

Supporting Information.

A. Materials

Methanol (BakerDRY, Mallinckrodt Baker) and lithium perchlorate (battery grade, Sigma-Aldrich) were used as received, without further purification. Me₂Fc (95%, Sigma-Aldrich) was sublimated at room temperature and stored under an inert atmosphere until use. Me₂FcBF₄ was synthesized as described previously.¹

B. VLS-Catalyzed Wire Growth

Si microwire arrays were grown using the vapor-liquid-solid (VLS) growth method, using thermally evaporated Au or Cu (ESPI, 99.9999%) as the VLS growth catalyst. Degenerately doped (111)-oriented n-Si wafers with a resistivity of $\rho < 0.007 \text{ } \Omega\text{-cm}$ and with 300 nm of thermal oxide (Addison Engineering, Inc.) were used as the growth substrates. A positive photoresist (Microchem S1813) was used to pattern the wafers with 3 μm diameter circular holes, with a 7 μm center-to-center spacing, in a square (for Au) or hexagonal (for Cu) array. The exposed thermal oxide was etched in buffered HF(aq) (BHF, Transene Inc.) for 4 min. Immediately following the HF etch, 400 nm of Au or Cu was thermally evaporated onto the patterned growth substrate. Lift-off was performed in acetone, and the patterned wafers were then cleaved into 1.3 x 2.0 cm pieces. To perform VLS growth, the samples were annealed in a tube furnace at 1000° C for 20 min with 500 sccm of H₂ at atmospheric pressure. Wire growth was induced by introduction of SiCl₄ (6N, Strem) in 50 sccm of He into the reactor for 20 min. After VLS growth, the Au VLS catalyst was subsequently removed by a 10 s BHF etch followed by etching in a Au etchant solution (gold etch TFA, Transene Inc.) for 45 min. The Cu growth catalyst was likewise removed by a 10 s BHF etch, immediately followed by an etch in 6:1:1 (by

volume) of H₂O:HCl:H₂O₂ at 70° C (RCA 2) for 15 min. Prior to photoelectrochemical measurements, the Si wire arrays were etched for 5 s in 5% HF(aq), rinsed with > 18 MΩ-cm resistivity H₂O, and dried thoroughly under a stream of N₂(g).

C. Four-point Resistance and Gate-Dependent Measurements

Four-point resistance measurements were performed as described previously.² After removal of the VLS catalyst, an area of 3 x 3 mm of Si microwires was mechanically removed from the growth substrate with a razor blade, and the microwires were suspended in isopropanol. The wires were then spin-coated onto a silicon wafer that had been coated with 300 nm of Si₃N₄ (University Wafer). Contacts were patterned on individual wires using a lift-off resist (LOR10A, Microchem) and a positive photoresist (S1813, Microchem). Immediately following a 5 s BHF etch, 800 nm of Al (5N, Kurt J. Lesker) and 200 nm of Ag (4N, Kurt J. Lesker) were deposited by electron-beam evaporation onto the patterned wafer, to form ohmic contacts to the wires. The conductivity of the wires was measured with varying gate bias potentials, between -10 V and +10 V, to determine the carrier type in the wires. For both Au and Cu catalyzed wires, three wire arrays were sampled to measure the variability in wire dopant density among growths, and, for each growth, at least ten wires were measured. For Au catalyzed wire arrays, the measured resistivities of wires from three different arrays were 1400 ± 900 Ω-cm, 800 ± 700 Ω-cm, and 600 ± 300 Ω-cm. For Cu catalyzed wire arrays, the measured resistivities of wires from three different arrays were 310 ± 70 Ω-cm, 1000 ± 600 Ω-cm, and 600 ± 400 Ω-cm. The resistivities of wires from the arrays measured for their *J-E* performance are provided in the main article.

D. Electrode Fabrication

To fabricate electrodes for photoelectrochemical measurements, wire arrays were cleaved into 4 x 4 mm samples. The backs of the samples were scratched with a SiC scribe that was coated in Ga:In eutectic, to make ohmic contact to the Si substrate. The samples were then mounted with Ag print (GC Electronics) on a coiled wire that was passed through a glass tube, so that the electrode was positioned in a face-down configuration. The active area of the electrodes was defined using Loctite 9460 F epoxy, and the back contact and wire coil were insulated using Hysol 1C epoxy. Prior to electrochemical measurements, the electrodes were placed for 2 h in an oven heated to 70° C, to further cure the epoxy to obtain enhanced chemical stability. Electrode areas were measured with a high-resolution scanner, and were calculated using Adobe Photoshop software. Electrode areas were ~0.03 cm².

E. Photoelectrochemical Measurements

Current density vs. potential (*J-E*) measurements were performed with bottom illumination in an air-tight, flat-bottomed glass cell. The electrolyte solution consisted of 200 mM of dimethylferrocene (Me₂Fc), 0.4 mM of Me₂FcBF₄, and 1.0 M LiClO₄ in 30 mL of methanol. The cell was assembled and sealed under an inert atmosphere (< 10 ppm O₂) before being placed under a positive Ar pressure outside of the dry box. A methanol bubbler was used to prevent evaporation of the solution during an Ar purge. The three-electrode cell consisted of a high-area Pt mesh as the counter electrode, a Pt wire in a Luggin capillary filled with the cell's solution as the reference electrode, and a Si working electrode. The solution potential versus the reference was continuously monitored using a 4-digit voltmeter (Keithley), and deviated from the reference by <10 mV. *J-E* measurements were obtained at a scan rate of 5 mV s⁻¹ using a Princeton Applied Research (PAR) Model 273 potentiostat in conjunction with CoreWare software.

The cell was illuminated using a 150 W Xe lamp with an AM 1.5 G filter (Newport/Oriel) coupled to a UV-enhanced Al mirror, to direct the light through the bottom of the cell. The incident light intensity was calibrated using a Si photodiode that was placed in the solution at the position of the working electrode. The light intensity was adjusted until the short-circuit photocurrent density on the Si diode was the same as the value produced by 100 mW cm⁻² of AM 1.5G illumination. The cell was vigorously stirred during *J-E* measurements. Data were collected and averaged for six wire array samples, for both Au- and Cu-catalyzed Si microwire arrays.

To demonstrate the correction for concentration overpotential losses, 25 mM Me₂FcBF₄ was added to the cell. A 1 W 808 nm diode laser (Thorlabs) was used as the illumination source, and *J-E* data were collected by matching the *J*_{sc} value to the value of *J*_{sc} that was obtained under simulated AM 1.5 G illumination. This process required ~60 mW cm⁻² of 808 nm illumination. Corrections for the concentration overpotential (η_{conc}) and series resistance (*R*_s) losses were performed according to eqs. 1 and 2.

$$\eta_{\text{conc}} = \frac{k_{\text{B}}T}{nq} \left\{ \ln \left(\frac{J_{1,\text{a}}}{-J_{1,\text{c}}} \right) - \ln \left(\frac{J_{1,\text{a}} - J}{J - J_{1,\text{c}}} \right) \right\} \quad (1)$$

$$E_{\text{corr}} = E_{\text{meas}} - iR_{\text{s}} - \eta_{\text{conc}} \quad (2)$$

where *k*_B is Boltzmann's constant; *T* is the absolute temperature; *q* is the (unsigned) charge on an electron; *n* is stoichiometric number of electrons transferred in the electrode reaction (*n* = 1 for Me₂Fc⁺⁰); and *J*_{1,a} and *J*_{1,c} are the anodic and cathodic mass-transport-limited current densities, respectively. A Pt foil working electrode of comparable area to the Si working electrodes was used to measure *J*_{1,a} and *J*_{1,c}, and *R*_s of the cell. The limiting anodic current density was 80 mA

cm^{-2} and the limiting cathodic current densities were 0.15 and 9.8 mA cm^{-2} , for 0.4 mM and 25 mM Me_2FcBF_4 , respectively. The measured value of R_s was dependent on the placement of the working electrode with respect to the Luggin capillary, and typically varied from 50–150 Ω . A value of $R_s = 50 \Omega$ was used in the calculations to avoid overcorrection of the data, resulting in conservative, potentially underestimated, values for the intrinsic fill factor and photoelectrode efficiency of the $\text{Si}/\text{CH}_3\text{OH}-\text{Me}_2\text{Fc}^{+/0}$ contact.

F. Angle-resolved Spectral Response and Optical Measurements

For angle-resolved spectral response measurements, side-facing electrodes of high-fidelity Si microwire arrays with dimensions of $\sim 8 \times 8$ mm were fabricated as described previously for photoelectrochemical measurements performed under 1 Sun. Care was taken to ensure that all electrodes had the same orientation in all three dimensions, with the long $14 \mu\text{m}$ axis of the hexagonal pattern oriented vertically, as the axis of rotation (θ_y). Angle-resolved spectral response measurements were performed using an apparatus that has been described previously, which consisted of a chopped ($f = 30$ Hz) Fianium supercontinuum laser coupled to a monochromator, with two rotational stages to allow for rotation around both the θ_x and θ_y axes.³ A custom, air-tight, round-bottom flask with a side window was utilized for angle-resolved spectral response measurements, allowing free rotation about the θ_y axis. The configuration of the electrochemical cell was identical to that of the cell that was used for J - E measurements, except that 10 mM Me_2Fc was used, to reduce light absorption from this reagent. The working electrode was poised at the solution potential of the cell, referenced by a Pt wire in solution. The photoelectrode was aligned in the cell by utilizing the reflected optical diffraction pattern, and normal incidence ($\theta_{x,y} = 0^\circ$) was determined by minimizing the photocurrent of each electrode. A calibrated Si photodiode (Thorlabs) that was positioned inside the cell was used to calculate

the Γ_{ext} of the Si microwire array photoelectrodes. The cell was constantly purged with Ar, and no degradation of the response of the Si working electrode was observed over the duration of the experiment.

After electrochemical measurements, the electrodes were thoroughly rinsed, and polydimethylsiloxane (PDMS; Sylgard 184, Dow Corning) was drop-cast into the electrodes. To ensure a uniform thin film, a transparency was placed on top of the curing PDMS, to create a thin film (< 1 mm) that exhibited little optical distortion. The PDMS was allowed to cure at room temperature for 48 h, and the transparency was then removed from the top of the film. Si wires embedded in PDMS were subsequently peeled off of the electrode using a razor blade, and the films were mounted onto a quartz slide. Optical transmission and reflection measurements as a function of wavelength (λ) and incident angle of illumination (θ_y) were performed on the peeled-off films using an integrating sphere.³ The optical diffraction patterns of the arrays were used to orient the films relative to the rotational axes (θ_x , θ_y). The maximization of transmission in the films was taken to be normal incidence to the wire array, and was 4° off specular. This angle corresponded to the off-cut of the (111) growth substrate, which caused the microwires to grow at 4° from the surface normal.

References.

1. J. R. Maiolo, H. A. Atwater and N. S. Lewis, *J Phys Chem C*, 2008, **112**, 6194-6201.
2. M. D. Kelzenberg, D. B. Turner-Evans, B. M. Kayes, M. A. Filler, M. C. Putnam, N. S. Lewis and H. A. Atwater, *Nano Lett*, 2008, **8**, 710-714.
3. M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis and H. A. Atwater, *Nat Mater*, 2010, **9**, 239-244.
4. J. R. Maiolo, B. M. Kayes, M. A. Filler, M. C. Putnam, M. D. Kelzenberg, H. A. Atwater and N. S. Lewis, *J Am Chem Soc*, 2007, **129**, 12346-12347.

SI Figure Captions.

Figure S1. Two-point and four-point resistivity measurements of an undoped Si microwire. The inset is a scanning electron microscope image of a contacted single wire for the measurement (scale bar 40 μm).

Figure S2. Scanning electron microscope image of the top of a Si microwire after chemical etching had been performed to remove the metallic Cu VLS catalyst (scale bar 1 μm).

Table S1. Figures of Merit of Si Microwire Array Cells				
	V_{oc} (mV)	J_{sc} (mA cm^{-2})	ff	Efficiency (%)
Au Catalyzed (AM 1.5 G)	334 ± 21	10.0 ± 1.3	0.34 ± 0.05	1.1 ± 0.3
Au Catalyzed (808 nm)	332 ± 18	10.2 ± 1.2	0.47 ± 0.04	2.7 ± 0.7
Corrected Au	334 ± 21	10.4 ± 1.4	0.57 ± 0.05	2.0 ± 0.5
Au Wires Removed	223 ± 38	1.0 ± 0.2	0.20 ± 0.04	0.04 ± 0.01
Cu Catalyzed (AM 1.5 G)	437 ± 8	7.9 ± 0.6	0.40 ± 0.02	1.4 ± 0.1
Cu Catalyzed (808 nm)	435 ± 10	7.8 ± 0.4	0.60 ± 0.02	3.4 ± 0.2
Corrected Cu	437 ± 8	8.0 ± 0.7	0.61 ± 0.04	2.1 ± 0.1
Wires Removed	274 ± 1	1.4 ± 0.1	0.22 ± 0.002	0.08 ± 0.006
Previous Result ⁴	389 ± 18	1.43 ± 0.14	0.16 ± 0.02	0.09 ± 0.01

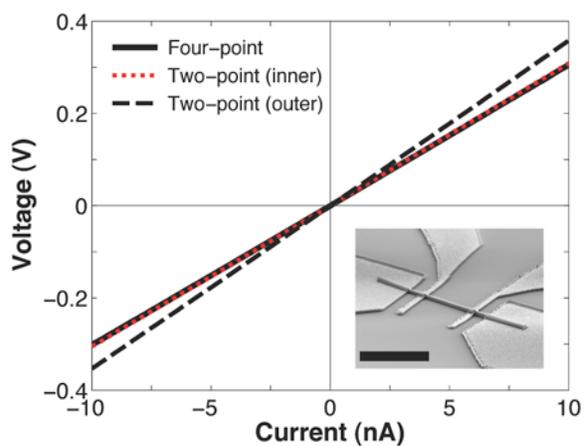


Figure S1.

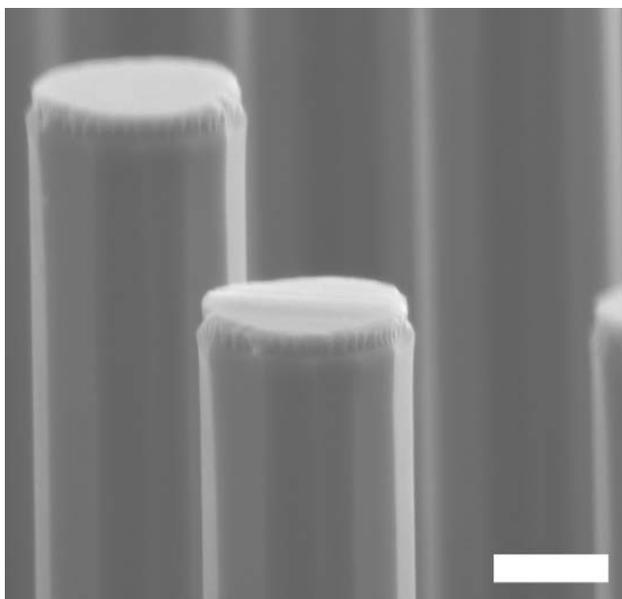


Figure S2.