Electronic Supplementary Information

Three-dimensional interconnected network of nanoporous CoP nanowires as an efficient hydrogen evolution cathode

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Experimental section

Materials

Cobalt nitrate ($Co(NO_3)_2.6H_2O$), Urea ($CO(NH_2)_2$) and sodium hypophosphite (NaH_2PO_2) were purchased from Aladdin Industrial All the chemical reagents used as received 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 Three-Dimensional Interconnected Network of np-CoP NWs

Typically, titanium plate was cleared by ultrasonic with acetone, ethanol and deionized water. While 4 mmol $Co(NO_3)_2.6H_2O$ and 20 mmol $CO(NH_2)_2$ were dissolved in 40 ml deionized water stirring for 15 min to form a clear solution. Then, it was transferred into a glassware with titanium plate substrate heating to 90 °C for 12 h. After cooled down to room temperature, the precursor was rinsed with deionized water several times in order to remove the free particle debris and the residual reactant. Finally, the precursor was annealed at 300 °C for 1 h in a crucible with 0.3 g of NaH_2PO_2 in Ar flow.

Characterizations

Powder X-ray diffraction (XRD) data were recorded on a RigakuD/MAX 2550 diffractometer. SEM measurements were made on a XL30 ESEM FEG microscope. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 microscopy (Tokyo, Japan). The BET surface area, pore volume and pore size were measured on a Quantachrome NOVA 1000 system at liquid N_2 temperature.

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 platinum wire as the counter electrode. In all measurements, SCE was used as the reference, and all the potentials reported in our work were vs. the reversible hydrogen electrode (RHE). The potential, measured against a SCE electrode, was converted to the potential versus RHE according to $E_{vs\ RHE} = E_{vs\ SCE} + E^{o}_{SCE} + 0.059pH$. For HER test in neutral environment (pH = 7), a phosphate buffer solution (1 M) was used as the electrolyte. LSVs were performed in the range from -1.2 V to -0.4 V vs. SCE. Durability test was also carried out by CVs but in the range from -1.0 to -0.6 V vs. SCE. While in base environment (pH 14), 1 M KOH solution was used as the electrolyte. LSVs were performed in the range from -1.6 V to -0.8 V vs. SCE. Durability test was also carried out by CVs but in the range from -1.4 to -0.8 V vs. SCE.

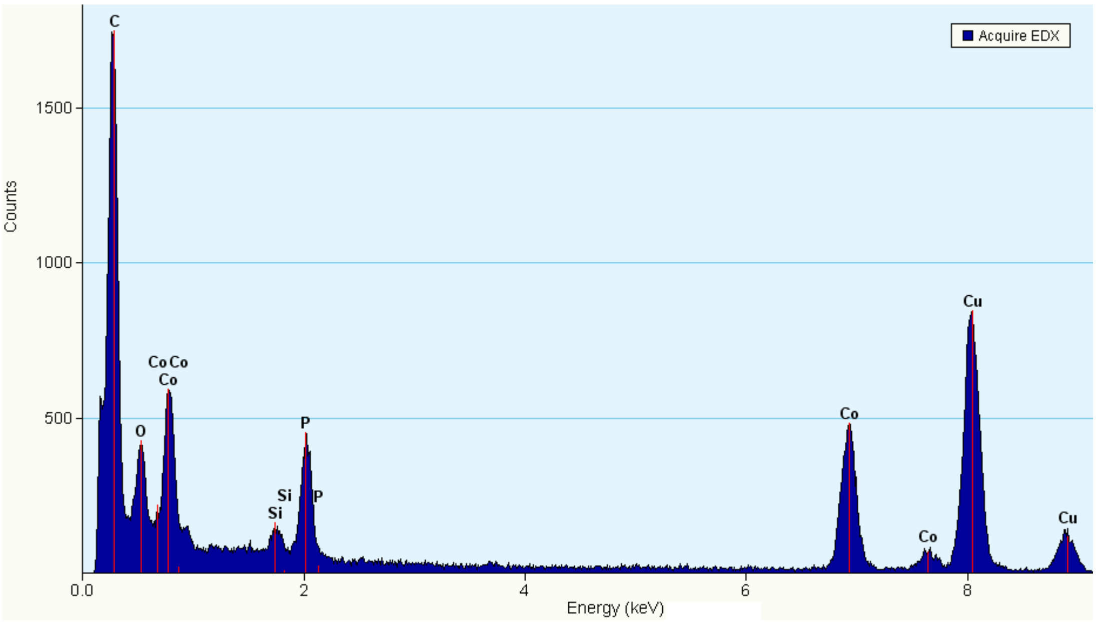

Fig. S1 EDS of the 3D interconnected network of np-CoPNWs.

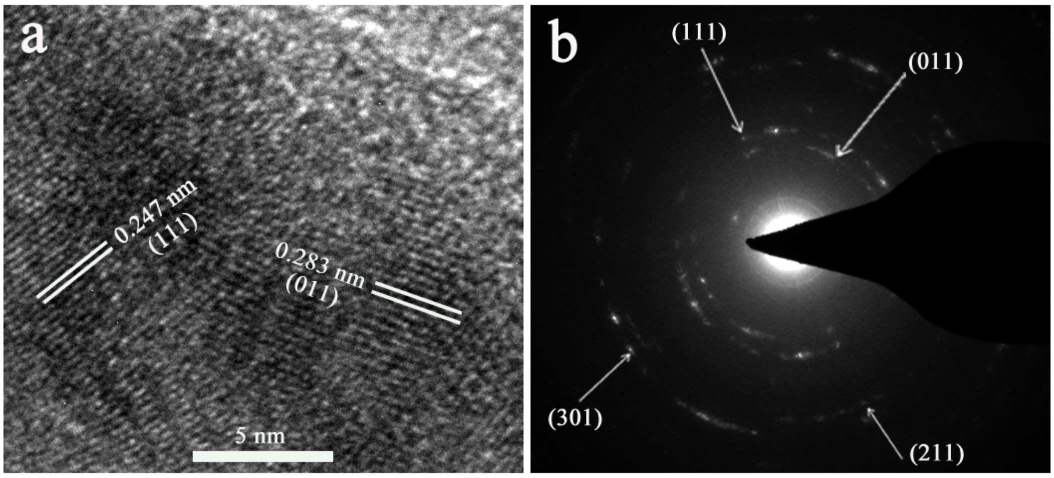

Fig. S2 HRTEM image of np-CoP NWs and selected area electron diffraction pattern from np-CoP NWs.

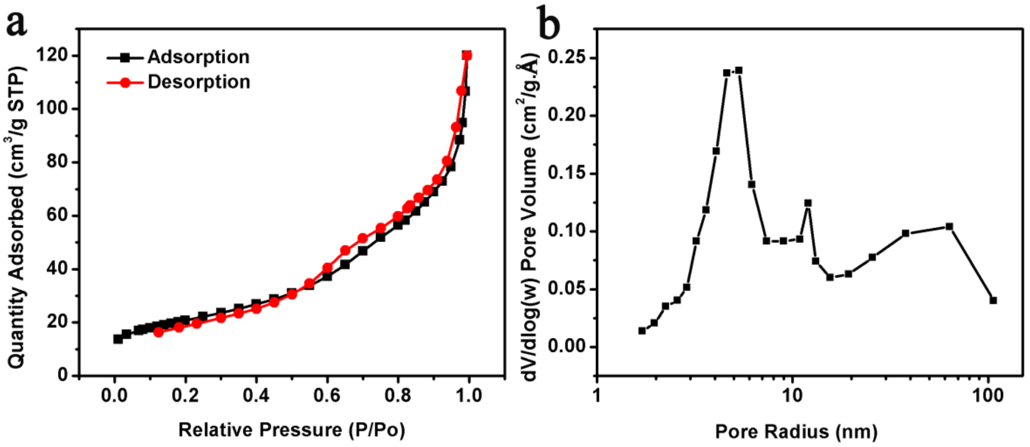

Fig. S3 (a) Nitrogen adsorption/desorption isotherm plot and (b) BJH pore-size distribution curve of np-CoP NWs.

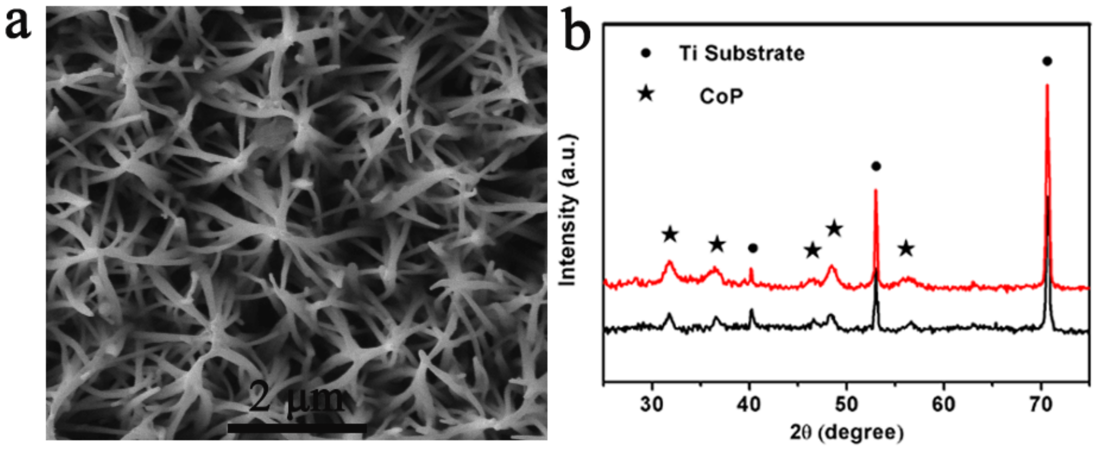

Fig. S4 (a) SEM image and (b) XRD patterns of np-CoP NWs/Ti before (black) and after (red) 3000 CV cycles in 0.5 M H_2SO_4solution.

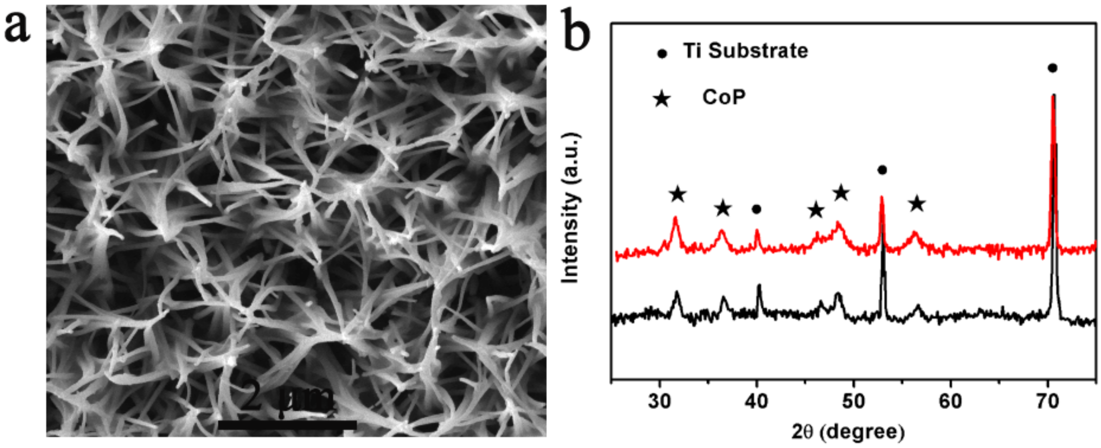

Fig. S5 (a) SEM image and (b) XRD patterns of np-CoP NWs/Ti before (black) and after (red) 1000 CV cycles in 1 M phosphate buffer solution.

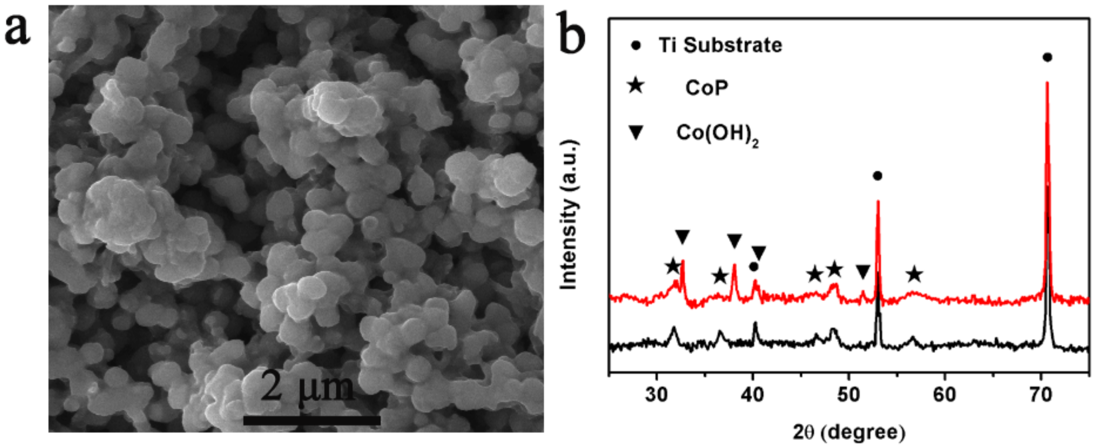

Fig. S6 (a) SEM image and (b) XRD patterns of np-CoP NWs/Ti before (black) and after (red) 100 CV cycles in 1 M KOH solution.

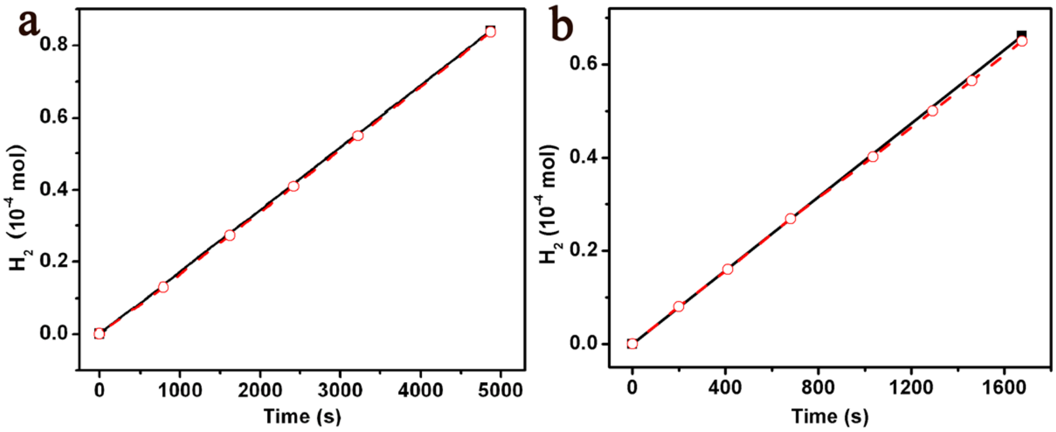

Fig. S7 The amount of theoretically calculated (solid) and experimentally measured (circle) hydrogen versus time for np-CoP NWs/Ti at an overpotential of 350 mV in (a) 1 M phosphate buffer solution and 300 mV in (b) 1 M KOH solution.

Table S1 Comparison of performances for HER catalysts under acidic conditions.

Catalyst	**Loading**	**Electrolytes**	**Current density (j)**	**Overpotential**	**Ref.**
Np-CoP NWs/Ti	0.8 mg cm^{-2}	0.5 M H_2SO_4	**5 mA cm^{-2}**	**48 mV**	This work
			10 mA cm^{-2}	**72 mV**	
			20 mA cm^{-2}	**95 mV**	
MoS_2/RGO	0.28 mg cm^{-2}	0.5 M H_2SO_4	10 mA cm^{-2}	150 mV	7b
MoS_2 film	0.06 mg cm^{-2}	0.5 M H_2SO_4	2 mA cm^{-2}	190 mV	7d
Exfoliated MoS_2 nanosheets	~	0.5 M H_2SO_4	10 mA cm^{-2}	187 mV	7e
NiMoN/C	0.25 mg cm^{-2}	0.1 M $HClO_4$	5 mA cm^{-2}	~220 mV	7f
W_2S	~	0.5 M H_2SO_4	10 mA cm^{-2}	225 mV	8b
Bulk MoB	2.5 mg cm^{-2}	1.0 M H_2SO_4	20 mA cm^{-2}	~240 mV	9
Bulk Mo_2C	1.4 mg cm^{-2}	1.0 M H_2SO_4	20 mA cm^{-2}	~240 mV	9
NiP/Ti	1 mg cm^{-2}	0.5 M H_2SO_4	20 mA cm^{-2}	130 mV	17a
			100 mA.cm^{-2}	180 mV	
FeP	0.28 mg cm^{-2}	0.5 M H_2SO_4	10 mA cm^{-2}	~240 mV	17c
CoP/Ti	0.9 mg cm^{-2}	0.5 M H_2SO_4	20 mA cm^{-2}	95 mV	18
	2 mg cm^{-2}	0.5 M H_2SO_4	20 mA cm^{-2}	85 mV	
CoP/CNT	0.29 mg cm^{-2}	0.5 M H_2SO_4	10 mA cm^{-2}	122 mV	19
CoP/CC	0.92 mg cm^{-2}	0.5 M H_2SO_4	20 mA cm^{-2}	100 mV	20b

Supplementary Movie

This movie shows np-CoP NWs/Ti operated at anoverpotential of 150 mV to drive HER in 0.5 M H_2SO_4 solution. Generated hydrogen gas is efficiently released from the electrode in the form of tiny bubbles.