Supporting Information for:

520 mV, pH Independent, Open-Circuit Voltages of Si/Methyl Viologen$^{2+/+}$ Contacts Through Use of Radial n$^+$p-Si Junction Microwire Array Photoelectrodes

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MATERIALS AND METHODS

VLS-Catalyzed Wire-Array Growth

(111)-oriented p$^+$Si wafers with a resistivity of ρ<0.003 Ω-cm, were coated with 300 nm of thermal oxide (Silicon Quest International). The samples were then patterned with square arrays of 3 µm circular holes, with a hole-to-hole pitch of 7 µm, using a positive photoresist layer (Microchem S1813). The exposed SiO$_2$ was etched away with buffered HF(aq) (BHF, Transene Inc.). 300-500 nm of Cu (EPSI 6N) was then thermally evaporated onto the substrate and the excess material was lifted off with acetone. Growth substrates were cut into chips with dimensions of ~1.5 cm x 2 cm and were annealed in a tube furnace at 1000 °C for 20 min under a flow of 500 sccm H$_2$. Wire growth was performed by introducing SiCl$_4$ (Strem, 6N), and BCl$_3$ (0.25% in H$_2$, Mattheson) into the reactor chamber for 15-30 min. The wires were allowed to cool to ~650 °C under H$_2$ or He at ambient pressure before the samples were removed from the reactor.

Photoelectrochemical Characterization

1. pH Buffer Solutions. Three different buffer solutions were prepared by literature methods to compare the performance of the electrodes at different pHs: phthalate (pH 2.9), and phosphate (pH 5.9 and 8.9).[1,2] To improve the ionic conductivity of the solutions, 0.5 M K$_2$SO$_4$ (Aldrich) was added to each buffer, and the pH was adjusted with 0.1 M KOH or 0.1 M H$_2$SO$_4$. The pH of each solution was measured with a NexSens WQ-pH meter. Solutions were purged with Ar for a minimum of 10 min before addition of 50 mM methyl viologen (MV$^{2+/+}$) dichloride (Aldrich). The MV$^+$ radical cation species was generated by bulk electrolysis using the large carbon electrode as a cathode, and a Pt mesh counter electrode separated by a glass frit, to create well-defined Nernstian solution potential of -0.60 V to -0.59 V vs. SCE.

2. Current Density vs. Potential Measurements. Current density vs. potential (*J-E*) data were obtained at a scan rate of 20 mV s^{-1} with a Princeton Applied Research (PAR) Model 273 potentiostat using CorrWare software. To

remove any native oxide, all electrodes were dipped in BHF immediately before use. The illumination source was a 1 W, 808-nm diode laser (Thor Labs L808P1WJ). To calibrate the light intensity incident upon the Si sample, a Si photodiode (UDT UV-005) was mounted in solution parallel to each down-facing electrode. The laser beam was expanded to fill the entire area of both the working electrode and calibrated photodiode. Photoelectrochemical data were compared at an incident 808-nm light intensity of 60 mW cm^{-2}, because the maximum short-circuit current density obtainable for Si under such conditions is similar to the maximum short-circuit current density obtainable for Si under 100 mW cm^{-2} of Air Mass 1.5 (AM 1.5) solar illumination.[3] For all electrodes, the cathodic limiting current density measured in the solution containing 3 mM MV^{+} was directly compared to that measured in a solution that contained no MV^{+} to ensure that light intensity was correctly measured.

3. Conversion of Current Density into an External Quantum Yield. When using a monochromatic illumination source, it is appropriate to describe the current in terms of the quantum yield. The external quantum yield (Φ_{ext}) is the fraction of photons incident on the photoelectrochemical cell that produce minority carriers that are collected as current. The current density can be converted to Φ_{ext} using the following equation:

$$\Phi_{ext} = \frac{\text{electrons collected}}{\text{photons absorbed}} = \frac{\left(\frac{i}{qA_{Si}}\right)}{\left(\frac{P}{A_{PD}}\right)\left(\frac{\lambda}{hc}\right)}$$

(S1)

where i is the current in mA, q is the unsigned electronic charge, A_{Si} and A_{PD} are the areas of the Si working electrode and the photodiode detector, respectively, P is the power incident on the photodiode in mW, λ is the wavelength in nm (808 nm in this work), h is Planck's constant, and c is the speed of light. The number of incident photons is calculcated from the current density of the calibrated Si photodiode parallel to the working electrode.

Data Correction for Concentration Overpotenial and Uncompensated Resistance

To determine the intrinsic behavior of the semiconductor material, the measured data were corrected for the concentration overpotential and uncompensated resistances that are present in unoptimzed electrochemical cell designs. To calculate the fill factor, *ff*, and the photocathode efficiency, η_{808}, inherent to the photoelectrode, a polished glassy carbon electrode was used to determine the limiting anodic ($J_{l,a}$) and cathodic ($J_{l,c}$) current densities, as well as the uncompensated resistance (R_{cell}) of the cell (eqn S2).[4,5] Raw *J-E* data were then corrected for both losses (eqn S3), and the corrected data were used to calculate the ff_{corr} and $\eta_{808,corr}$ that are reported in Table S1.

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

(S2)

$$E_{\text{corr}} = E_{\text{raw}} - iR_{\text{cell}} - \eta_{\text{conc}} \qquad \text{(S3)}$$

The correction parameters were very similar for all three of the buffered electrolytes: $R_{\text{cell}} = 15$ to $20\ \Omega$, $J_{\text{l,a}} = 3$ to $5\ \text{mA cm}^{-2}$, $J_{\text{l,c}} = -40$ to $-50\ \text{mA cm}^{-2}$. While the data correction did not change the value of V_{oc}, it slightly changed the J_{sc} used to calculate the ff_{corr} for samples that did not reach a saturation current density at the solution potential ($E_{\text{corr}} = 0$).

	V_{oc} / mV	J_{sc} / mA cm^{-2}	$\Phi_{\text{ext, sc}}$	ff_{raw}	ff_{corr}	$\eta_{\text{808, raw}}$	$\eta_{\text{808, corr}}$
			n$^+$-p Si Wire Array (best)				
pH 2.9	545	9.69	0.25	0.65	0.72	5.8%	6.4%
pH 5.9	537	9.62	0.25	0.65	0.71	5.6%	6.1%
pH 8.9	535	9.45	0.25	0.65	0.73	5.5%	6.2%
			n$^+$-p Wire Array Electrodes (average)				
pH 2.9	527 ± 25	7.75 ± 2.74	0.20 ± 0.07	0.62 ± 0.05	0.67 ± 0.07	$4.3 \pm 2.0\%$	$4.7 \pm 2.3\%$
pH 5.9	519 ± 26	7.95 ± 2.37	0.20 ± 0.06	0.64 ± 0.01	0.69 ± 0.03	$4.4 \pm 1.6\%$	$4.8 \pm 1.8\%$
pH 8.9	518 ± 23	7.78 ± 2.36	0.20 ± 0.06	0.62 ± 0.05	0.68 ± 0.07	$4.2 \pm 1.8\%$	$4.7 \pm 2.1\%$
			p-Si Wire Array Electrodes				
pH 2.9	418 ± 14	7.31 ± 0.50	0.19 ± 0.01	0.45 ± 0.02	0.48 ± 0.02	$2.3 \pm 0.2\%$	$2.5 \pm 0.2\%$
pH 5.9	378 ± 15	8.21 ± 1.07	0.21 ± 0.03	0.44 ± 0.02	0.48 ± 0.03	$2.2 \pm 0.3\%$	$2.5 \pm 0.3\%$
pH 8.9	228 ± 8	8.31 ± 0.73	0.21 ± 0.02	0.40 ± 0.01	0.53 ± 0.03	$1.3 \pm 0.1\%$	$1.7 \pm 0.3\%$
			n$^+$-p Si Planar Electrodes				
pH 2.9	560 ± 19	24.0 ± 4.5	0.61 ± 0.12	0.45 ± 0.02	0.58 ± 0.04	$10.2 \pm 2.0\%$	$13.5 \pm 2.6\%$
pH 5.9	550 ± 15	27.4 ± 1.0	0.70 ± 0.02	0.38 ± 0.03	0.52 ± 0.04	$9.5 \pm 1.0\%$	$13.5 \pm 1.4\%$
pH 8.9	554 ± 13	25.8 ± 0.4	0.66 ± 0.01	0.41 ± 0.00	0.61 ± 0.05	$9.8 \pm 0.1\%$	$13.8 \pm 0.5\%$
			p-Si Planar Electrodes				
pH 2.9	530 ± 34	22.2 ± 3.2	0.57 ± 0.08	0.55 ± 0.05	0.63 ± 0.06	$10.8 \pm 2.0\%$	$12.4 \pm 2.6\%$
pH 5.9	371 ± 17	22.7 ± 4.6	0.58 ± 0.12	0.43 ± 0.00	0.58 ± 0.03	$6.0 \pm 1.0\%$	$8.2 \pm 1.8\%$
pH 8.9	264 ± 8	20.1 ± 3.4	0.41 ± 0.18	0.24 ± 0.05	0.41 ± 0.13	$2.1 \pm 0.8\%$	$3.8 \pm 1.9\%$

Table S1: Photoelectrochemical performance data for each type of electrode measured under 60 mW cm^{-2} of 808 nm illumination in aqueous solution with 50 mM MV$^{2+/+}$

REFERENCES

(1)   *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 2010.
(2)   To compare the effect of the buffer, a pH 5.9 phthalate buffer was made to directly compare the effect of phosphate/phthalate. No appreciable difference in performance or stability was discerned between these two buffers.
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