

Electrocatalytic Hydrogen Evolution Using Amorphous Tungsten Phosphide Nanoparticles

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(Reference numbers refer to those documented in the main text)

Supplementary Figures

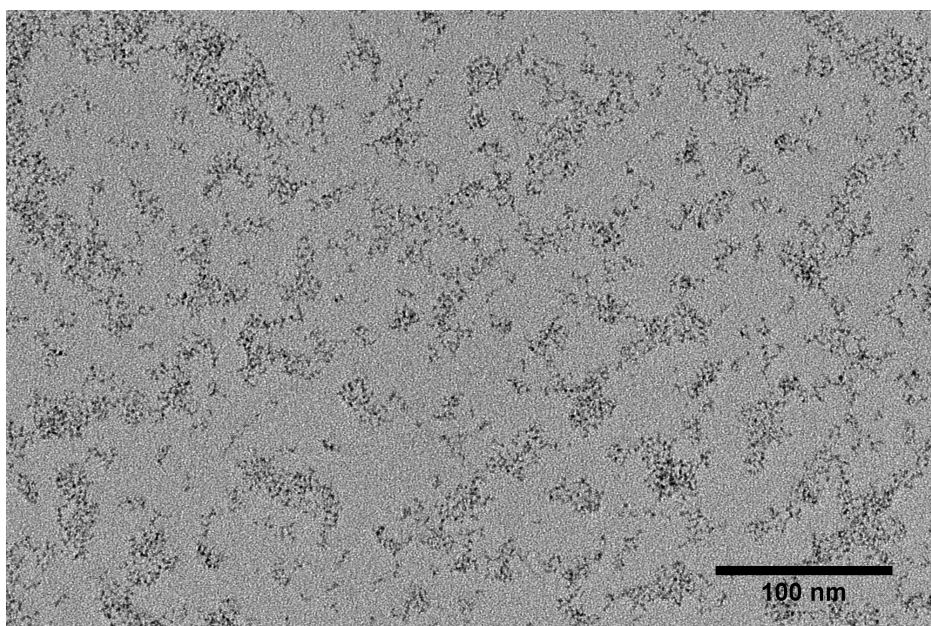


Figure S1. TEM image (wide area) of the as-synthesized amorphous WP nanoparticles.

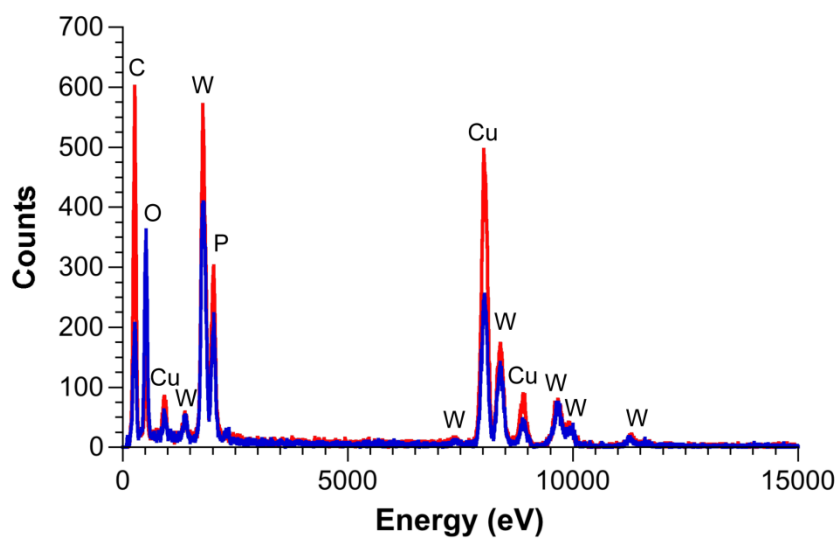


Figure S2. EDS spectra of the amorphous WP nanoparticles as-synthesized (red), as well as after annealing under $\text{H}_2(5\%)/\text{Ar}(95\%)$ at 450°C (blue).

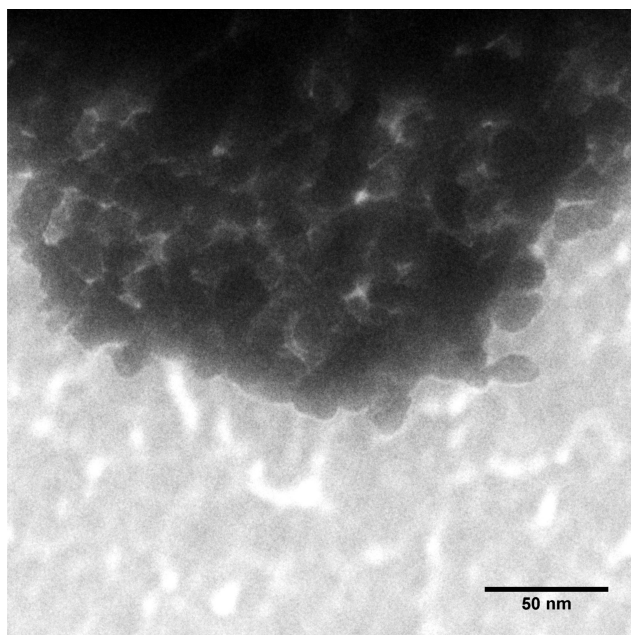


Figure S3. TEM image of amorphous WP nanoparticles after annealing under $\text{H}_2(5\%)/\text{Ar}(95\%)$ at 450°C .

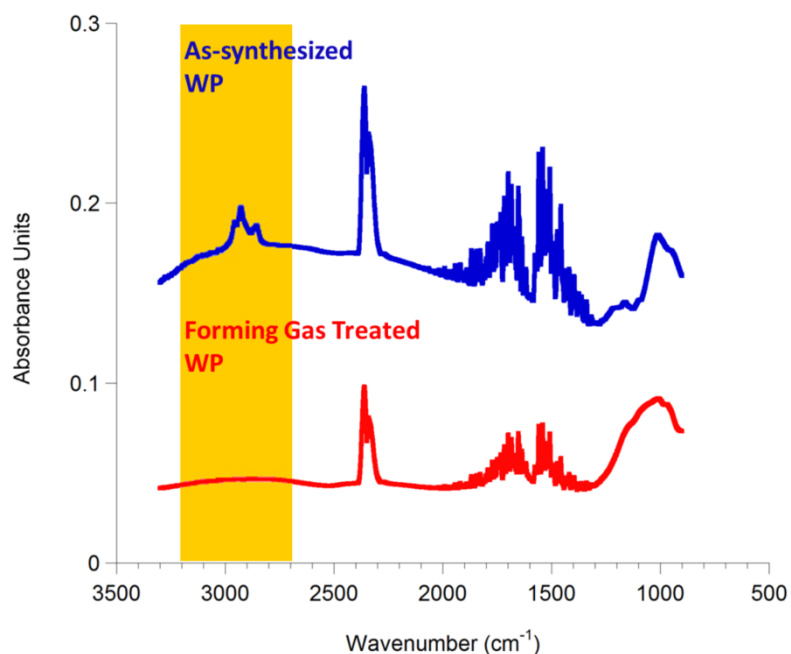


Figure S4. DRIFT spectra of the amorphous WP nanoparticles as-synthesized (top) and after heating to 450 °C in H₂(5%)/Ar(95%).

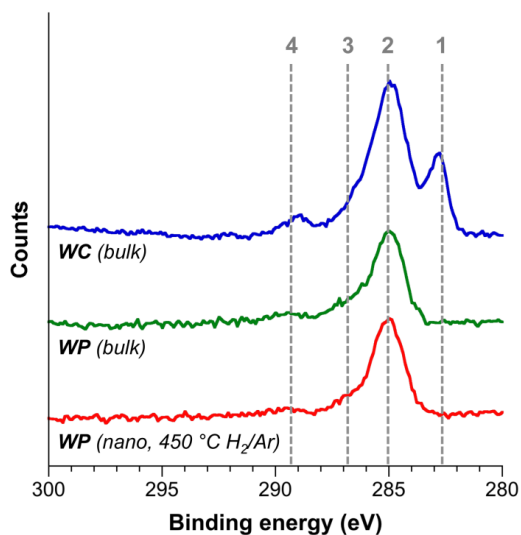


Figure S5. XPS spectra showing the C 1s region for the amorphous WP nanoparticles, along with bulk WC and bulk WP (the sample annealed at 800 °C) for comparison. The dashed numbered lines correspond to the following peak assignments: metal carbide (#1), adventitious carbon (#2), C-O (#3), and carbonate (#4). The WP C 1s spectra contained no significant contribution from tungsten carbide type carbon (282.7 eV).

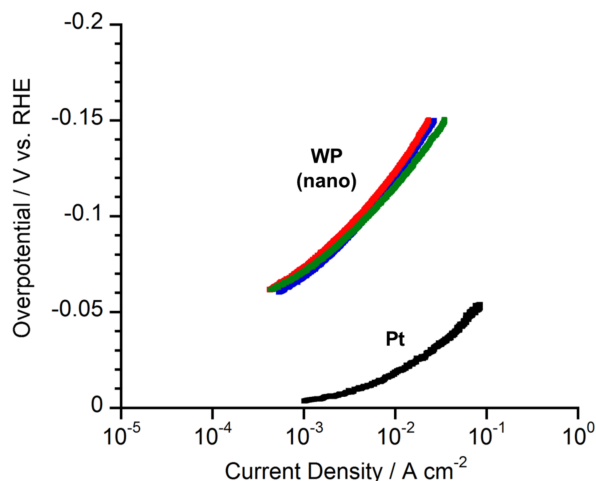


Figure S6. Tafel analysis [plots of overpotential vs. $\log [| (\text{current density}) |]$] for Pt and three distinct WP/Ti electrodes, using iR corrected data. For Pt, the extrapolated exchange current density was $4.6 \times 10^{-3} \text{ A cm}^{-2}$ and the slope of the linear region of the Tafel plot was $30 \text{ mV decade}^{-1}$. Both of these values are consistent with the behavior expected for Pt.^{9,20} For the amorphous WP nanoparticles, the extrapolated exchange current density was $4.5 \times 10^{-5} \text{ A cm}^{-2}$ and the slope of the linear region of the Tafel plot was $54 \text{ mV decade}^{-1}$. This suggests that the HER mechanism on WP is different from that on Pt. While the slopes of the Tafel plots for the WP/Ti electrodes do not match any of those expected for standard HER mechanisms (29 , 38 , or $116 \text{ mV decade}^{-1}$), they are comparable to Tafel slopes reported for other nanostructured catalysts in non-noble metal systems, including Ni_2P ($46 \text{ mV decade}^{-1}$),⁹ CoP ($50 \text{ mV decade}^{-1}$),¹¹ and WS_2 ($55 \text{ mV decade}^{-1}$).¹⁴

Experimental Details

Chemicals and Materials. Tungsten hexacarbonyl [99%, $\text{W}(\text{CO})_6$, Strem Chemicals, Lot #21669500], squalane [98%, $\text{C}_{30}\text{H}_{62}$, Alfa-Aesar, Lot #10169326], trioctylphosphine [tech. 90%, $\text{P}(\text{C}_8\text{H}_{16})_3$, Sigma-Aldrich, Lot #SHBC8966V], titanium foil [99.7%, 0.25 mm thickness], and sulfuric acid [99.999%, Sigma-Aldrich] were used as received. High-quality colloidal Ag paint was purchased from SPI Supplies and two-part epoxy [HYSOL 9460] was purchased from McMaster-Carr.

Synthesis of Amorphous Tungsten Phosphide Nanoparticles. [Caution: This reaction should be considered to be highly flammable and corrosive, as it has the potential to liberate phosphorus, which is highly pyrophoric. Therefore, it should only be carried out under rigorously air-free conditions by appropriately trained personnel.] Squalane (7.0 mL, 13 mmol) and trioctylphosphine (3.0 mL, 6.7 mmol) were added to a 50-mL three-necked, round-bottom flask equipped with a reflux condenser, a thermometer adapter, a thermometer, a rubber septum, and a borosilicate-coated stir bar. The mixture was moderately stirred and heated to 120°C under vacuum, to remove any water that was present. After placing the solution under an Ar

atmosphere, 352 mg (1 mmol) of $\text{W}(\text{CO})_6$ was added. The reaction mixture was then heated to 320 °C for 2 h. At ~ 270 °C the solution began to darken, and turned black at 320 °C. After remaining for 2 h at 320 °C, the heating mantle was turned off to allow the reaction to slowly cool until the temperature reached 200 °C. At this point, the heating mantle was removed, to allow the sample to cool to room temperature more rapidly. After transferring the reaction solution to a centrifuge tube, the nanoparticles were collected by adding hexanes (5 mL) and ethanol (15 mL) to the tube, followed by centrifugation (12,000 rpm, 3 min). The particles were then resuspended in hexanes (5 mL), and this process was repeated two additional times. After isolating the final product, the particles were redispersed in hexanes and placed in a vial (20 mL) for use.

Preparation of Working Electrodes. Protocols for preparing electrodes were modified slightly from previous reports.^{9,13b} First, a stock solution of the WP nanoparticles, at a concentration of 10 mg mL⁻¹, was prepared in hexanes. Next, WP nanoparticles were deposited onto 0.2 cm² pieces of Ti foil using 5-μL increments of the solution, up to a total of 20 μL. The WP-decorated Ti foils were allowed to dry, heated at 450 °C in 5% H₂/Ar, then attached to a polyvinylchloride-coated Cu wire. The conductive surfaces, with the exception of the WP-decorated side, were insulated from the solution using a two-part epoxy.

Electrochemical Measurements. All electrochemical measurements were performed in 0.50 M H₂SO₄ using a two-compartment, three-electrode cell and a Princeton Applied Research Versastat 3 potentiostat. The two compartments were separated by a Nafion® membrane to prevent contamination of the working electrode by the contents of the counter electrode solution. A mercury/mercurous sulfate (Hg/Hg₂SO₄) electrode and a Pt mesh electrode were used as the reference and counter electrodes, respectively. Raw electrochemical data were collected without any corrections for uncompensated resistance. To apply an iR correction, the uncompensated Ohmic resistance value for each electrode in the electrolyte solution was measured prior to the electrochemical testing of the electrode using the high frequency pulse iR determination function of the Versastat 3 potentiostat. The uncompensated resistance was ~ 31 Ω for bulk WP and ~ 11 Ω for amorphous WP nanoparticles in 0.50 M H₂SO₄. A sweep rate of 2 mV s⁻¹, with rapid stirring using a magnetic stir bar, was used to acquire the polarization data. Research-grade H₂(g) was continuously bubbled through the solution at ~1 atm to maintain a constant value for the RHE potential. The RHE potential was determined after electrochemical characterization of the tungsten phosphide nanoparticles by measurement of the open-circuit potential of a clean Pt mesh electrode in the electrolyte solution. For galvanostatic stability measurements, the current density was held at 10 mA cm⁻² for 18 h. Cyclic voltammetric sweeps, to further evaluate the acid stability, were carried out between +0.2 V and -0.3 V (vs. RHE) at 100 mV s⁻¹.

Quantitative Hydrogen Yield Measurements. To quantify the H₂ yield in 0.50 M H₂SO₄(aq) (two-electrode, single compartment cell with a graphitic carbon counter electrode), a cathodic current of 10 mA was passed continuously through a 0.2 cm² WP/Ti working electrode over a duration of 50 min (3000 s). This resulted in the passage of 30 C of total charge. The H₂(g) that

was evolved was collected in an inverted graduated cylinder, placed above the working electrode, that contained the electrolyte solution. The WP/Ti electrodes produced a volume of $\text{H}_2(\text{g})$ that was equivalent to the volume collected above comparable Pt nanoparticle electrodes. Each produced 3.97 ± 0.03 mL of gas. This volume of gas is comparable to the theoretical faradaic H_2 yield of 3.74 mL calculated for 30 C of charge at 1 atm and 20 °C. To avoid any possible Pt contamination, the Pt electrodes were evaluated after completion of the WP/Ti yield measurements.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS D8 Advance diffractometer with Cu $\text{K}\alpha$ radiation and a LynxEye 1-D detector. Simulated XRD patterns were produced using CrystalMaker / CrystalDiffract. All samples for microscopic analysis were prepared by drop-casting 0.7 μL of dilute, dispersed WP in hexanes onto a Cu grid (400 mesh, coated with Formvar and carbon, Electron Microscopy Sciences). Transmission-electron microscopy (TEM) images were collected using a Philips 420 microscope (80 kV). High-resolution TEM (HRTEM) images were obtained using a JEOL 2010 microscope (LaB₆, 200 kV). Scanning transmission-electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDS) was performed using a JEOL 2010F field emission microscope, which was equipped with an EDAX solid-state X-ray detector. STEM-EDS data were processed using ES Vision software (Emispec). The W L-shell and P K-shell transitions were used for quantitative EDS analysis, since these transitions do not overlap appreciably. X-ray photoelectron spectroscopic (XPS) measurements were collected on a Kratos Axis Ultra (monochromatic Al $\text{K}\alpha$ source, 14 kV, 20 mA, 280 W X-ray power) with a photoelectron take-off angle of 90° from the sample surface plane. All spectra were referenced to the $\text{C}_{1\text{s}}$ peak (285 eV). Diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected using a Bruker IFS 66/s spectrometer. Nanoparticle samples were diluted in KBr for analysis and DRIFT spectra were processed with Bruker OPUS 6.0 software.