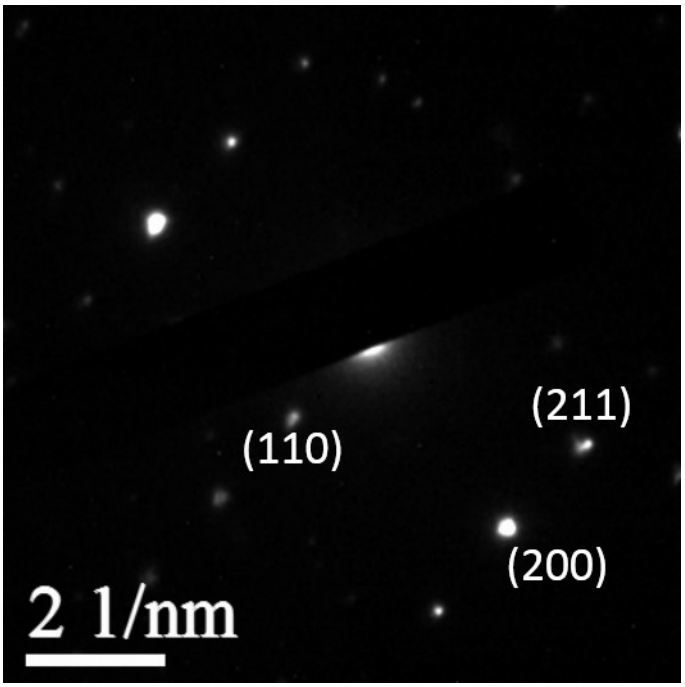
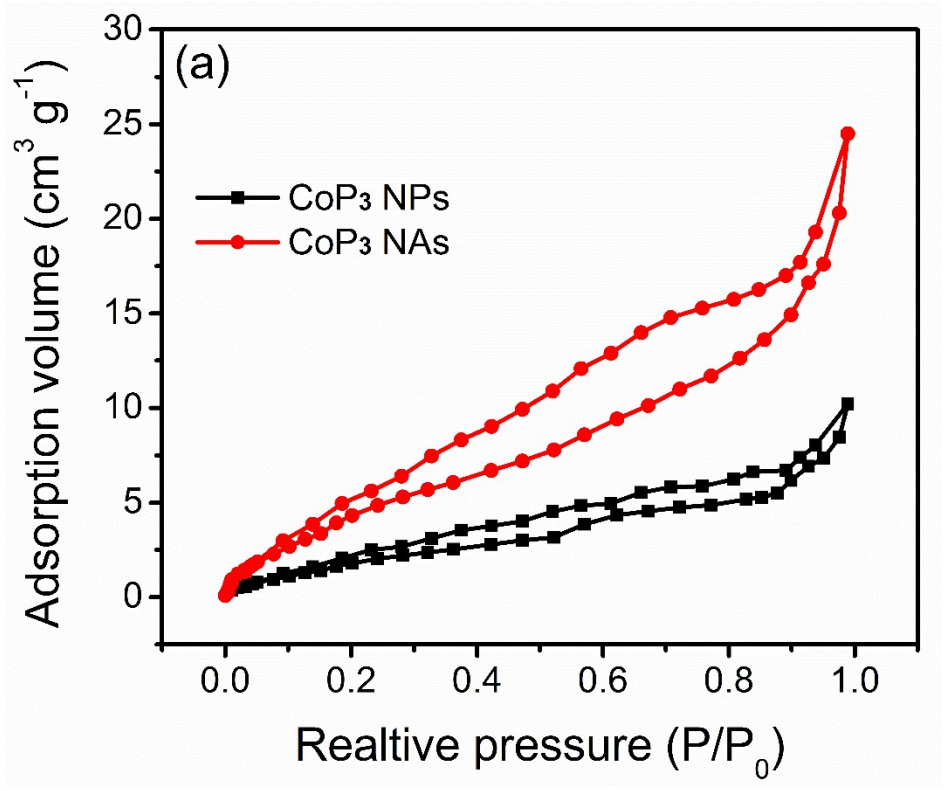


Fig. S4 SAED pattern of CoP_3 nanoneedles.



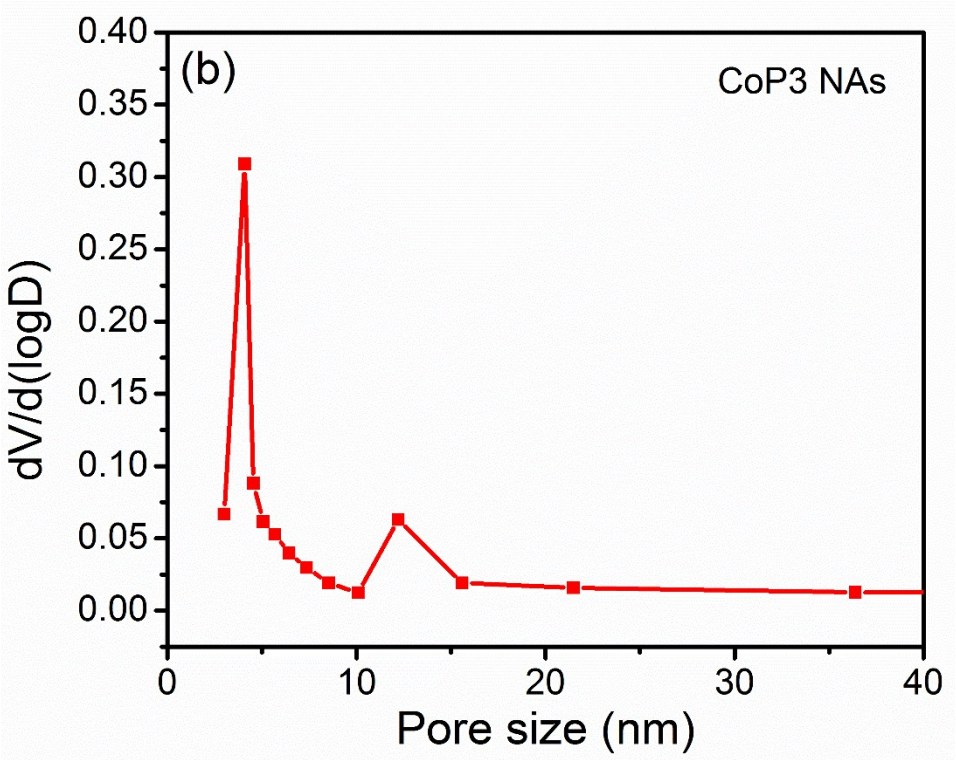


Fig. S5 (a) Nitrogen adsorption/desorption isotherm and (b) the BJH pore-size distribution curve (inset) of CoP_3 NAs/CFP.

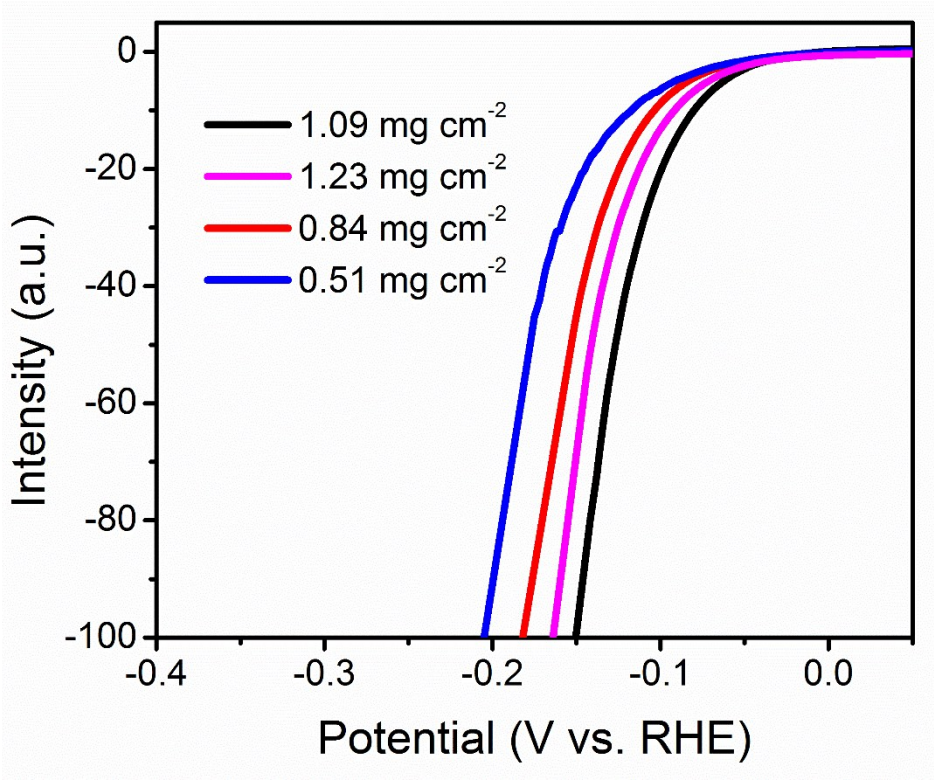


Fig. S6 Polarization curves of the CoP_3 NAs/CFP with different CoP_3 loading in 0.5 M H_2SO_4 with a scan rate of 2 mV/s.

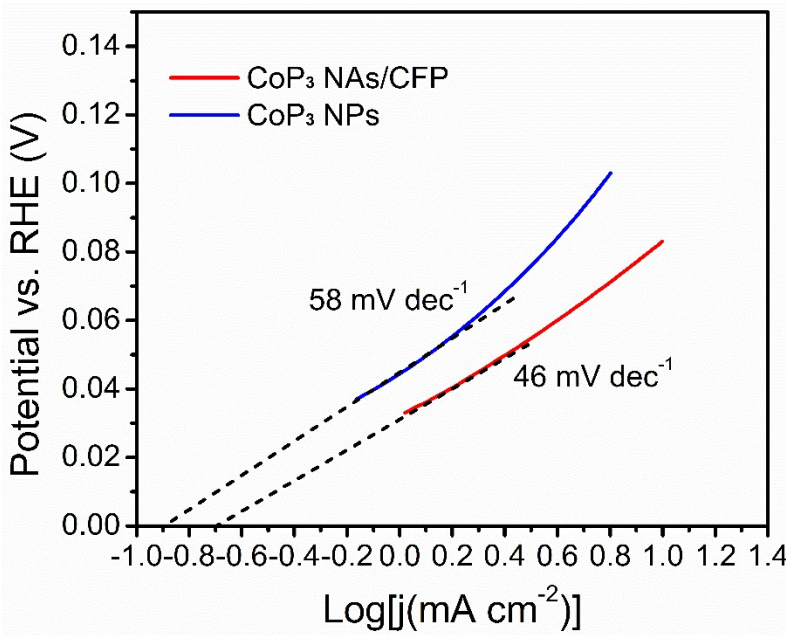


Fig. S7 Calculated exchange current density of the CoP_3 NAs/CFP by applying extrapolation method to the Tafel plot.

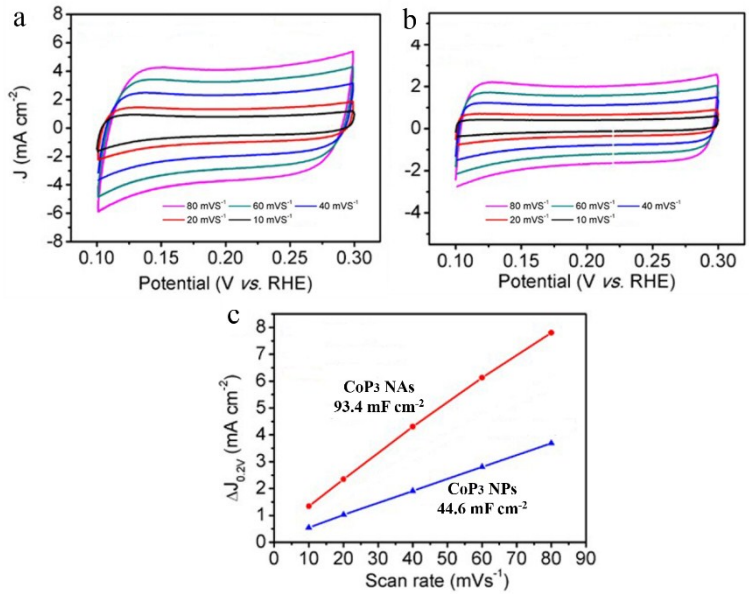


Fig. S8 Cyclic voltammograms in the region of 0.1-0.3 V *vs.* RHE at various scan rates and the corresponding linear fitting of the capacitive currents vs. scan rates to estimate the double layer capacitance: (a) CoP_3 NAs/CFP and (b) CoP_3 NPs/CFP; (c) The capacitive currents were measured at 0.20 V *vs.* RHE plotted as a function of scan rate.

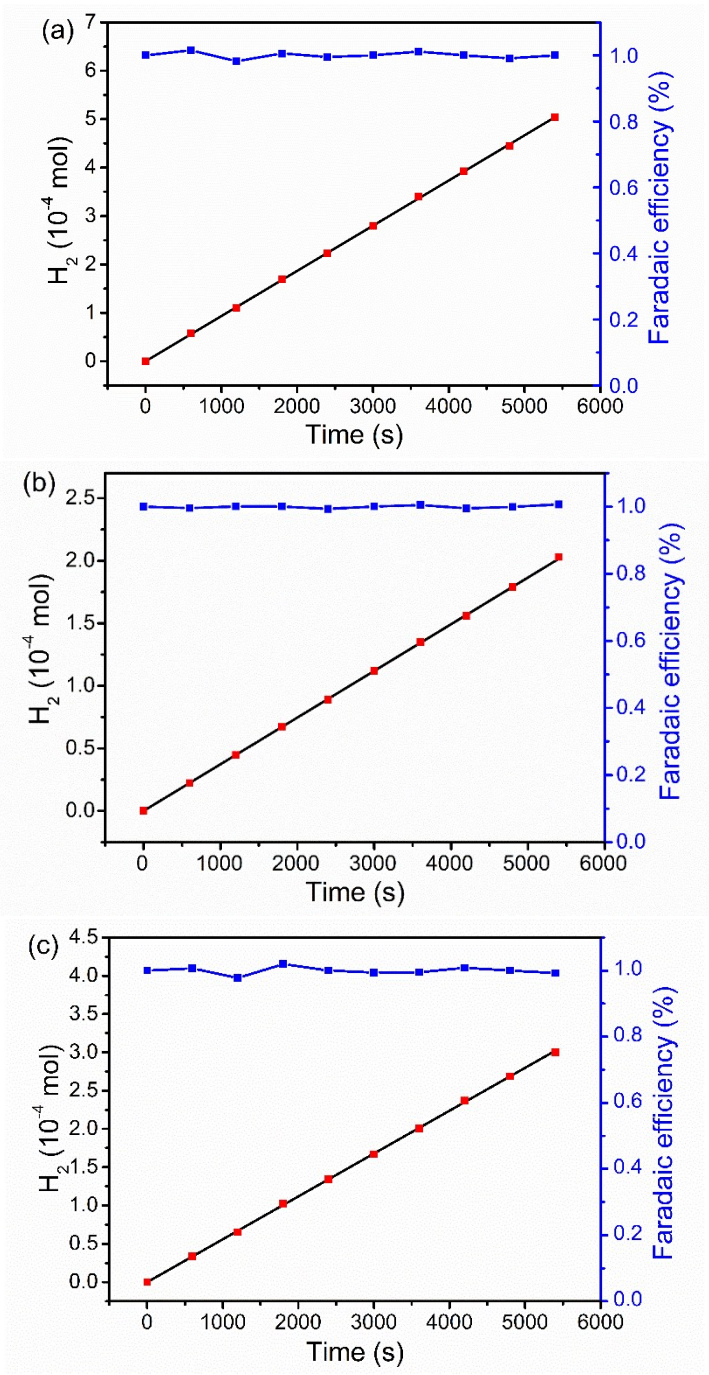


Fig. S9 The amount of H_2 theoretically calculated (solid) and experimentally measured (red sphere) versus time for CoP_3 NAs/CFP at (a) pH 0 under an overpotential of 115 mV for 90 min, (b) pH 6.8 under overpotentials of 200 mV for 60 min. and (c) pH 14 under overpotentials of 160 mV for 60 min.

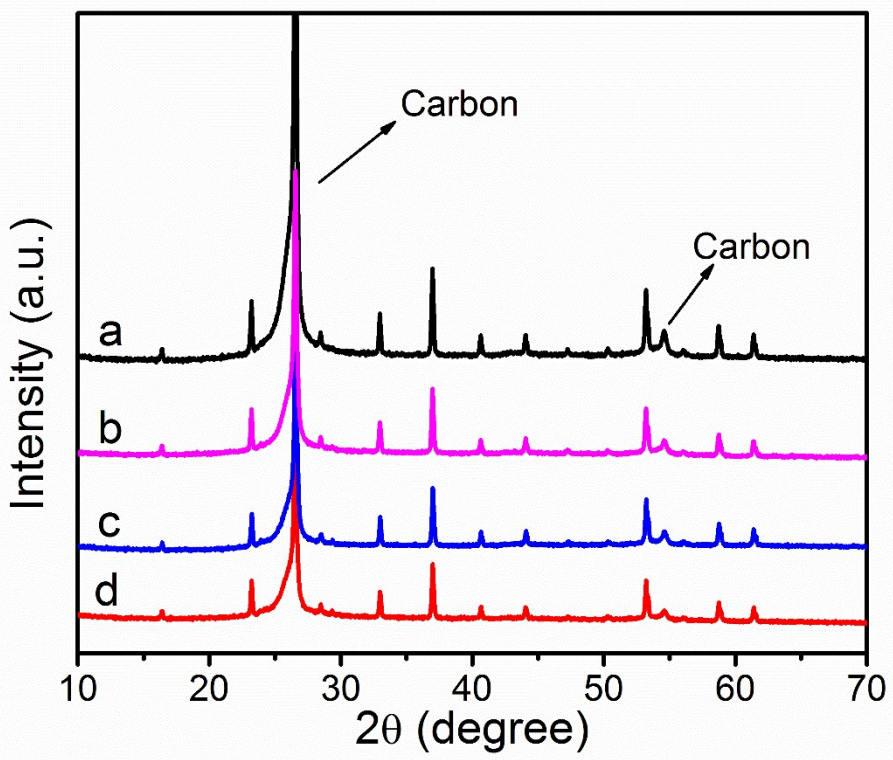


Fig. S10 XRD patterns of CoP_3 NAs/CFP (a) before and after 5000 cycles CV scanning at (b) pH 0, (c) pH 6.8, and (d) pH 14.

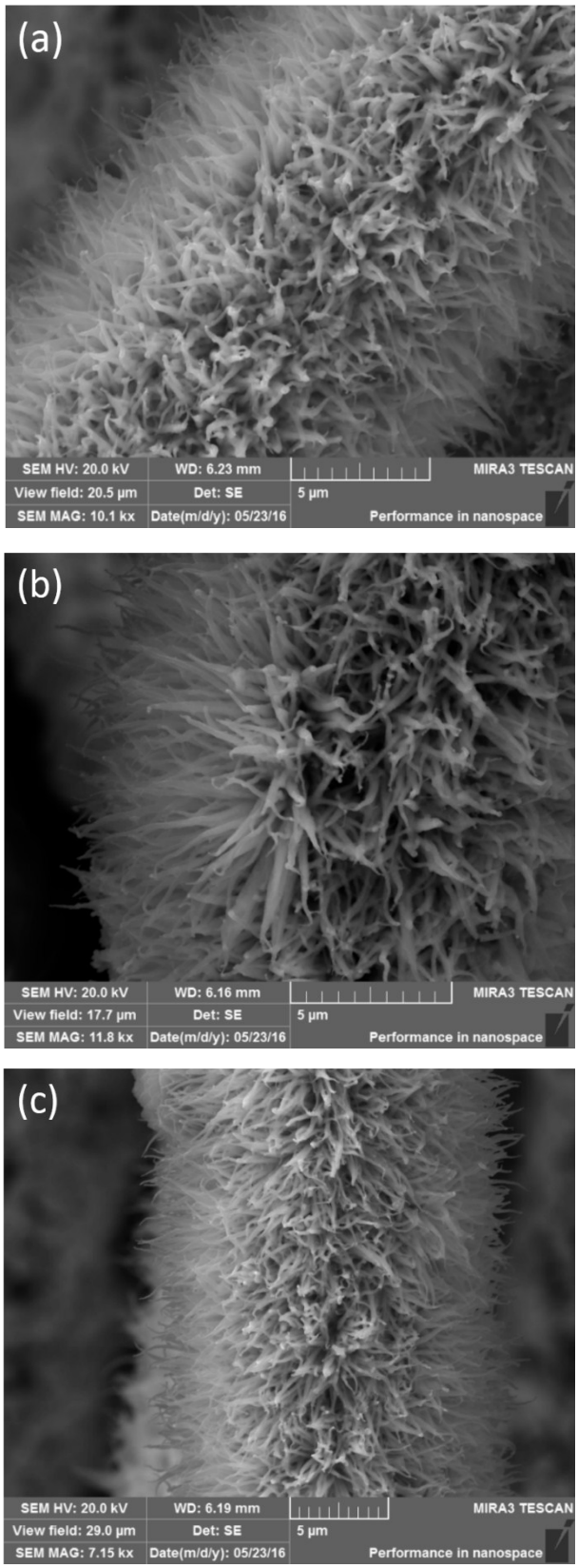


Fig. S11 SEM images of CoP_3 NAs/CFP after 5000 cycles CV scanning at (a) pH 0, (b) pH 6.8, and (c) pH 14.

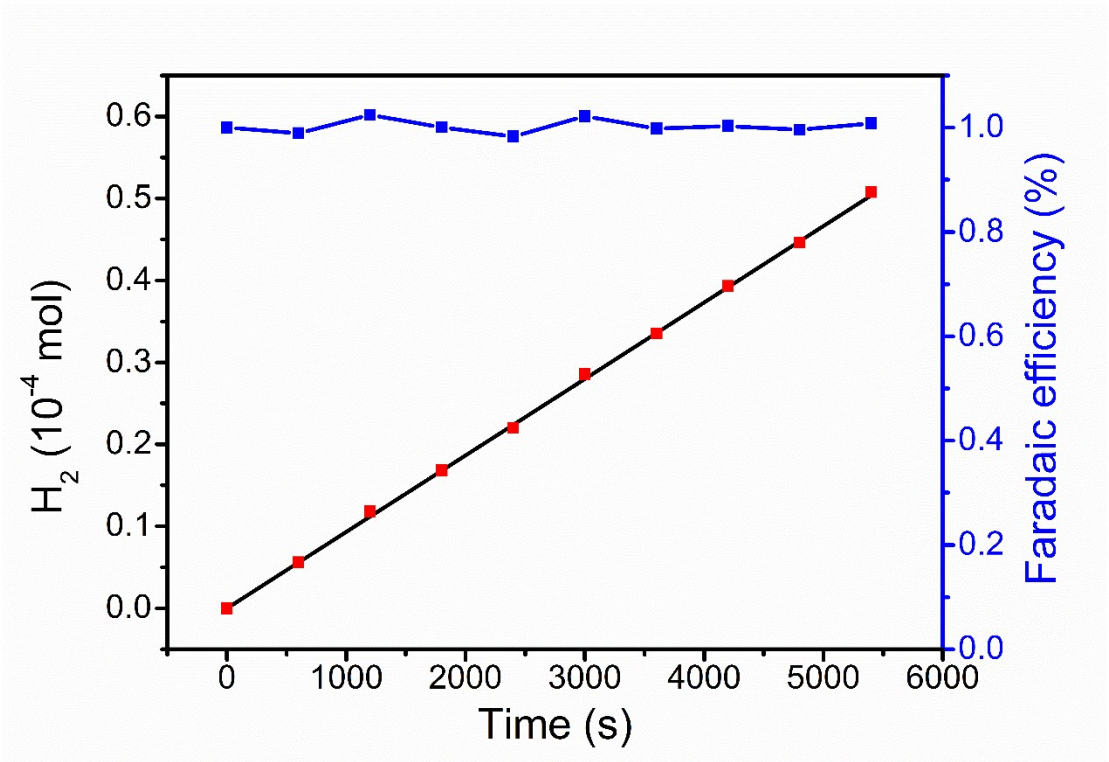


Fig. S12 The amount of O_2 theoretically calculated (solid) and experimentally measured (red sphere) versus time for the CoP_3 NAs/CFP at pH 14 under overpotentials of 334 mV for 90 min.

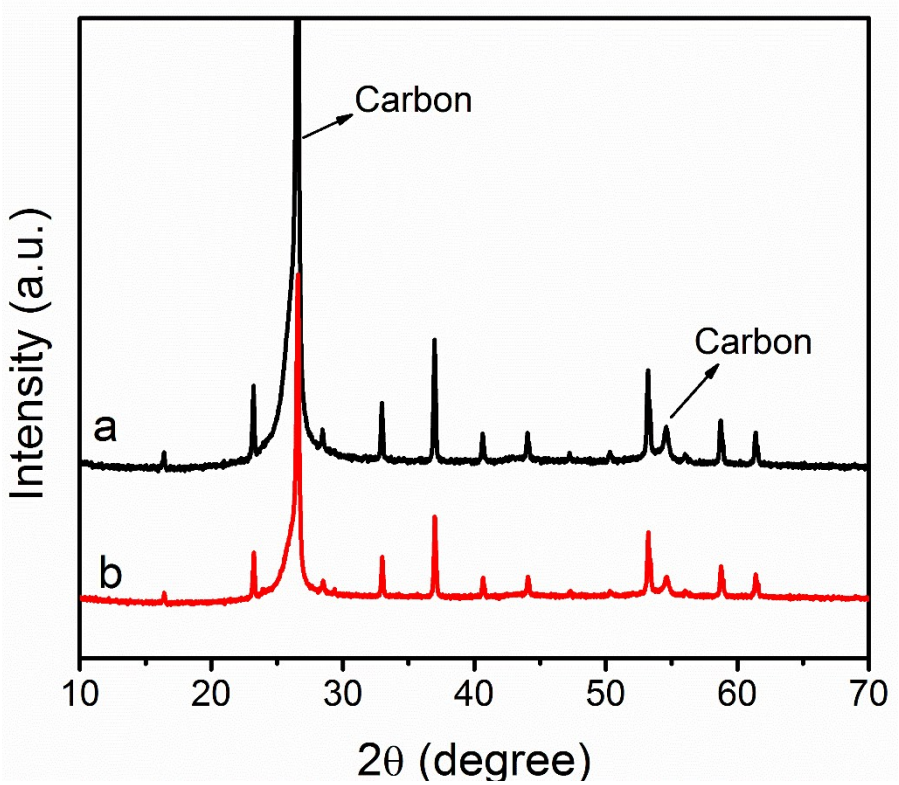


Fig. 13 XRD patterns of the CoP_3 NAs/CFP before and after 5000 cycles CV scanning at pH 14.

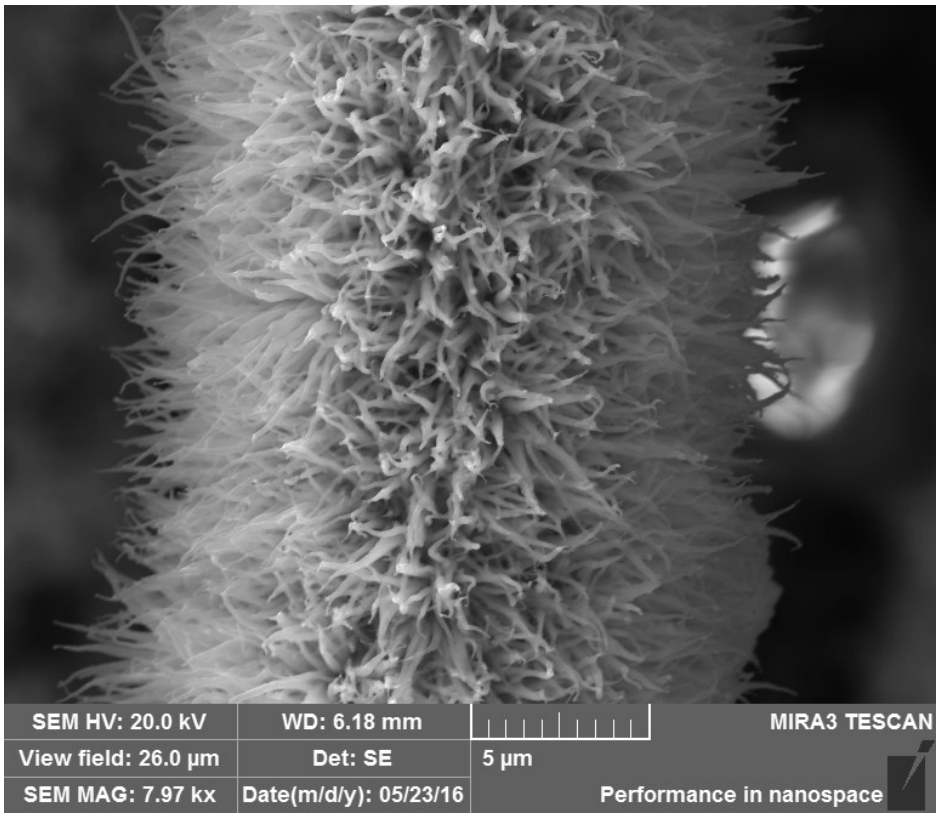


Fig. S14 SEM images of the CoP_3 NAs/CFP after 5000 cycles CV scanning at pH 14 for OER.

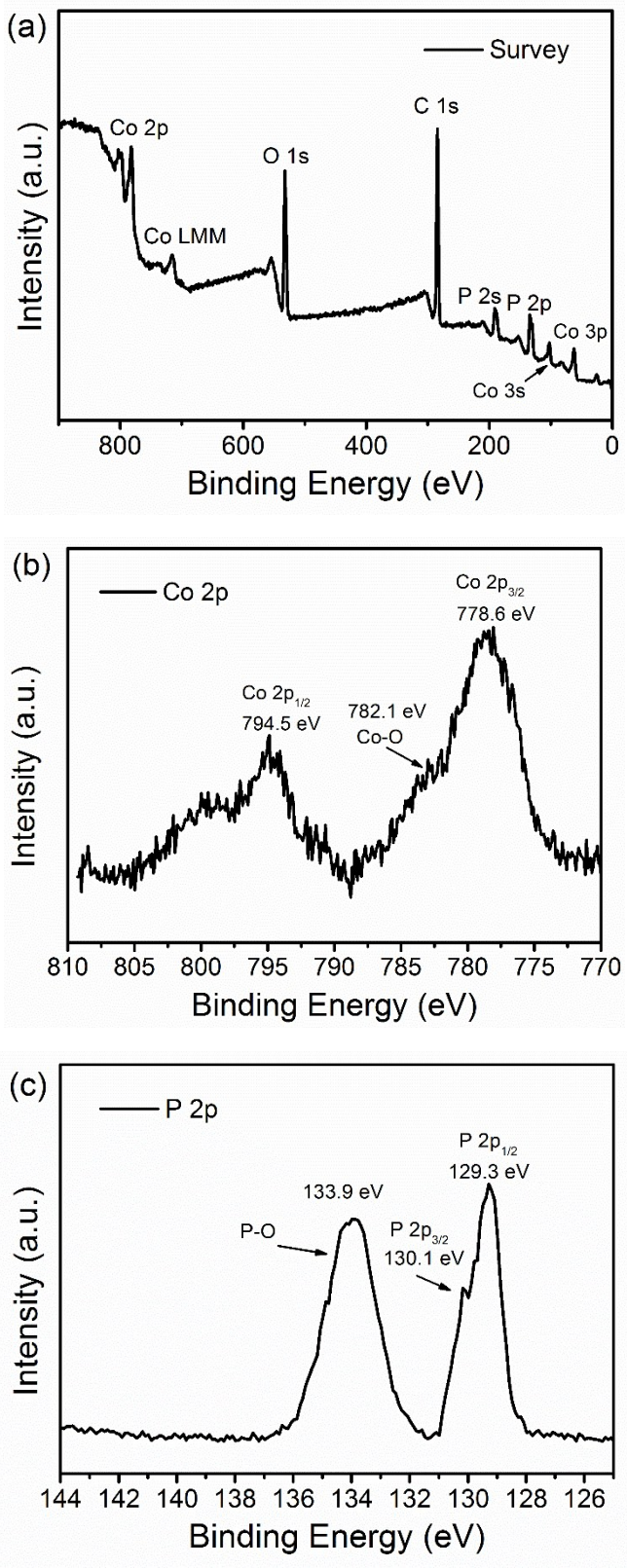


Fig. S15 XPS spectra of the CoP_3 NAs/CFP: (a) survey spectrum, (b) Co 2p, and (c) P 2p.

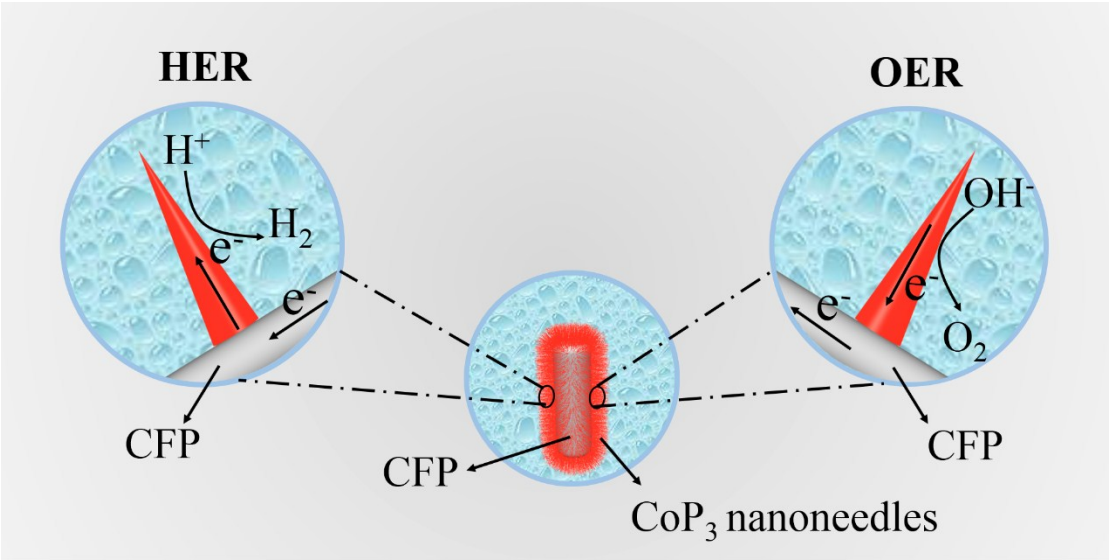


Fig. S16 A schematic diagram to illustrate the operating principle of the HER and OER based on the CoP_3 NAs/CFP.

Table S1. Comparison of HER performance in acid media for CoP_3/CFP with other TMPs HER electrocatalysts.

Catalyst	Onset η (mV)	Current density (*j*, mA cm^{-2})	η at the corresponding *j* (mV)	Exchange current density (mA cm^{-2})	Ref.
FeP nanosheets	100	10	240	-	*Chem. Commun.*, 2013, 49, 6656
FeP NWs/Ti	38	10	55	0.42	*Angew. Chem. Int. Ed.*, 2014, 53, 12855
FeP NWs	-	10	96	0.17	*Chem. Commun.*, 2016, 52, 2819.
FeP NPs	38	10	112	-	*Nanoscale*, 2015, 7, 4400
FeP NAs	-	10	85	-	*J. Mater. Chem. A*, 2014, 2, 17263
FeP_2/C	-	5	500	$1.75*10^{-3}$	*J. Mater. Chem. A*, 2015, 3, 499
Ni_2P NPs	-	20	130	$2.7*10^{-3}$	*J. Am. Chem. Soc.*, 2013, 135, 9267
Ni_2P/graphene	37	10	102	0.049	*J. Power Sources*, 2015, 297, 45
Ni_2P/CNs	40	10	92	-	*J. Power Sources*, 2015, 285, 169
NiP_2/CC	-	10	116	0.26	*Nanoscale*, 2014, 6, 13440
Se doped NiP_2	-	10	84	-	*ACS Catal.*, 2015, 5, 6355
Cu_3P NWs	62	10	143	0.18	*Angew. Chem. Int. Ed.*, 2014, 53, 9577
MoP Bulk	50	30	180	0.034	*Energy Environ. Sci.*, 2014, 7, 2624
MoP NPs	40	10	125	0.086	*Adv. Mater.*, 2014, 26, 5702
MoP_2 NPs/Mo	-	10	143	0.06	*Nanoscale, 2016, 8, 8500*
MoP_2 nanosheets	-	10	58	-	*J. Mater. Chem. A*, 2016, 4, 7169
WP	50	10	120	-	*Chem. Commun.*, 2014, 50, 11026

α-WP_2	**54**	**10**	**161**	**0.017**	***ACS Catal.*, 2015, 5, 145**
β-WP_2	**56**	**10**	**148**	**0.013**	***J. Power Sources*, 2015, 278, 540**
Co2P	**-**	**10**	**95**	**-**	***Chem. Mater.*, 2015, 27, 3769**
CoP/CC	**38**	**10**	**67**	**0.288**	***J. Am. Chem. Soc.*, 2014, 136, 7587**
CoP NPs	**-**	**20**	**85**	**-**	***Angew. Chem. Int. Ed.*, 2014, 53, 5427**
CoP/CNs	**40**	**10**	**122**	**0.13**	***Angew. Chem. Int. Ed.*, 2014, 53, 6710**
CoP3/NAs	**30**	**10** **100**	**65** **137**	**0.209**	**This work**

NPs (nanoparticles); CNs (Carbon Nanotubes); CC (Carbon Cloth); NWs (Nanowires); NAs (Nanoneedle Arrays)

Table S2. Comparison of HER performance in neutral media for CoP_3/CFP with other HER electrocatalysts.

Catalyst	Current density (*j*, mA cm^{-2})	Potential at the corresponding *j* (mV)	Ref.
Mo_2B	1	250	*Angew. Chem. Int. Ed.*, 2012, 51, 12703
Mo_2C	1	200	*Angew. Chem. Int. Ed.*, 2012, 51, 12703
H2-CoCat/FTO	2	385	*Nat. Mater.*, 2012, 11, 802
Co-S/FTO	2	83	*J. Am. Chem. Soc.*, 2013, 135, 17699
$CuMoS_4$	2	210	*Energy Environ. Sci.*, 2012, 5, 8912
WP	10	200	*ACS Appl. Mater. Interfaces*, 2014, 6, 218740
WP_2	10	298	*J. Power Sources*, 2015, 278, 540
MoP_2 NPs/Mo	10	211	*Nanoscale*, 2016, 8, 8500
MoP_2 nanosheets	10	67	*J. Mater. Chem. A*, 2016, 4, 7169
CoP NWs	2	65	*J. Am. Chem. Soc.*, 2014, 136, 7587
CoP_3	10	165	This work

Table S3. Comparison of HER performance in alkaline media for CoP_3/CFP with other HER electrocatalysts.

Catalyst	Current density (j, mA cm^{-2})	Potential at the corresponding j (mV)	Ref.
Ni wire	10	350	*ACS Catal.*, 2013, 3, 166
MoB	10	225	*Angew. Chem. Int. Ed*, 2012, 51, 12703
NiP_2	10	102	*Nanoscale*, 2014, 6, 13440
WP	10	250	*ACS Appl. Mater. Interfaces*, 2014, 6, 218740
WP_2	10	225	*J. Power Sources*, 2014, 136, 7587
MoP_2 nanosheets	10	85	*J. Mater. Chem. A*, 2016, 4, 7169
MoP_2 NPs/Mo	10	194	*Nanoscale*, 2016, 8, 8500
CoP nanowires	10	209	*J. Am. Chem. Soc.*, 2014, 136, 7587
CoP3	10	119	This work

Table S4. Comparison of OER performance in alkaline media for CoP_3/CFP with other OER electrocatalysts.

Catalyst	Current density (j mA cm^{-2})	Potential at the corresponding j (mV)	Ref
NiOOH/Ni_5P_4	10	290	*Angew. Chem. Int. Ed*, 2015, 54, 12361
Ni-P/CF	10	325	*J. Power Sources*, 2015, 299, 342
Co-P film	10	345	*Angew. Chem. Int. Ed*, 2015, 54, 6251
CoP NPs	10	360	*ACS Catal.*, 2015, 5, 4066
CoP nanorods	10	320	*ACS Catal.*, 2015, 5, 6874
CoP hollow	10	427	*ACS Appl. Mater. Interfaces*, 2016, 8, 2158
CoP_2/RGO	10	300	*J. Mater. Chem. A*, 2016, 4, 4686
CoP_3 NAs/CFP	10	334	This work
	50	407	