Supporting Information

A. VLS–Catalyzed Wire Growth

Arrays of undoped Si microwires were grown on both on planar n^+- and p^+-Si(111) substrates using the vapor–liquid–solid (VLS) method, with thermally evaporated Cu (ESPI, 99.9999%) as the VLS growth catalyst. The degenerately doped (111)–oriented n^+- and p^+-Si wafers were patterned with 3 μm diameter circular holes, with a 7 μm center-to-center spacing, in a square array using a positive photoresist (Microchem S1813). The wafers were etched in buffered HF(aq) (BHF, Transene Inc.) for 5 min to remove the exposed thermal oxide, and 450–600 nm Cu was thermally evaporated onto the patterned growth substrates. The wafers were thoroughly rinsed in acetone and isopropyl alcohol, and then cleaved into 1.3 x 2.0 cm pieces. The lithographically patterned planar substrates with the Cu catalyst were annealed in a tube furnace at 1000º C for 20 min with 500 sccm of H_2 (Research grade, ALPHAGAZ™ 2, Air Liquide) at atmospheric pressure. VLS wire growth occurred at 1000 ºC using $SiCl_4$ (99.9999%-Si PURATREM, Strem) in 50 sccm of H_2, without the introduction of dopants, for 20–45 min.

B. Corrections of *J-E* Data for Concentration Overpotential and Series Resistance

The *J-E* data from the $Me_2Fc^{+/0}$–CH_3OH cell were corrected for concentration overpotential (η_{conc}) and series resistance (R_s) losses using eq. 1 and 2:

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

$$E_{corr} = E_{meas} - iR_s - \eta_{conc} \quad (2)$$

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 $Me_2Fc^{+/0}$); and $J_{l,a}$ and $J_{l,c}$ 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 $J_{l,a}$ and $J_{l,c}$, and R_s of the cell. The measured limiting anodic current density was 72 mA cm^{-2} and the limiting cathodic current densities were 0.15 and 15 mA cm^{-2}, for 0.4 mM and 40 mM Me_2FcBF_4, respectively. The value of R_s varied from 40–300 Ω, due to variations in the electrode placement relative to the Luggin capillary reference; a conservative value of R_s = 50 Ω was used in the calculations to avoid overcorrection of the data.

In *J-E* measurements, the electrode areas were less than 0.03 cm^{-2}, to limit resistance losses within the electrochemical cell, but greater than 0.02 cm^{-2}, such that the electrode areas could be accurately measured. Electrodes with areas less than 0.02 cm^{-2} exhibited measurable effects from epoxy creeping into the wire array, and also exhibited artificially enhanced photocurrent from light scattering into the array from the surrounding epoxy. For all *J-E* measurements, the light calibration was confirmed by measurements using a planar, single crystal n-Si photoelectrode with an area of ~0.03 cm^{-2} in the electrochemical cell. The behavior of these electrodes has been well established under 1 Sun illumination.

C. Chemical–mechanical polishing of Si microwire arrays

After removal of the Cu VLS catalyst, arrays of Si microwires of dimensions of ~ 3 cm x 2 cm were cleaved in half longitudinally. Half of the array was reserved for the fabrication of unpolished, control electrodes. The other half of the array was again cut in half, to create to smaller chips for more uniform polishing. Each chip was mounted on a flat, 1 inch diameter stainless steel mounting block using a small amount of mounting wax (Quickstick 135, South

Bay Technology) on a hot plate at ~ 150 ºC. The array was subsequently infilled with mounting wax, and the wax was allowed to equilibrate within the array for 30 min; the resulting array was completely filled to the tops of the wire arrays with wax. Additional mounting wax was placed around the perimeter of the array, to prevent the removal of wires at the edge of the array during polishing. The array infilled with wax was polished using a succession of aluminum oxide suspensions of 3 μm, 1 μm and 0.3 μm with polishing cloth (MultiTex™, South Bay Technology). The array was thoroughly rinsed in > 18 M Ω-cm resistivity H_2O periodically and between different suspensions. To gauge the polishing rate, the focal planes of the top most wires and the shortest wires were determined using an optical microscope. Polishing was terminated shortly after all of the wires were the same height, and the array was then subjected to a final polish using a colloidal silica suspension (SBT, 0.02–0.06 μm).

SI Figure Captions.

Figure S1. *J-E* behavior of lightly doped Si microwire arrays grown on an n^+-Si substrate, in contact with the $Me_2Fc^{+/0}$–CH_3OH redox system, with an increased concentration of Me_2FcBF_4 and the corrected *J-E* response.

Figure S2. A) Top view SEM image of a mechanically polished Si microwire array, scale bar = 4 μm B) Side view SEM image of the same array. Scale bar = 20 μm.

Table S1. Figures of merit of undoped Si microwire array photoelectrodes.

Figure S1.

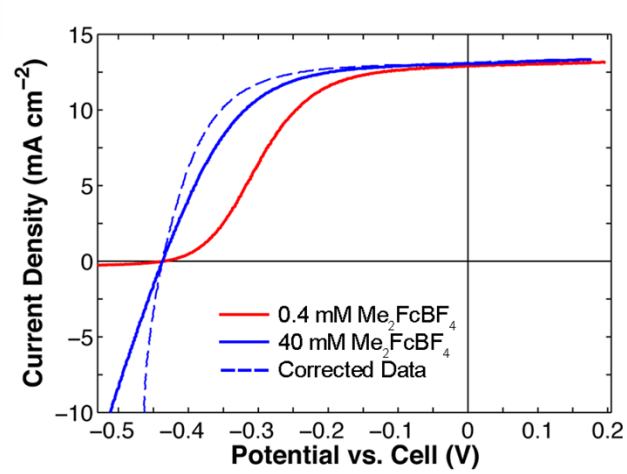

Figure S2.

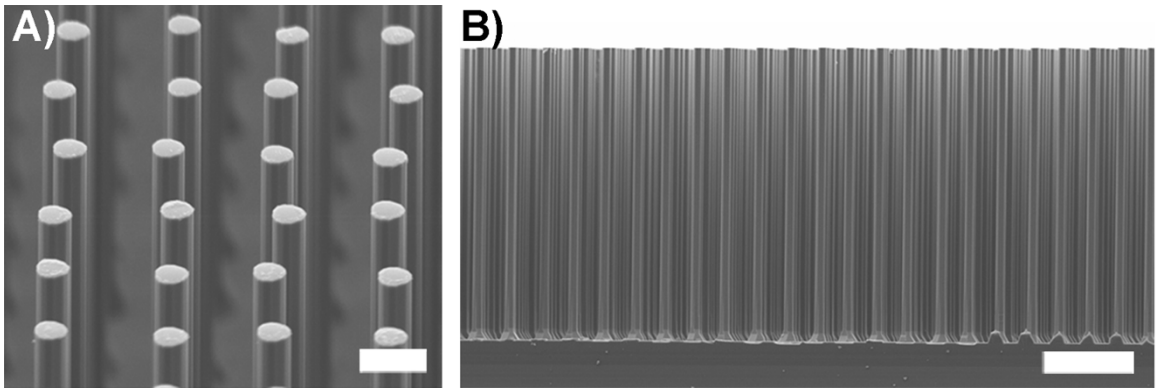

Table S1.

	V_{oc} (mV)	J_{sc} (mA cm^{-2})	*ff*	Efficiency (%)
n^+/i-Si/ $Me_2Fc^{+/0}$–CH_3OH				
i-Si on n^+ substrate (ELH)	445 ± 13	12.8 ± 2.1	0.41 ± 0.03	2.3 ± 0.3
i-Si on n^+ substrate (808 nm)	436 ± 14	12.8 ± 2.1	0.58 ± 0.02	5.9 ± 1.0
Corrected i-Si on n^+ substrate	445 ± 13	12.9 ± 2.1	0.62 ± 0.04	3.5 ± 0.6
Wires Removed, n^+ substrate	7.5 ± 0.7	0.9 ± 0.01	0.34 ± 0.07	0.002 ± 0.003
p^+/i-Si/ $CoCp_2^{+/0}$–MeCN				
i-Si on p^+ substrate (ELH)	421 ± 14	10.9 ± 0.3	0.32 ± 0.02	1.5 ± 0.1
Wires Removed, p^+ substrate	253 ± 1	1.75 ± 0.11	0.27 ± 0.05	0.11 ± 0.01
p^+/i-Si/ $Me_2Fc^{+/0}$–CH_3OH				
i-Si on p^+ substrate (ELH)	0.14 ± .07	0.10 ± 0.03		
i-Si on p^+ substrate (dark)	0.42 ± .09	0.17 ± 0.04		
n^+/i-Si/ $CoCp_2^{+/0}$–MeCN				
i-Si on n^+ substrate (ELH)	0	0.02 ± 0.01		
i-Si on n^+ substrate (dark)	0	0.04 ± 0.02		