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Supporting Information
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CoP As An Acid-Stable Active Electrocatalyst For The Hydrogen-Evolution Reaction: Electrochemical Synthesis, Interfacial Characterization And Performance Evaluation

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Physical Characterization

Grazing Incidence X-Ray Diffraction

Grazing incidence X-ray diffraction data was acquired with a Bruker D8 Discover diffractometer equipped with a Cu Kα source and a VÅNTEC-500 2-dimensional detector. The X-rays were collimated through a 0.1 mm diameter capillary and incident at fixed grazing angle of 0.3° above the plane of the sample while the detector was swept to encompass the full 2θ range.

Faradaic Efficiency Calculation

Gas collection: CoP (electrodeposited on Cu) and an iridium film were epoxied into two chambers of an airtight plastic chassis and separated by a Nafion membrane. Electrodes were operated in 0.50 M sulfuric acid electrolyte with a constant current of 10 mA. Hydrogen and oxygen were collected in two eudiometers and gas volume was measured at regular intervals, as shown in Figure S2. For more than 5 hours of operation, during which 162 Coulombs of charge passed between the electrodes, a faradaic efficiency of 100% was observed for both cathodic and anodic reactions with a 2:1 ratio of hydrogen to oxygen produced.

Atomic Force Microscopy

Atomic force micrographs were collected with a Bruker Dimension Icon microscope with a Nanoscope V controller in tapping operation.

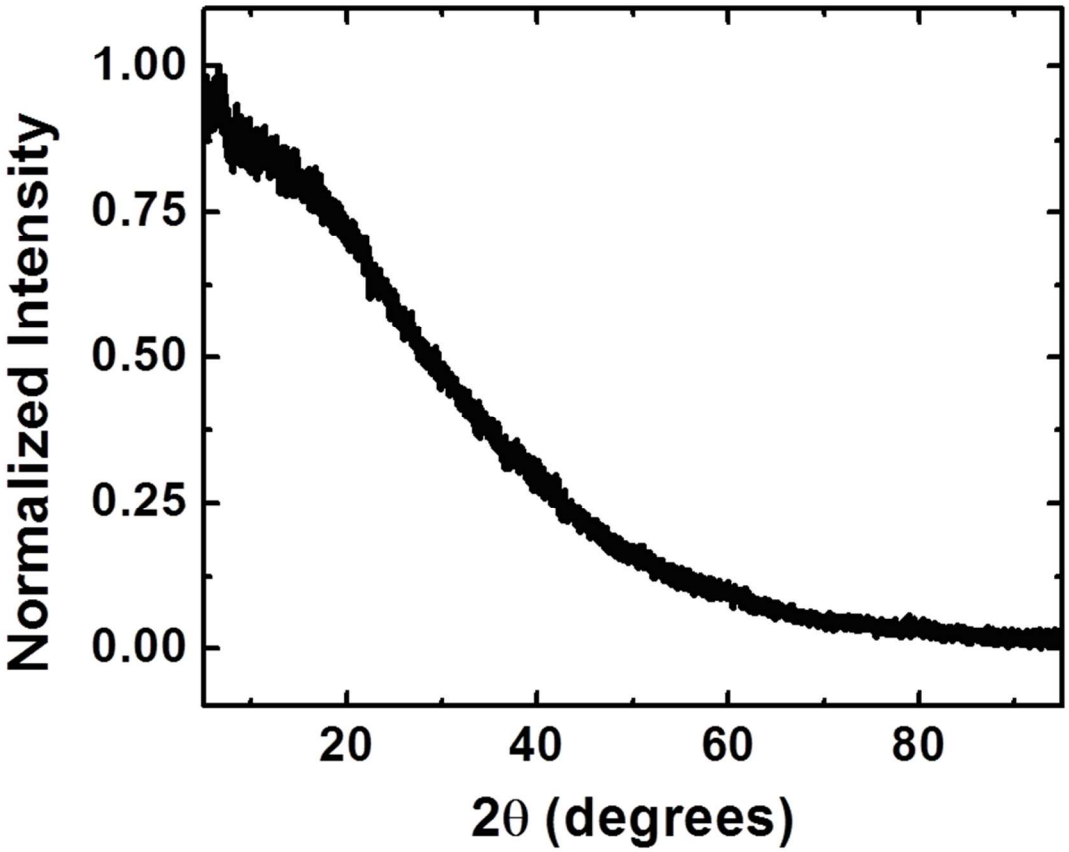

Figure S1. Grazing incidence X-ray diffraction pattern of cobalt phosphide thin film. The absence of distinct reflections suggests a lack of crystallinity.

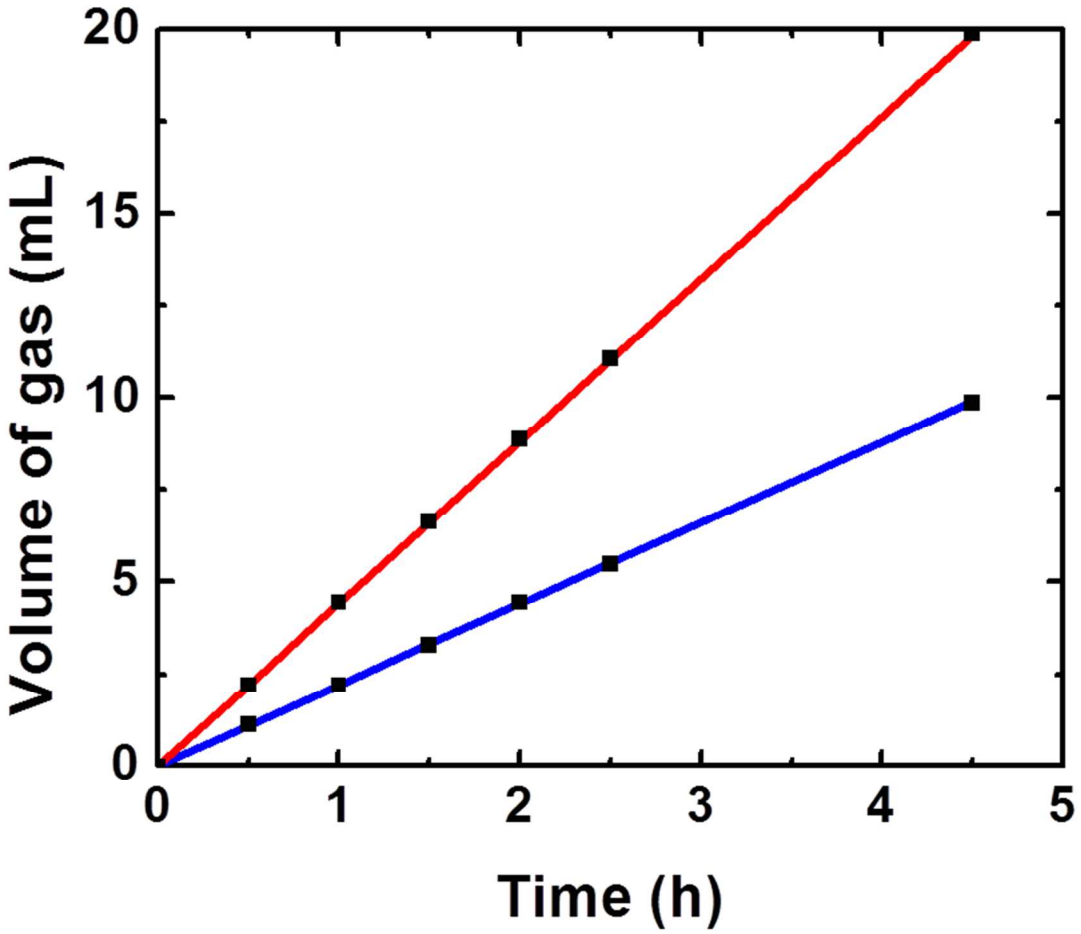

Figure S2. Faradaic efficiency of CoP cathode and Ir anode in a two-electrode configuration. Current density was held at 10 mA and gas products were collected in two eudiometers. Volume of H_2 (red) and O_2 (blue) was recorded over regular intervals, and overlaid with expected gas production over time.

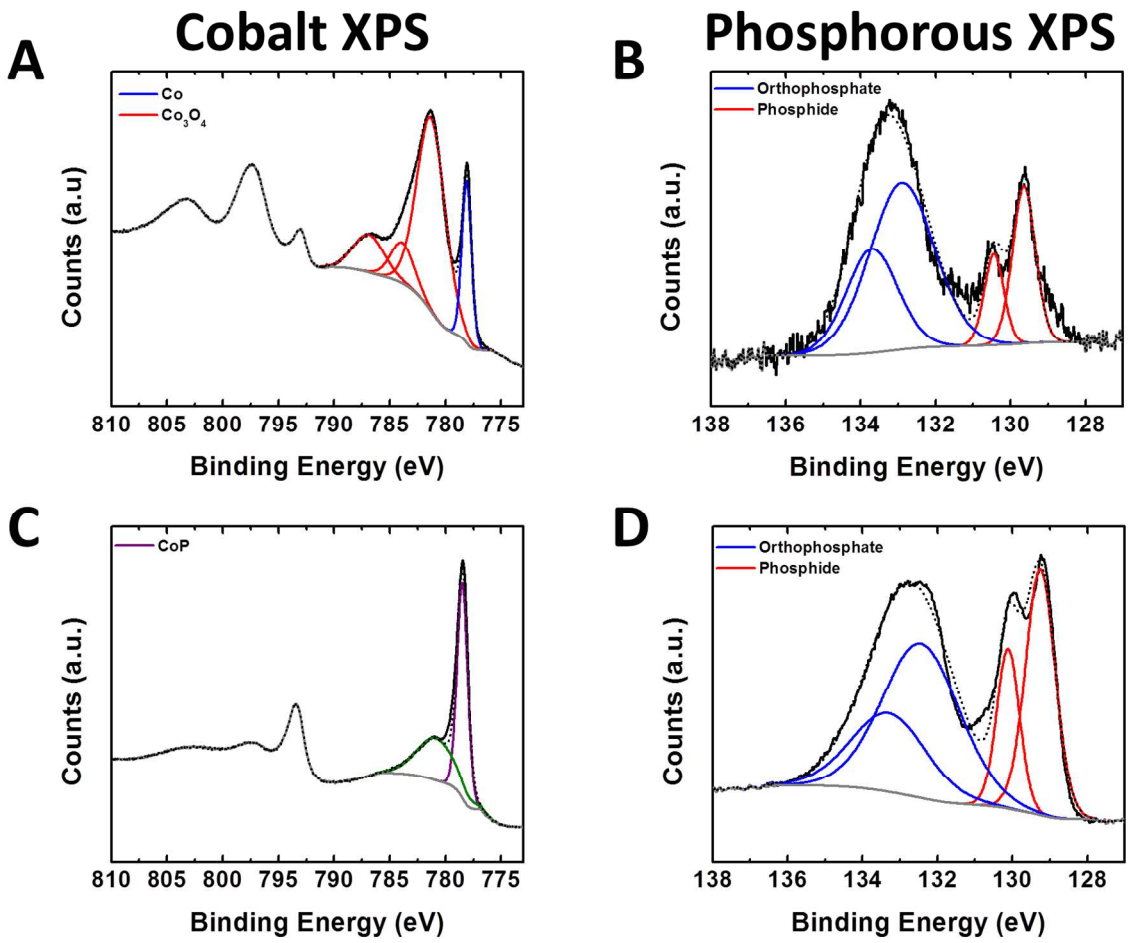

Figure S3. High-resolution X-ray photoelectron spectra of (A) Co 2p region of the as-deposited thin film; (B) P 2p region of the as-deposited thin film; (C) Co 2p region after voltammetry; (D) P 2p region after voltammetry.

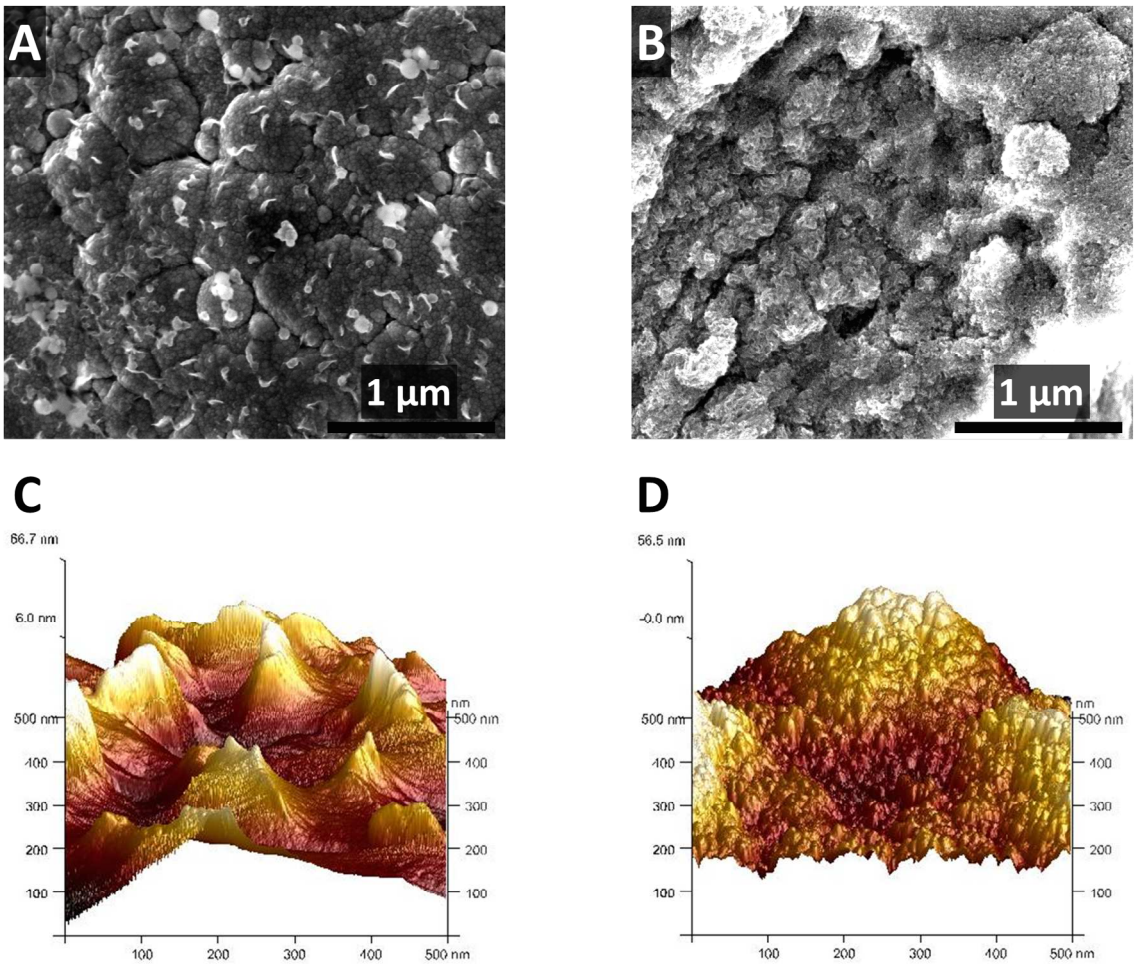

Figure S4. Scanning-electron micrographs of the films before (A) and after (B) voltammetry; Atomic force micrographs of the films before (C) and after (D) voltammetry.

	Co	C	O	P
As-Deposited	15%	34%	49%	2%
After Voltammetry	12%	33%	43%	12%

Table S1. Table of atomic abundances derived from the quantitative analysis of XPS peaks for the as-deposited film and resultant material after voltammetry.

	Orthophosphate	Phosphide
As-Deposited	75%	25%
After Voltammetry	62%	38%

Table S2. Ratio of phosphorous oxidation states derived from the quantitative analysis of XPS peaks for the as-deposited film and resultant material after voltammetry.