

Supplementary Information for:

Comparison of the Performance of CoP-Coated and Pt-Coated Radial-Junction
n⁺p-Silicon Microwire-Array Photocathodes for the Sunlight-Driven Reduction of Water
to H₂(g)

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Electrode Preparation

Reactive ion etching of Si(100) substrate (B-doped, resistivity of 14.6 ohm-cm) was used to form 4 μm diameter Si microwires (MWs) at an 11 μm pitch, with the wires being 50 μm in length. Radial n^+ junctions on the p-Si microwires were formed by vapor-phase P diffusion from phosphoryl chloride (POCl_3) at 900 $^\circ\text{C}$. Ohmic contacts to the back of the Si(100) substrates were made by electron-beam evaporation of 150 nm of Al, followed by a 5 min anneal at 800 $^\circ\text{C}$ under forming gas (5% $\text{H}_2(\text{g})$ in $\text{N}_2(\text{g})$). The Si MW arrays were etched for 10 s in 0.5 M $\text{HF}(\text{aq})$ (Transene, Inc.) and were dried under a stream of $\text{Ar}(\text{g})$. Centrifugation was then promptly performed in 25 mL falcon tubes in a swinging-head centrifuge, with the tubes filled with ~ 15 mL of polydimethylsiloxane (PDMS, Dupont). The PDMS was cured overnight while centrifuging at 3000 rpm. Si MW arrays were then loaded into the bottom of the falcon tubes and centrifugation of the particles was performed at 3000 rpm with a suspension of the CoP nanoparticles (0.2 mg/mL) in hexane for 5 min (the suspension was sonicated immediately prior to application of 15 μL for a 0.1 cm^2 sample). A Cahn microbalance was used to determine the geometric mass loading (mg cm^{-2}) by weighing samples before and after deposition of particles. After deposition of the particles, the catalyst was activated by annealing at 450 $^\circ\text{C}$ for 30 min under forming gas. Ga-In eutectic was scratched onto the back side of the wire arrays, and Ag paint (SPI) was then applied to the back side of the arrays. A Cu wire was affixed to the array using Ag paint. The Cu wire was then threaded through a glass tube. Hysol 9460 epoxy was used to adhere the glass tube to the back side of the electrode and to seal the back and sides of the electrode. The epoxy was cured overnight.

Synthesis of Pt nanoparticles: A solution of 0.10 mM H_2PtCl_6 (Sigma, ACS Reagent), 0.10 mM sodium polyacrylate (M_w 2100, Aldrich), and 0.50 mM ascorbic acid (Sigma, ACS Reagent) was prepared in 250 mL of degassed, deionized H_2O with a resistivity of $\sim 18.2 \text{ M}\Omega\text{-cm}$ obtained from a Barnsted Nanopure column. The solution was stirred for 1 h under $\text{N}_2(\text{g})$, prior to cooling overnight with the subsequent addition of 2.0 g of NaOH. The suspension was left overnight, centrifuged, and then washed with deionized H_2O three times before suspending the particles in isopropanol.

Synthesis of CoP nanoparticles: synthesized and characterized as previously reported.¹

Electrochemical Measurements

Photoelectrochemical measurements were performed in 0.50 M $\text{H}_2\text{SO}_4(\text{aq})$. Experiments were performed in a Pyrex electrochemical cell in a conventional three-electrode configuration, with a Ag/AgCl reference electrode (BASi) in saturated KCl(aq) and a high-purity carbon cloth counter electrode (FuelCellStore). During a typical acquisition with a Gamry Reference 600 potentiostat, $\text{H}_2(\text{g})$ was constantly purged into the solution (except for the H_2 determination case), to maintain a constant, reversible (H^+/H_2) Nernstian potential in the solution. The solution was rapidly stirred with a magnetic stir bar, to minimize mass-transport limitations and to minimize any effects due to bubble formation. Potentially detrimental oxidative processes were minimized by limiting the scans to potentials that were negative of the open-circuit potential.

The cell was illuminated with an ELH-type W-halogen lamp equipped with a dichroic rear reflector. The light intensity was calibrated using a Si photodiode (Thorlabs UDT UV-005) that had been mounted in the same orientation as the Si working electrodes.

The Si photodiode was calibrated, in turn, against a NIST-traceable secondary standard Si cell that had been calibrated and produced a specified short-circuit current density under 100 mW cm^{-2} of illumination by Air Mass 1.5 G sunlight. Prior to data collection, trace metal impurities were removed by soaking the cell overnight in aqua regia, then thoroughly rinsing the cell with $18 \text{ M}\Omega$ resistivity H_2O . After each set of experiments, a Pt electrode was used to determine the reversible hydrogen potential, and thereby to calibrate the reference electrode.

We have not extended the measurement time nor have we compared the stability of the Si/Pt system to that of the Si/CoP system for extended time periods.

Spectral Response

Photoelectrochemical spectral response measurements were performed using illumination from a 150 W Xe lamp that was passed through an Oriel monochromator (0.50 mm slits), then chopped at 30 Hz, and focused to a beam spot that illuminated a portion of the electrode area in solution. A calibrated Si photodiode (Thorlabs UDT UV-050) was used to measure the light intensity incident on the electrode. Another Si photodiode was used to measure the beam-split portion of the illumination, with this Si photodiode providing a continuous calibration of the light intensity from the monochromator. A Gamry G 300 potentiostat was used to maintain the potential of the Si working electrode at -0.20 V vs RHE and to record the current produced by the sample. The signal components were measured by use of independent lock-in detection of the sample channel and the calibration channel.

Characterization

Scanning-electron microscopy (SEM) was performed using a Phenom Pro (Phenom World) electron microscope. The substrate was affixed to the sample chuck using Cu tape.

A FEI model TF30ST transmission-electron microscope with 300 kV field emission, equipped with a HAADF STEM detector and a CCD camera, was used to image Pt nanoparticles that were dispersed on a copper mesh supported by a Cu grid.

Although the images in Figure 1 are displayed with different tilt angles for convenience of viewing, when these images were loaded into software such as ImageJ, with the appropriate calibration indicated by the scale bar, the diameters and lengths of the wires were found to be the same in all three cases.

The CoP nanoparticles were monodisperse (Figure S2), whereas the Pt nanoparticles (Figure S1) were dispersed in a carbonaceous conductive matrix that may more readily adhere to a hydrophobic Si-H surface than the CoP. These factors may contribute to the differences in the distributions of the Pt and CoP nanoparticle on the MW arrays (Figure 1).

In some cases, i.e. with a highly resistive radial emitter or with no emitter present, a more uniform distribution of catalyst on the tops, sides, and bottoms of the wire arrays would be more optimal than deposition only at the bottoms of the wire arrays as described herein. Electrodeposition could be used to obtain a more uniform placement of the electrocatalyst onto microwire arrays.²

H₂ Faradaic Yield

H₂(g) generation was determined by quantitative volumetric collection of the gas evolved in the catholyte chamber in a two-electrode setup consisting of an H-tube made from volumetric burets. The gas formed at the cathode was collected after passage of -100 C with the electrode held at a current density of -10 mA cm⁻². The electrode area was 0.050 cm². The volume of the collected gas was in excellent agreement with the amount of H₂(g) expected assuming 100% Faradaic efficiency for H₂(g) production. The counter electrode was an IrO_x-coated Ti wire.

Calculation of Photocathode Efficiency

The ideal regenerative-cell efficiency was calculated by using the measured three-electrode characteristics of the photoelectrode in conjunction with an ideally nonpolarizable counterelectrode operating at the Nernstian potential $E(\text{O}_2/\text{H}_2\text{O})$. Hence, $\eta_{\text{IRC}} = \frac{ff \cdot V_{\text{oc}} \cdot J_{\text{sc}}}{P_{\text{in}}}$, where P_{in} is the input solar power, V_{oc} is the difference between the open-circuit potential and $E(\text{O}_2/\text{H}_2\text{O})$, J_{sc} is the current density observed at $E(\text{O}_2/\text{H}_2\text{O})$, and the fill factor is calculated as fractional maximum power with respect to the quantity $V_{\text{oc}} \cdot J_{\text{sc}}$.

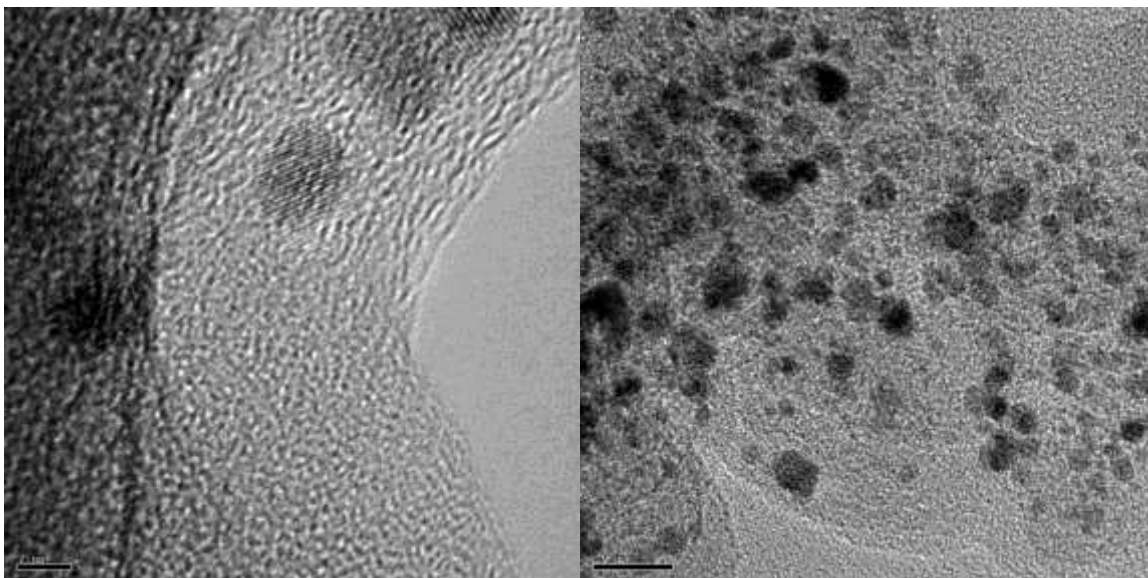


Figure S1. Transmission-electron micrographs of ~ 3 nm mean diameter crystalline Pt nanoparticles, with diameters ranging from 1 to 8 nm. The scale bar on the left image is 2 nm, whereas the bar on the right indicates 10 nm.

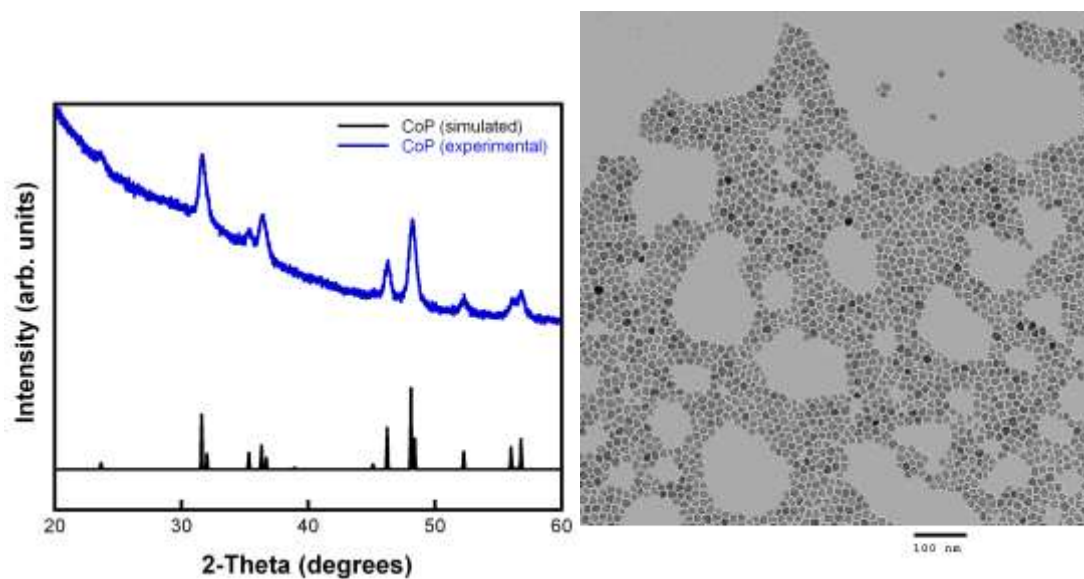


Figure S2. Powder x-ray diffraction (left) and transmission-electron micrograph (right) of ~ 13 nm diameter crystalline CoP nanoparticles. The scale bar indicates 100 nm.

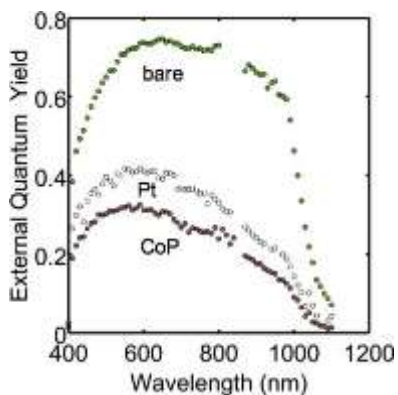


Figure S3. Spectral response for bare (top), Pt-coated (middle), and CoP-coated (bottom) n^+p Si MW arrays in contact with $H_2(g)$ -saturated 0.50 M H_2SO_4 . The data points that were acquired near complex Xe arc-lamp spectral features were omitted due to artifacts.

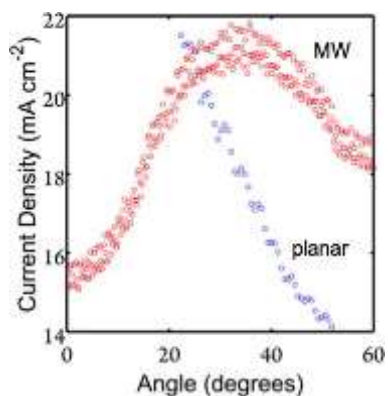


Figure S4. Dependence of photocurrent on the angle of illumination. The blue data were obtained using a CoP-coated planar n^+p Si photocathode (0.050 mg cm^{-2} mass loading), whereas the red data were obtained using a CoP-coated n^+p Si microwire-array photocathode (2.0 mg cm^{-2} mass loading), both at 1 Sun of simulated AM1.5G solar illumination in 0.50 M H_2SO_4 .

Comparison Between Calculated Resistance and Measured Series Resistance

The sheet resistance of $100 \Omega \text{ sq}^{-1}$ for a 100 nm (t) thick emitter yields a calculated resistivity of $0.001 \Omega \text{ cm}$ (ρ). The resistance for a single wire of radius $2 \mu\text{m}$ (r) along the radial emitter on a $50 \mu\text{m}$ (L) tall wire is 398Ω ($R_{\text{wire}} = \frac{\rho L}{2\pi r t}$, where L , r and t are the wire length, radius and emitter thickness, respectively). For an entire wire array, the total resistance decreases by the number of parallel resistors ($R_{\text{array}} = \frac{R_{\text{wire}}}{N_{\text{wires}}}$). A 0.1 cm^2 geometric array on an $11 \mu\text{m}$ pitch ($8.26 \times 10^5 \text{ wire cm}^{-2}$) therefore produces a total calculated emitter-based resistance of 0.0048Ω . The measured series resistance was determined by the measurement of the area ($A = \int_0^{J_{\text{sc}}} V dJ$) under the J - E data³, yielding ($R_{S,f} = 2 \cdot (\frac{V_{\text{oc}}}{J_{\text{sc}}} - \frac{A}{J_{\text{sc}}^2} - \frac{nk_b T}{q} \cdot \frac{1}{J_{\text{sc}}})$) a value of 285Ω .

Table S1. *J-E* parameters for n⁺p-Si planar and microwire photocathodes.

Catalyst	Loading (mg cm ⁻²)	J_{ph} (mA cm ⁻²)	ff	V_{oc} (V vs RHE)	Illumination (mW cm ⁻²)
Bare (planar)	0	30	NA	0.44	100
Pt (planar)	0.10	23	0.40	0.43	100
	0.20	12	0.49	0.48	100
Pt (MW)	0.50	7.8	0.49	0.37	30
	0.50	14	0.46	0.44	100
	0.50	30	0.43	0.46	330
CoP (planar)	0.050	28	0.15	0.41	100
	0.20	12	0.52	0.49	100
	2.0	0.19	0.54	0.29	100
CoP (MW)	2.0	8.5	0.35	0.45	30
	2.0	17	0.24	0.48	100
	2.0	21	0.23	0.52	330

References

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- (3) Pysch, D.; Mette, A.; Glunz, S.W. A Review and Comparison of Different Methods to Determine the Series Resistance of Solar Cells. *Sol. Energ. Mat. Sol. C.*, **2007**, *91*, 1698.