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Supporting information

Improving the hydrogen evolution activity of Co_xP nanoparticles by hydrogenation

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Experimental details, Figure S1-S6 and Table S1

Experimental section

Catalyst preparation

In a typical process, 1.19 g of Co $(OH)_2$ and 1.33 g of $NaH_2PO_2 \cdot H_2O$ was grinded in a agate mortar, then the obtained mixture was calcinated in argon atmosphere at 250−400 ^oC for 3h. The collected product was dispersed ultrasonically into a 2.0 M HCl solution and kept on stirring for 12 h. A black powder was obtained after washed by deionized water for several times and dried in an oven at 100 ^oC overnight. Hydrogenation was performed on all as-prepared samples at 350 ^oC for 6h under pure hydrogen environments.

Characterizations

The crystal structure of products was characterized by a Rigaku Miniflex X-ray Diffractometer (XRD) with a CuKα (λ= 0.15418 nm) radiation source. The morphologies and structure of the samples were observed by transmission electron microscopy (TEM, FEI Tecnai F20 STEM) with the electron accelerating voltage of 200 kV. A small amount of powder sample dispersed in ethanol was dropped onto a thin holey carbon film, and dried overnight before TEM measurement. XPS data were collected using a Kratos Axis 165 X-ray photoelectron spectrometer with an Al/Mg dual-anode X-ray source, using a photon beam of 1486.6 eV.

All electrochemical measurements were carried out in a three-electrode system at room temperature. A Pt wire, an Ag/AgCl electrode, and 0.5 M H_2SO_4 were used as the counter electrode, reference electrode, and electrolyte, respectively. The working electrode was prepared by coating a mixture slurry of catalyst powder, carbon black

and polyvinylenedifluoride (weight ratio = 8:1:1) in 0.05 mL N-methyl-2-pyrrolidone solution on a titanium foil. The mass loading is about 0.7 mg cm^{-2} (catalyst loading ≈ 0.56 mg cm^{-2}). Linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} and electrochemical impedance spectroscopy (EIS) analysis using a 10 mV amplitude AC signal over a frequency range from 100 kHz to 10 mHz were performed on a electrochemical workstation. The commercial Pt/C was used as the state-of-the-art HER catalyst for comparison. All polarization curves were iR-corrected for an ohmic drop obtained from Nyquist plot. Reversible hydrogen electrode (RHE) calibration was carried out using Ag/AgCl as the reference electrode. The calibration was performed in the high purity hydrogen saturated 0.5 M H_2SO_4 electrolyte with a Pt wire as the working electrode. The long−term stability test was measured at a constant voltage over the duration of 6000 s.

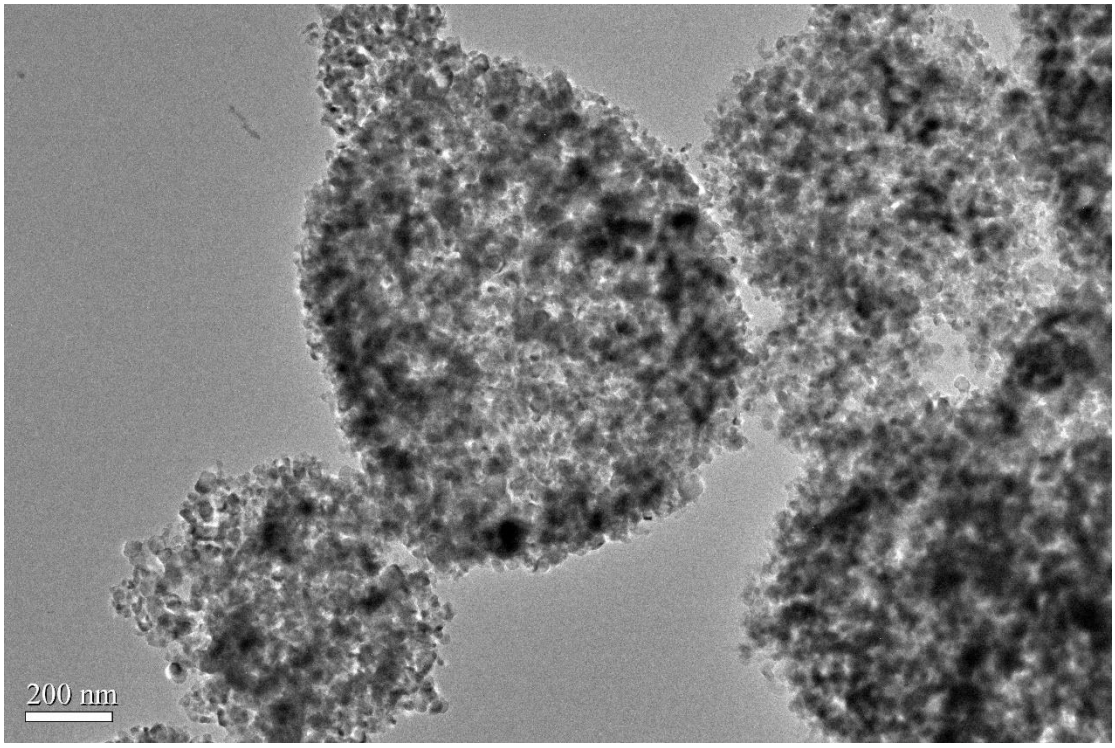

Fig. S1. TEM images of the pristine Co_xP nanoparticles.

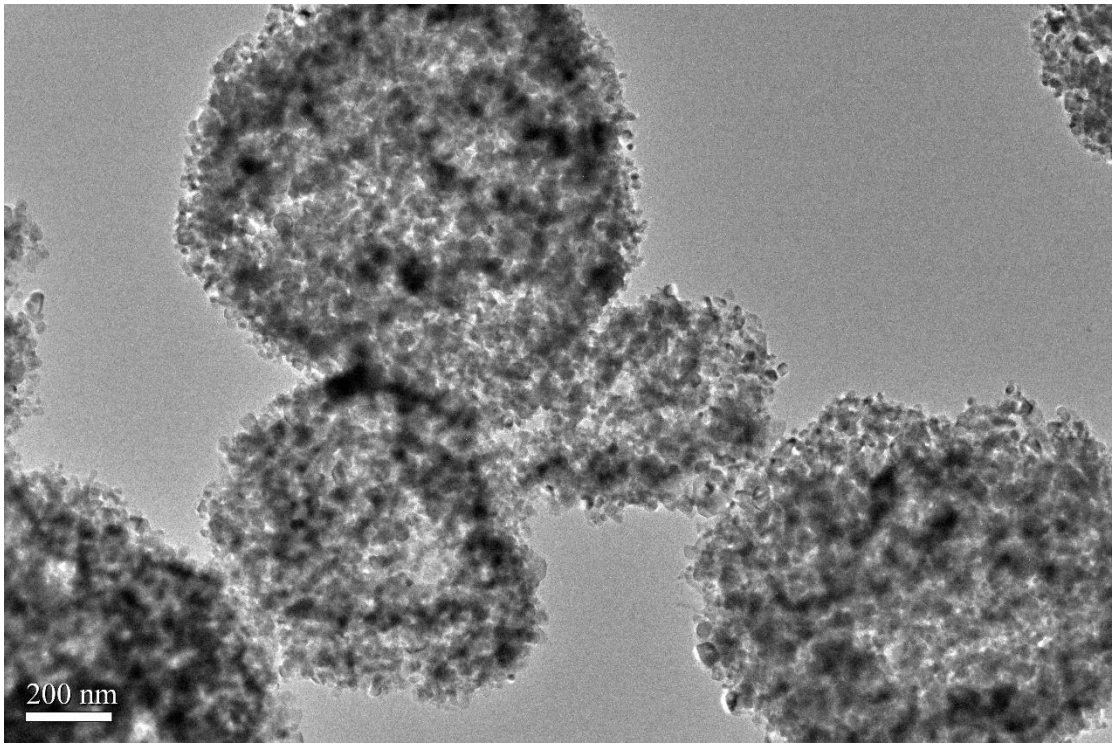

Fig. S2. TEM images of the pristine Co_xP nanoparticles.

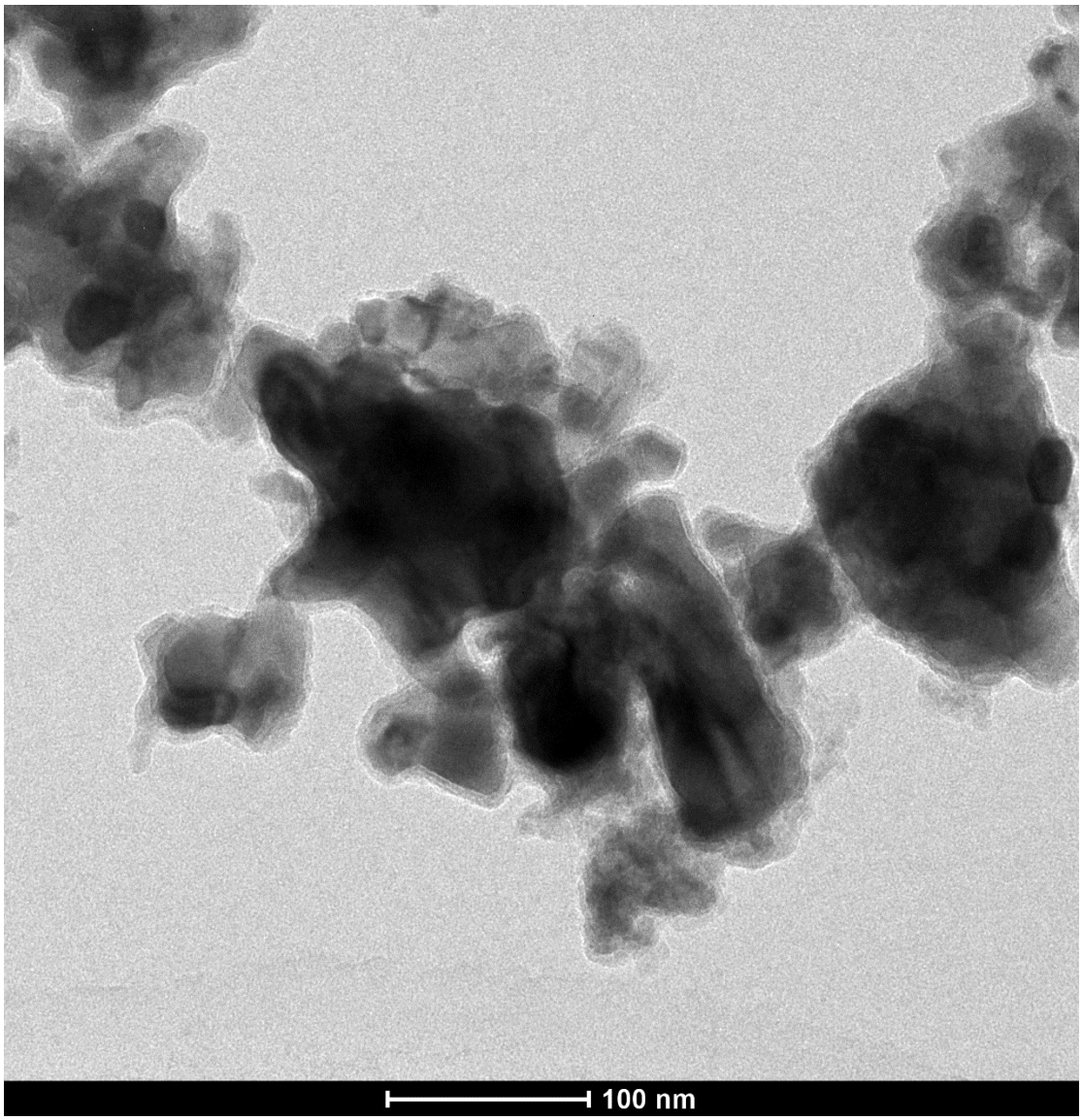

Fig. S3. TEM images of the hydrogenated Co_xP nanoparticles.

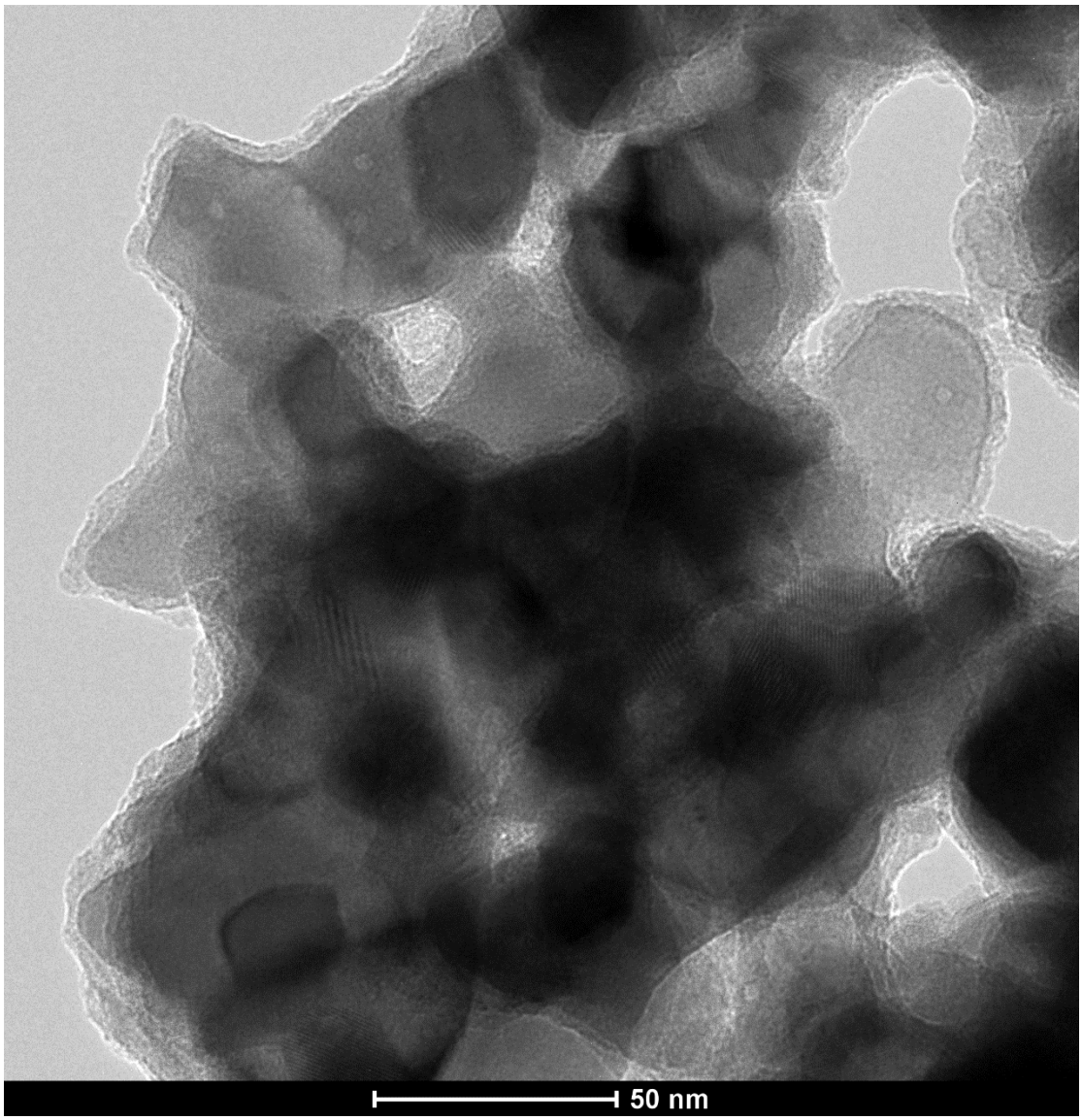

Fig. S4. TEM images of the hydrogenated Co_xP nanoparticles.

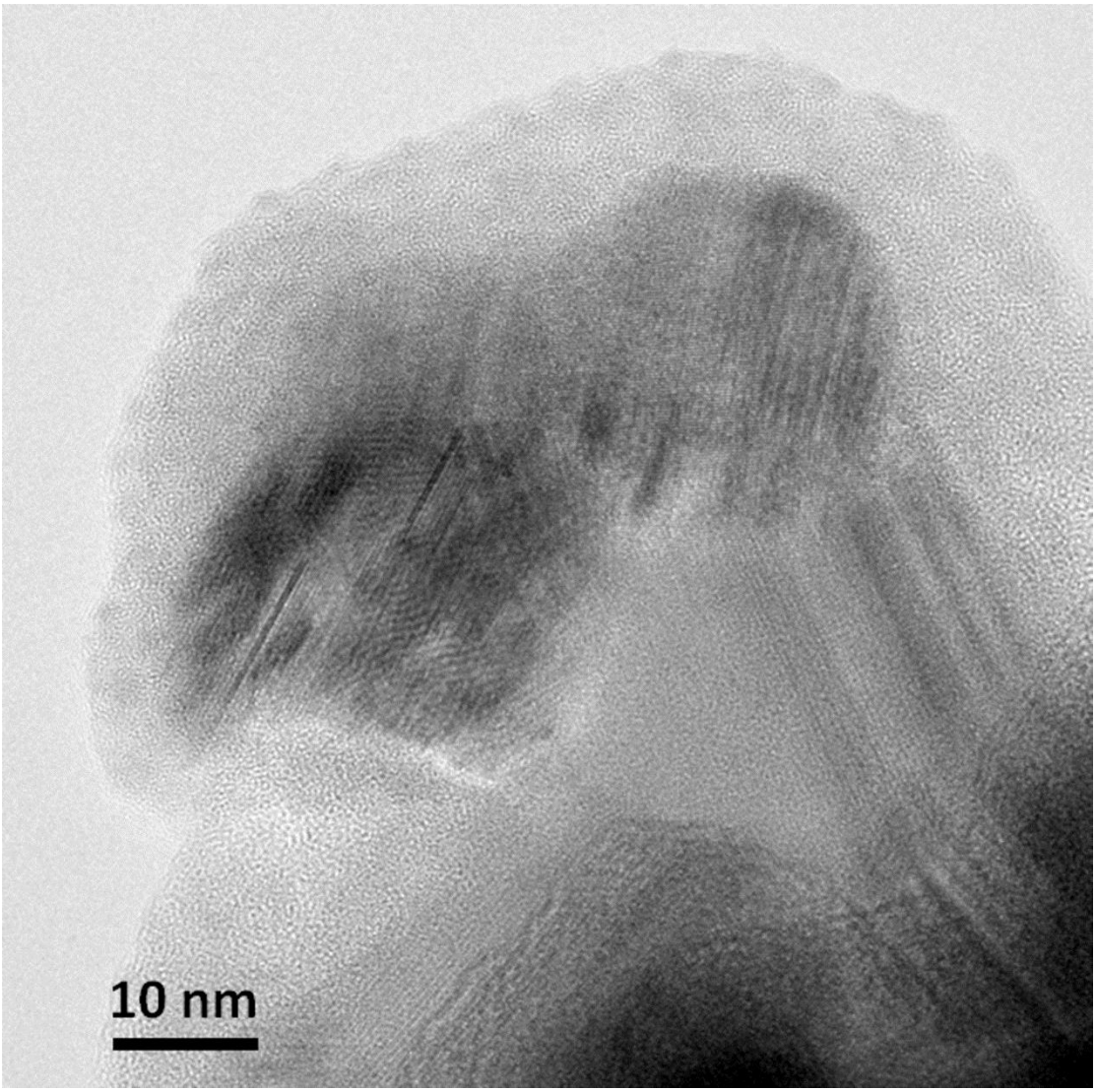

Fig. S5. HRTEM images of the hydrogenated Co_xP nanoparticles.

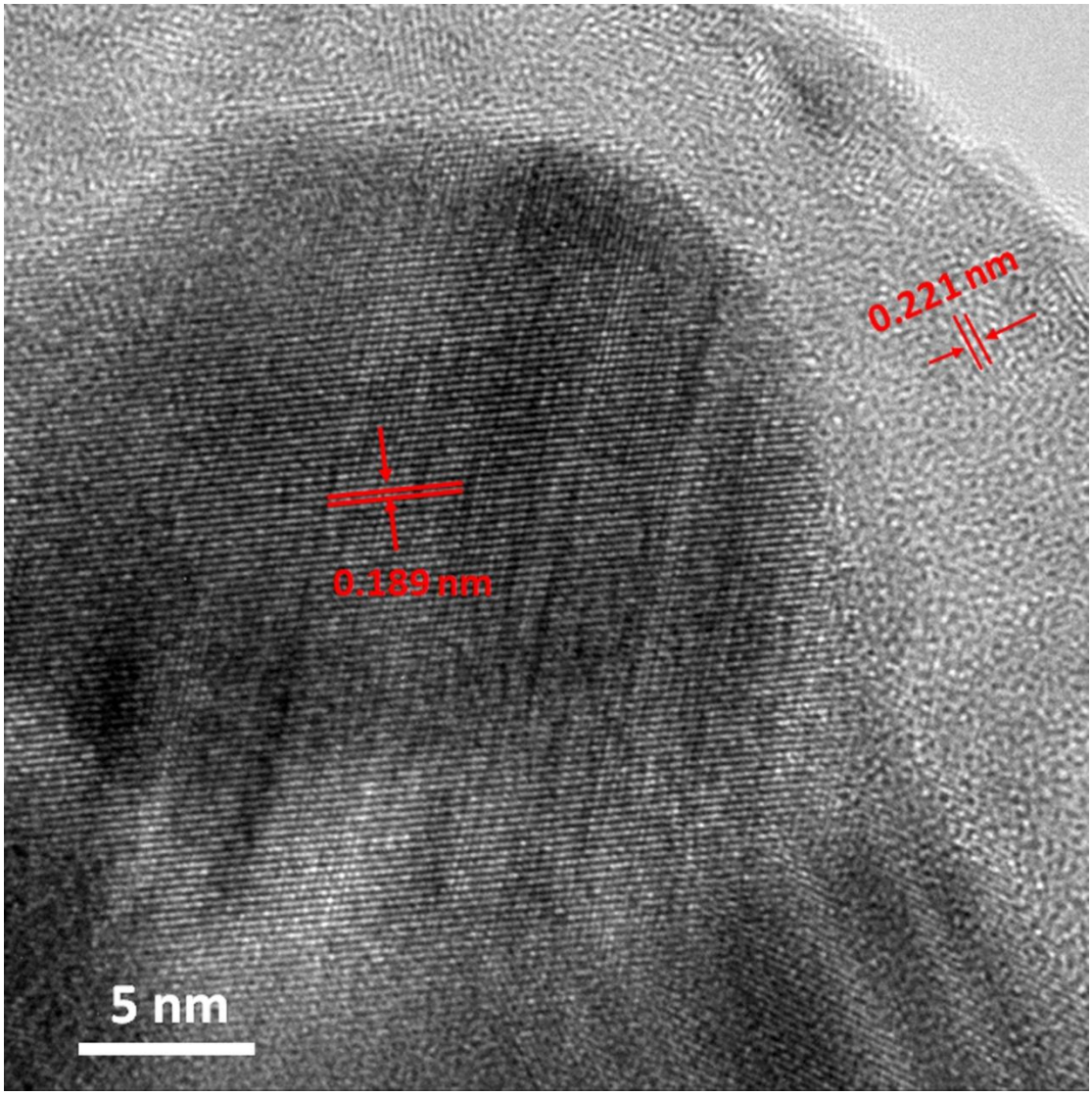

Fig. S6. HRTEM images of the hydrogenated Co_xP nanoparticles.

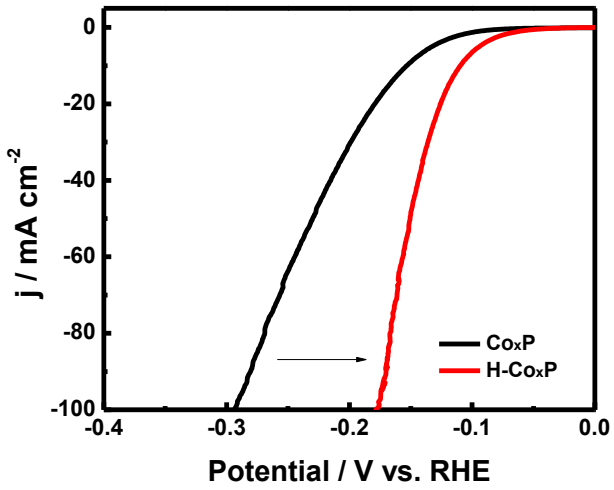

Fig. S7. Comparison of the polarization curves of the pristine and hydrogenated Co_xP ($H\text{-}Co_xP$) nanoparticles using a graphite electrode as the counter electrode.

Table S1. Comparison of the various HER catalysts at a current density of 10 mA cm^{-2} in 0.5 M H_2SO_4.

Catalyst	Electrolyte	η_{10} (mV)	Ref
H-Co_xP	0.5 M H_2SO_4	110	This work
Porous Co_2P/CoP	0.5 M H_2SO_4	150	14a
Co_2P	0.5 M H_2SO_4	134	13
CoP/carbon cloth	0.5 M H_2SO4	67	14e
CoP/carbon	0.5 M H_2SO_4	122	14c
Porous FeP	0.5 M H_2SO_4	240	16
MoP	0.5 M H_2SO_4	140	17
W_2P	0.5 M H_2SO_4	161	18
Cu_3P	0.5 M H_2SO_4	143	26
N,P-doped graphene	0.5 M H_2SO_4	420	27
MoS_2	0.5 M H_2SO_4	215	28
MoS_x	1.0 M H_2SO_4	215	29
MoS_x-graphene	0.5 M H_2SO_4	180	30
WS_2	0.5 M H_2SO_4	220	31
WSe_2	0.5 M H_2SO_4	230	32
$CoSe_2$	0.5 M H_2SO_4	193	33
$MoS_{2(1-x)}Se_{2x}$	0.5 M H_2SO_4	161	34
$WS_{2(1-x)}Se_{2x}$	0.5 M H_2SO_4	260	35