

Supporting information

One-pot, large-scale, facile synthesis of CoxP nanocatalysts for electrochemical hydrogen evolution

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2. Experimental section

2.1 Catalyst preparation

In a typical process, 1.19 g of Co (OH)₂ and 1.33 g of Na₂HPO₂·H₂O was grinded in a agate mortar, then the obtained mixture was calcinated in argon atmosphere at 250–400 °C 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 °C overnight. Hydrogenation was performed on all as-prepared samples at 350 °C for 6h under pure hydrogen environments.

2.2 Characterizations

The crystal structure of products was characterized by a Rigaku Miniflex X-ray Diffractometer (XRD) with a CuK α (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 H₂SO₄ 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 polyvinylidene fluoride (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 $\approx 0.56 \text{ mg cm}^{-2}$). 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 $0.5 \text{ M H}_2\text{SO}_4$ electrolyte with a Pt wire as the working electrode. The long-term stability test was measured at a constant voltage over the duration of $15,000 \text{ s}$. The Faradaic efficiency was calculated by comparing the charge with the amount of hydrogen and oxygen produced with a gas chromatography equipped with a thermal conductivity detector (TCD).

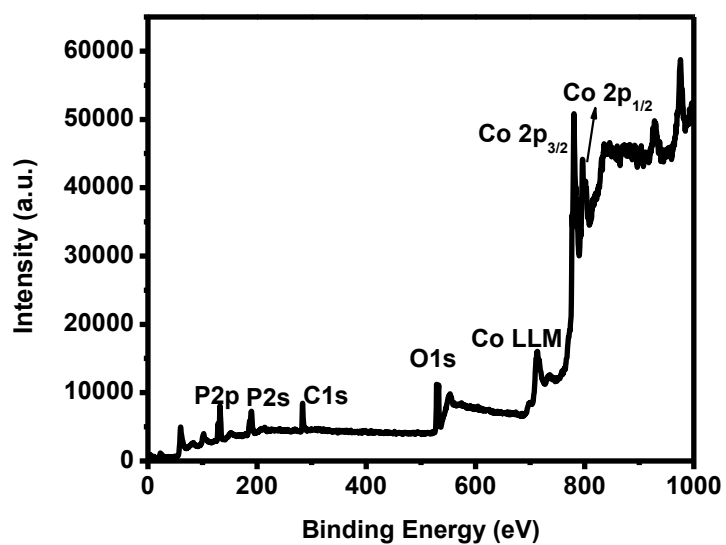


Fig. S1. The XPS survey of Co_xP nanoparticles.

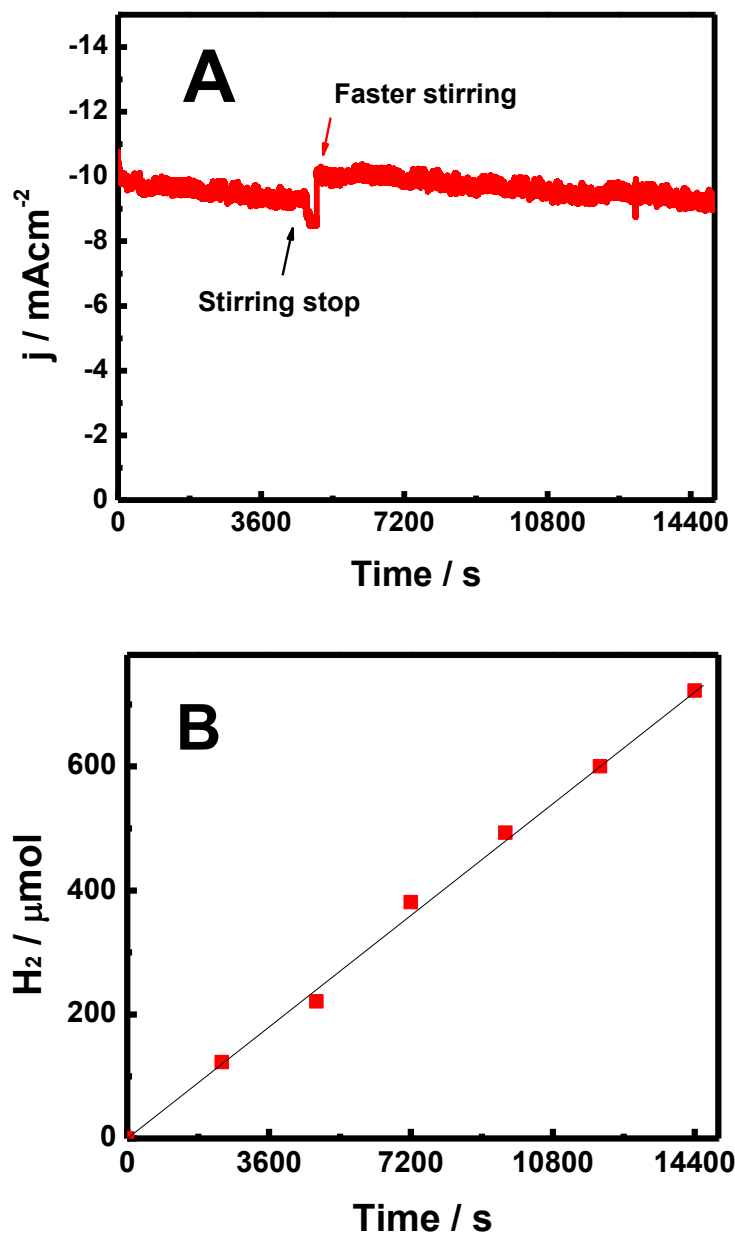


Figure S2. (A) Current–time characteristics of Co_xP for the stability test at an overpotential of 150 mV, and (B) the corresponding H_2 produced.