

Supporting Information for:

OPERANDO SPECTROSCOPIC ANALYSIS OF COP FILMS
ELECTROCATALYZING THE HYDROGEN-EVOLUTION REACTION

FADL H. SAADI^{†,‡,¶}, AZHAR I. CARIM^{§,¶}, WALTER S. DRISDELL^{‡,#}, SHERAZ GUL[#], JACK H.
BARICUATRO[‡], JUNKO YANO^{*,‡,#}, MANUEL P. SORIAGA^{*,‡} AND NATHAN S. LEWIS^{*,‡,§,¶,⊥}

[†]Division of Engineering and Applied Sciences

[‡]The Joint Center for Artificial Photosynthesis

[§]Division of Chemistry and Chemical Engineering

[¶]Kavli Nanoscience Institute

[⊥]Beckman Institute

California Institute of Technology

Pasadena, CA 91125

[#]Molecular Biophysics and Integrated Bioimaging Division

Lawrence Berkeley National Laboratory

Berkeley, CA 94720

[¶]These authors contributed equally (FHS and AIC)

*Corresponding Authors: msoriaga@caltech.edu, jyano@lbl.gov, nslewis@caltech.edu

S1. Contents

This document contains a description of the experimental methods utilized in this work (Sections S2), reference Raman data (Section S3) additional standard P K-edge X-ray absorption spectra (Section S4), and a list of associated references (Section S5).

S2. Experimental Methods

Materials and Chemicals All materials and chemicals were used as received from the indicated suppliers without additional purification. H₂O with a resistivity $\geq 18.2 \text{ M}\Omega\cdot\text{cm}$ (Barnstead Nanopure System) was used throughout.

General Electrochemical Details Electrochemistry was performed using a Bio-Logic SP-200 potentiostat in conjunction with a three-electrode electrochemical cell. A saturated calomel electrode (SCE; CH Instruments) was used as the reference electrode. Electrocatalyst films were electrodeposited onto Cu substrates using an aqueous solution (pH = 5) of 0.20 M CoCl₂·6H₂O (99.998%, Alfa Aesar), 0.30 M NaPO₂H₂·H₂O (97+%, Alfa Aesar), 0.15 M H₃BO₃ (99.99%, Alfa Aesar), and 0.10 M NaCl (99.0+%, Macron Fine Chemicals). Deposition was effected by biasing the Cu electrode potentiostatically at -1.200 V vs. SCE for 0.50 min at room temperature. All analyses were performed in an aqueous solution of 0.500 M H₂SO₄ (A.C.S. Reagent, J. T. Baker). The uncompensated cell resistance (R_u) was determined from a single-point electrochemical impedance measurement obtained by applying a sine-wave modulated potential with an amplitude of 20 mV at a modulation frequency of 100 kHz centered at the open-circuit potential of the cell. Applied potentials during catalyst analysis were dynamically corrected for an uncompensated resistance that was 85% of the value of R_u .

Voltammetric Analysis A single-compartment cell that contained a graphite rod counter electrode (99%, Sigma-Aldrich) was utilized for deposition and analysis. Copper disks with a 5 mm diameter and 4 mm thickness (99.999%, Alfa Aesar) that had been mounted in PTFE rotating disk electrode tips (Pine Research Instrumentation) were utilized as catalyst substrates for the voltammetric experiments. The tips were mounted on a rotator, and the tips were suspended such that the Cu surface was immersed in deposition solution. After deposition of the

electrocatalyst film, the electrodes were removed from the cell, and the electrodes and the cell were rinsed with H₂O. The cell was then refilled with 0.500 M H₂SO₄ electrolyte, and the electrodes were replaced. Voltammetric data were then obtained by cycling the potential between -0.266 V and -0.406 V vs. SCE at a scan rate of 1 mV s⁻¹.

Raman Spectroscopy Raman spectra were collected with a Renishaw inVia Raman microprobe equipped with a Leica DM 2500 M microscope, a Leica N Plan L 50x objective (numerical aperture = 0.50), a 1800 lines mm⁻¹ grating, and a CCD detector configured in a 180° backscatter geometry. A 532 nm diode-pumped solid-state (DPSS) laser (Renishaw RL532C50) was used as the excitation source and a 1.58 mW radiant flux was incident on the surface of the sample. A $\lambda/4$ plate was used to circularly polarize the incident excitation. No polarizing collection optics were used. Square Cu foil sections (99.9999%, Alfa Aesar) \sim 1 cm² in area were utilized as catalyst substrates for Raman experiments. Single-compartment O-ring compression cells that confined the contact area between the electrolyte and the Cu foil to a circular area of 0.1 cm², and graphite rod counter electrodes, were used for deposition and analysis. After deposition of an electrocatalyst film, the Cu foil section was removed from the deposition cell, rinsed with H₂O, and dried under a stream of N₂(g). *Ex-situ* Raman spectra were then acquired. The electrocatalyst-coated Cu foil was then placed in the analysis cell along with 0.500 M H₂SO₄. The O-ring seal was located on the bottom wall of the analysis cell. The cell was equipped with a glass window on the top face that enabled *in-situ* and *operando* collection of Raman signals. Raman spectra were acquired *in-situ* after solution was added to the cell. The electrocatalyst film was then conditioned by cycling the potential 10 times between -0.266 V and -0.406 V vs. SCE at a scan rate of 15 mV s⁻¹. After conditioning, Raman spectra were then

obtained under *operando* conditions by acquiring spectra while the electrode was under potentiostatic control.

X-ray Absorption Spectroscopy Co K-edge X-ray absorption spectra (XAS), including both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data, were obtained at Beamline 7-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory. Monochromatic incoming radiation was obtained using a Si(220) double crystal that had been detuned to 50% of the flux maximum at the K-edge, to attenuate higher harmonics. The incident beam intensity was monitored by a N₂-filled ionization chamber that was positioned between the source and the sample. The fluorescence signal was collected at 90° from the source propagation vector by use of a 30-element Ge detector (Canberra Industries). P K-edge XAS measurements were performed at Beamline 14-3 at the SSRL. Monochromatic X-rays were produced using a Si(111) double crystal. The incident radiation intensity was monitored via a He-filled ionization chamber that was positioned between the source and the sample. The fluorescence signal was collected at 90° from the source propagation vector by use of a Vortex 4-element silicon drift detector (Hitachi High-Technologies Science).

Ex-situ Co K-Edge XAS of Co (99.995%, Alfa Aesar) and CoO (99.998%, Alfa Aesar) and P K-Edge XAS of K₃PO₄·7H₂O (98%, VWR), NaPO₂H₂·H₂O (99%, Sigma) and single-crystal GaP were acquired as standards. Powder standards were diluted with BN to minimize overabsorption effects. P K-edge XAS data were acquired under a He ambient to prevent atmospheric X-ray attenuation.

3 mm square, 0.5 μm thick Si₃N₄ membranes, enclosed by a 10 mm square Si frame, were utilized as substrates that were transparent to X-Rays. Electron-beam evaporation at a

deposition rate of 2 \AA s^{-1} at a base pressure of 5×10^{-6} Torr and a substrate temperature of $100 \text{ }^\circ\text{C}$ was used to deposit a 2 nm thick Ti adhesion layer and a 100 nm Cu film on one side of the framed Si_3N_4 membranes. A two compartment H-cell was utilized for deposition and analysis,^{1,2} and contained a porous glass frit to divide the two compartments. An Ir foil (99.7%, Goodfellow) counter electrode was utilized and isolated in one of the two compartments, whereas the reference electrode was placed in the other compartment. The compartment that housed the reference electrode had a square opening. The framed, Cu-coated Si_3N_4 membranes were affixed to the cell in this location by use of epoxy, with the Cu-coated portion of the electrode facing into the cell (Loctite Instant Mix). After deposition of an electrocatalyst film, the counter and reference electrodes were removed from the cell, and then the electrodes and the cell were rinsed with H_2O . *Ex-situ* XAS data were then acquired from the electrocatalyst films. During XAS acquisition, the excitation X-rays were directed at 45 degrees relative to the exposed Si_3N_4 face. The X-rays therefore entered the cell through the back of the catalyst film and provided a bulk probe of the entire CoP film thickness. For the P K-edge XAS experiments, the entire cell was enclosed in a He-filled bag to prevent atmospheric X-ray attenuation. After collection of the *ex-situ* spectra, the cell was refilled with 0.500 M $\text{H}_2\text{SO}_4(\text{aq})$ and the electrodes were replaced. The CoP film was then conditioned by cycling the potential 10 times between -0.266 V and -0.406 V vs. SCE at a scan rate of 15 mV s^{-1} . After conditioning, XAS data were then obtained under *operando* conditions while the electrode was under potentiostatic control.

X-ray absorption spectra were subjected to baseline correction and intensity normalization using the Athena software package based on IFEFFIT.^{3,4} For the Co K-edge EXAFS data, the background was fit using a five-domain cubic spline and the background was

then removed from the analyzed data. The resulting oscillations were plotted in k-space and then for analysis were Fourier-transformed into real space.

S4. Reference Raman Data

Figure S1a presents an *ex-situ* Raman spectrum acquired from crystalline CoP nanoparticles synthesized as described in previous work.⁵ The strong scatter at higher frequencies is likely due to organic residue from the wet nanoparticle synthesis. Figure S1b presents an expanded view of the low frequency part of the spectrum presented in Figure S1a. The observed Raman scatter in this region is attributed to phonon coupling in the crystalline material.

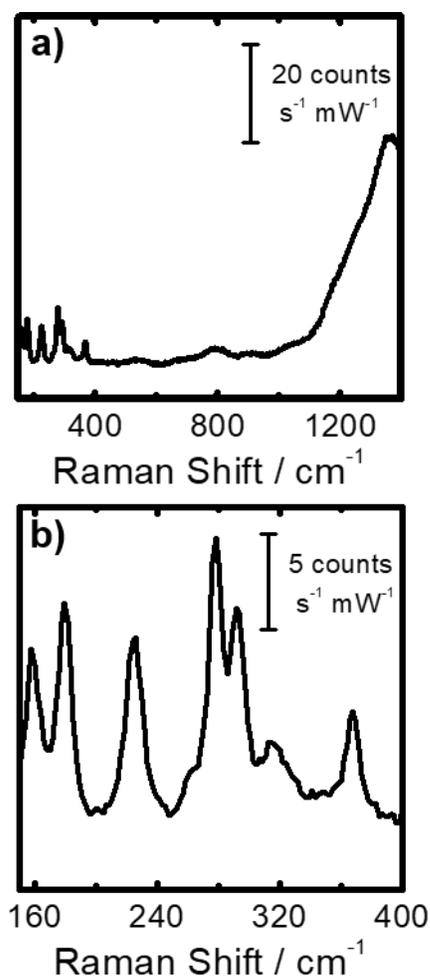


Figure S1. (a) *Ex-situ* Raman spectrum of crystalline CoP nanoparticles. (b) Same as (a) but expanded to highlight the low frequency scattering.

S4. Additional Standard P K-Edge X-Ray Absorption Spectra

Figure S2a presents the P K-edge X-ray absorption near-edge structure (XANES) spectrum for a K_3PO_4 standard material. Analogously, Figure S2b-d presents the first, second and third sequential spectra acquired from a NaPO_2H_2 material. Figure S2e presents the spectrum of a GaP standard material. Unlike with the K_3PO_4 and GaP standards, the spectra acquired from the NaPO_2H_2 standard evolved with each sequential spectral acquisition. A feature at 2149.4 eV was observed via the first spectral acquisition from the NaH_2PO_2 material. This feature was suppressed in the later spectra, whereas features at 2144.9 eV and 2152.2 eV appeared and increased in intensity. This behavior is consistent with beam-induced decomposition of the standard material to form a phosphate species (2152.2 eV) and a phosphide species (2144.9 eV).

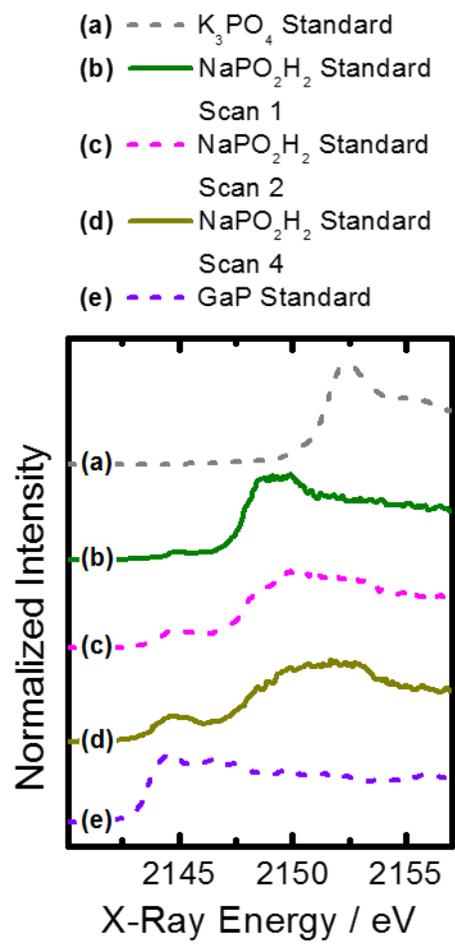


Figure S2. P K-edge X-ray absorption near edge structure (XANES) spectra of standard materials. (a) K_3PO_4 standard. (b)-(d) First, second and fourth sequential spectra acquired from a $NaPO_2H_2$ standard. (e) GaP standard.

S5. References

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