

Supporting Information for
“Unassisted solar-driven photoelectrosynthetic HI splitting using membrane-embedded Si microwire arrays”

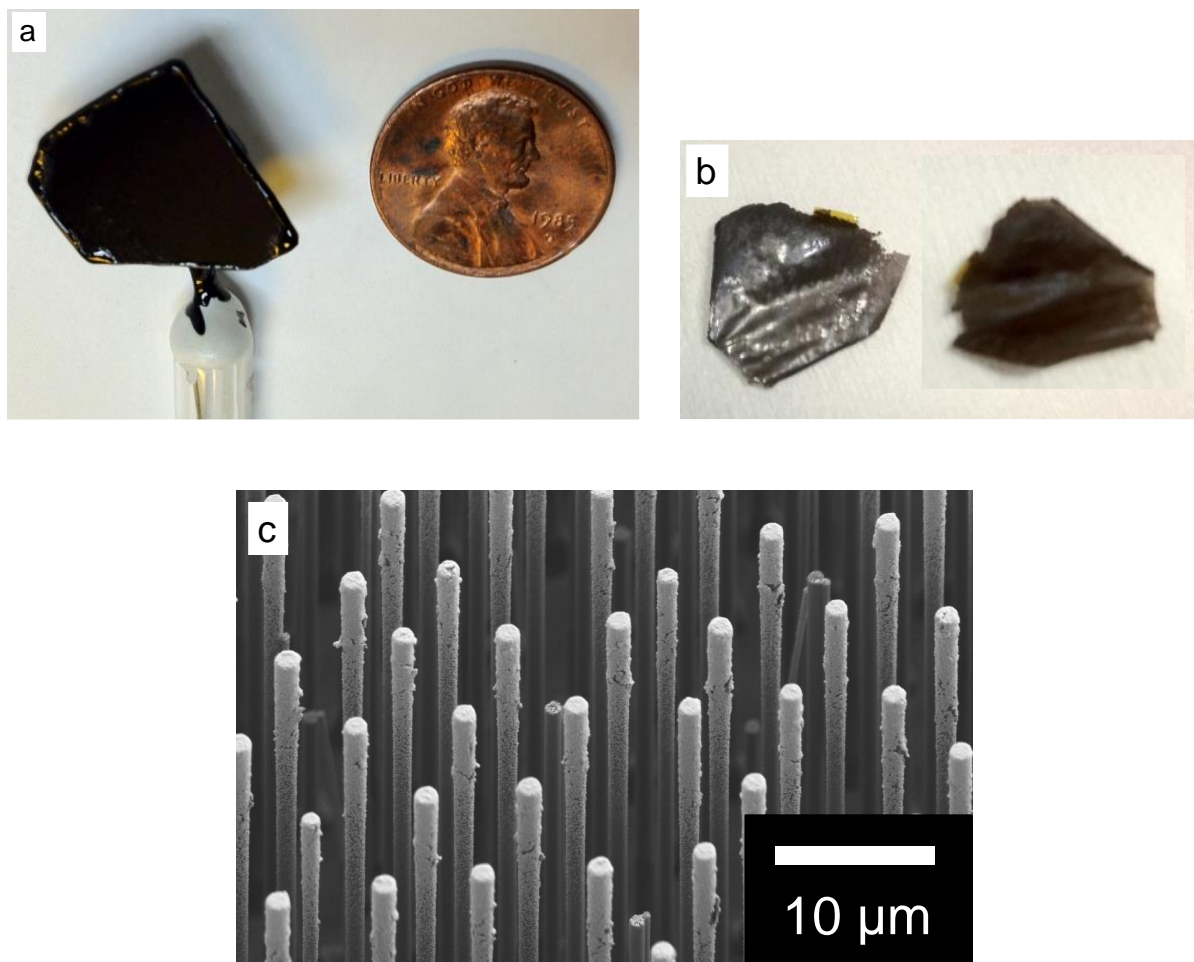


Figure S1. Digital photograph images of (a) a Nafion-embedded microwire-array electrode used to photoelectrochemically deposit Pt on the microwires, and (b) a fully functional, peeled composite membrane containing a partially embedded Si microwire arrays that demonstrated unassisted solar-driven HI splitting. Both images are referenced in size to the penny shown in panel a. (c) Scanning electron micrograph of microwires containing photoelectrochemically deposited Pt.

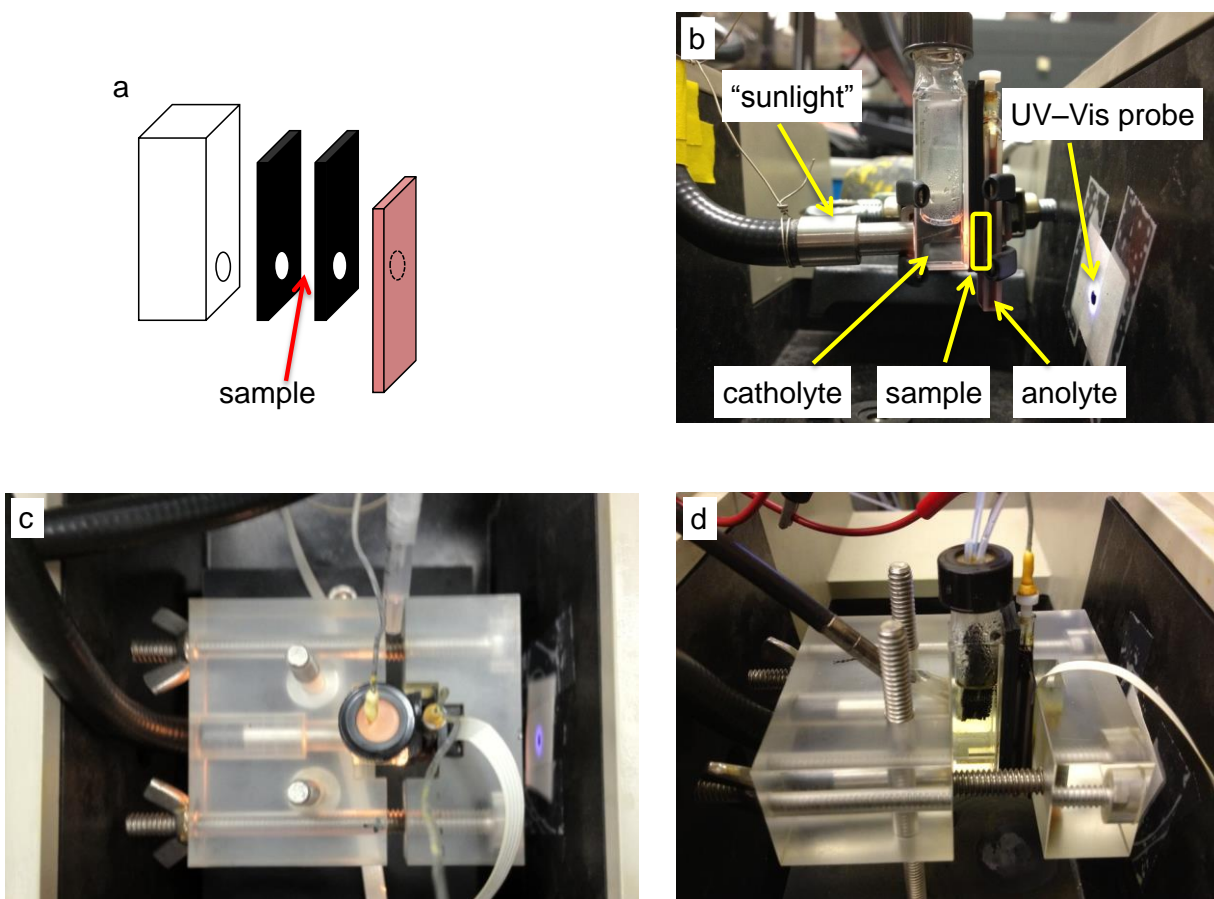


Figure S2. (a) Schematic showing the arrangement of a sample between two Viton sheets that had holes and that were capped by two borosilicate glass cuvettes having one hole each to wet the sample. The catholyte cell was clear while anolyte cell was red due to visible-light absorption by I_3^- . Digital photograph images of cell holders illustrating (b) an early design showing the excitation arrangement using the fiber optic, the location of the sample, and the probe beam path through the anolyte. Also shown are (c) an intermediate design with the features from panel b, plus a port for the fiber optic and an inductive stirrer to circulate the anolyte, and (d) a final design including the features from panel c, plus a port for a borescope to monitor bubble formation on the sample surface, a gas-tight cathode compartment to sample the headspace for evolved H_2 , and two electrodes in order to measure the potential difference between the cells.

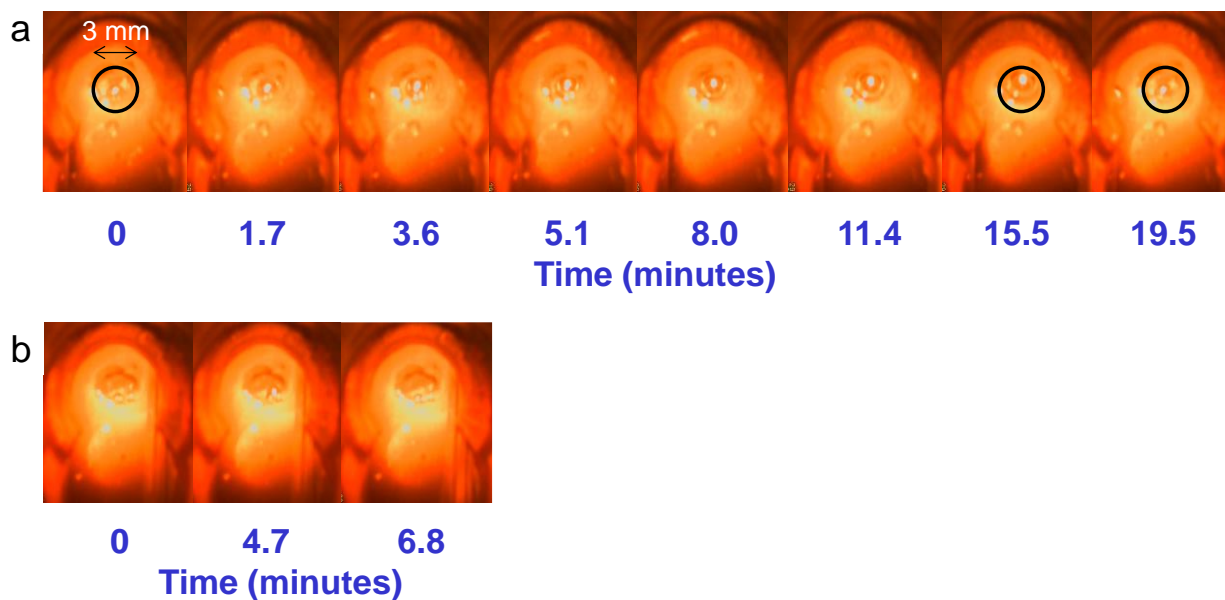


Figure S3. Real-time digital images using a borescope positioned on the photocathode side of the composite-material membrane (Figure S2d), demonstrating bubble formation due to light-driven H_2 evolution (**a**) over the first 19.5 min, and subsequently (**b**) 5.7 h later over a time-span of 6.8 min.

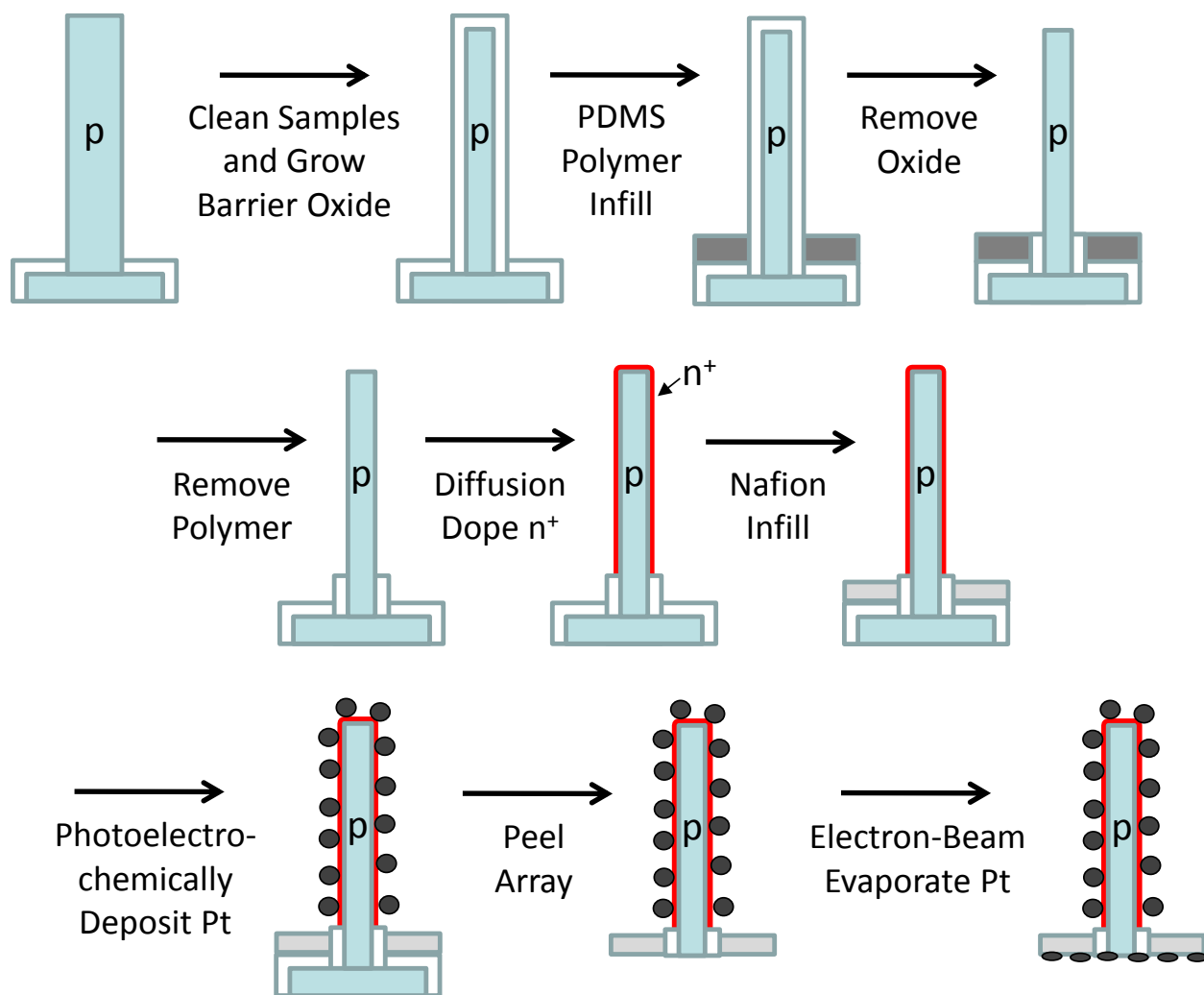


Figure S4. Schematic depiction of the general fabrication process for the free-standing composite membrane.

Additional Experimental Details

Chemicals

All chemicals were used as received unless noted otherwise. All water was filtered using a Barnsted Nanopure system which resulted in a resistivity $>18 \text{ M}\Omega\text{-cm}$.

Polydimethylsiloxane Deposition Protocol

Polydimethylsiloxane (PDMS) was cast from a freshly prepared and degassed solution that, unless noted otherwise, contained toluene, PDMS, and an initiator (5 mL: 1 g: 0.1 g). This solution was spin cast on the microwire arrays for 30 s at 150 RPM, then for 30 s at 750 RPM, and then for 60 s at 1500 RPM. The PDMS was subsequently cured at $60 \text{ }^\circ\text{C}$ overnight in a vacuum oven followed by a final cure at $150 \text{ }^\circ\text{C}$ for 30 min on a hot plate.

Materials Synthesis and Processing

Crystalline Si microwire arrays were grown on planar Si(111) wafer substrates pre-patterned with Cu in a hexagonal pattern having a $3 \text{ }\mu\text{m} \times 7 \text{ }\mu\text{m}$ array pitch (Montco Silicon Tech., Inc., Si(111) wafers, $610 - 640 \text{ }\mu\text{m}$ thick, B-doped, $0.005 - 0.010 \text{ }\Omega\text{-cm}$ resistivity, 300 nm thermal oxide). The microwire arrays were grown on a $\sim 2 \text{ cm} \times 3 \text{ cm}$ chip using flow rates of 450 sccm for H_2 , 50 sccm for SiCl_4 , and 1.5 sccm for BCl_3 for 18 min. These growth conditions produced microwires $\sim 65 \text{ }\mu\text{m}$ in height.

The samples were then cleaned via a standard procedure of HF($\sim 6 \text{ M}$, aq) for 10 s, followed by an RCA2 clean consisting of H_2O with equal parts HCl(12 M, aq) and H_2O_2 (9.8 M, aq) (6:1:1 v/v/v) at $70 \text{ }^\circ\text{C}$ for 20 min, then 10 s in HF($\sim 6 \text{ M}$, aq), 50 s in KOH(30 wt%, aq), 10 s in HF($\sim 6 \text{ M}$, aq), a second RCA2 etch at $70 \text{ }^\circ\text{C}$ for 20 min, immediately followed by rinsing with H_2O , drying under a stream of $\text{N}_2(\text{g})$, and subsequent thermal oxidation for 100 min at $1100 \text{ }^\circ\text{C}$ under an O_2 flow at 4 L min^{-1} , Figure S4. Oxide “boots” were defined using PDMS, per the procedure described above. The oxide was removed from the exposed regions of the microwires using a 5.5 min soak in buffered HF(aq) (Transene, Inc.), followed by a PDMS etch that consisted of *N*-methyl-2-pyrrolidone with tetra-*n*-butylammonium fluoride (2.7 M, aq) (3:1, v/v), until the PDMS had been completely removed. Prior to diffusion doping, the samples were then cleaned via a Piranha etch that consisted of H_2SO_4 with H_2O_2 (9.8 M, aq) (3:1, v/v) at $80 \text{ }^\circ\text{C}$ for 30 min, 10 s in HF($\sim 6 \text{ M}$, aq), an RCA1 clean consisting of H_2O with equal parts of NH_4OH (15 M, aq) and

H₂O₂(9.8 M, aq) (5:1:1, v/v/v) at 80 °C for 20 min, 10 s in HF(~6 M, aq), followed by another RCA2 clean. Samples were etched for 10 s in HF(~6 M, aq), followed by drying under a stream of N₂(g), and then were immediately placed into the first slot between solid-source ceramic CeP₅O₁₄ diffusion doping wafers (Saint-Gobain Ceramic Materials, PDS PH-900) on a quartz boat. The samples were placed into a furnace set at 900 °C with a 1 min push in, an 8 min soak, and a 1 min pull out. A p-type Si planar control that was placed in the second slot exhibited a sheet resistance of ~140 Ω/□.

Photoelectrode Fabrication and Photoelectrochemical Evaluation

All four edges of the growth substrate wafer were mechanically removed leaving a wafer (~1.5 cm x 2 cm) that was then diced into several ~3 mm x 3 mm pieces. Each piece was fashioned into an electrode by lightly scratching the back side with In–Ga eutectic and affixing the eutectic-coated electrode onto a coiled tinned Cu wire using Ag paint. The other end of the wire was then inserted into a glass tube and sealed using epoxy (Hysol 9460). The epoxy was left to cure overnight in a 60 °C oven and afterward the electrode was wetted with H₂O, etched for 15 s in HF(~6 M, aq), rinsed with H₂O, and then Pt was deposited potentiostatically (–100 mC cm^{–2}), as described above. Before use, each electrode was briefly etched in HF(~6 M, aq), and the current versus potential data were measured using a three-electrode setup with a Si microwire-array working electrode, a Pt wire or small carbon-cloth pseudo-reference electrode, and a Pt mesh or large carbon-cloth counter electrode. The electrolyte consisted of 12 M HCl under rapid stirring, a continuous H₂(g) purge, and 1 Sun of simulated solar illumination at an intensity of 100 mW cm^{–2} from an ELH-type W–halogen lamp with air blown onto the cell. The reversible potential for H₂(g) evolution (RHE) was determined using a Pt disk/button working electrode. The light intensity was determined using a calibrated Si photodiode (ThorLabs, Inc., FDS100) positioned at the location of the electrode, with the incident light passing through the borosilicate glass window of the electrochemical cell as well as through a thin path length of electrolyte.

Back-side Electrode Fabrication and Electrochemical Evaluation

A PDMS solution (2.5 mL toluene: 1 g PDMS: 0.1 g initiator) was spin cast onto oxide-booted p-type Si microwire arrays using the procedure described in the Supporting Information. Each partially PDMS-embedded Si microwire array was etched for 5 s with the PDMS etch described

in the Supporting Information, followed by a 10 min ozone etch, a 10 s etch in HF(~6 M, aq) and a rinse with H₂O, immediately followed by drying under a stream of N₂(g). Au was then thermally evaporated onto the microwires (300 nm planar equivalent; see Supporting Information), followed by covering the microwires in Ag paint, for structural stability. Once dried, the microwire–PDMS composite was mechanically removed from its growth substrate using a Teflon-coated steel razor blade. Pt was then evaporated onto the back side of the free-standing PDMS-embedded microwire array (5 nm planar equivalent) and the assembly was diced into smaller samples (~3 mm x 3 mm) using a razor blade. Each sample was fashioned into an electrode by mounting the Ag paint side of the sample onto a piece of Cu foil (99.9999%, Alfa Aesar) using Ag paint. The samples were then affixed to coiled tinned Cu wire using Ag paint, followed by inserting the other end of the wire into a glass tube and sealing the electrode using Hysol 9460 epoxy. After allowing the epoxy to cure overnight in a 60 °C oven, the electrode was wetted with H₂O, etched for 15 s in HF(~6 M, aq), and then immediately immersed in ~7.6 M HI that contained adventitious I₃⁻, under rapid stirring and a continuous Ar(g) purge. The current versus potential data were measured using a three-electrode setup with a back-side microwire–PDMS working electrode, a Pt wire pseudo-reference electrode, and a Pt mesh counter electrode. The reversible potential for I₃⁻ generation was determined using a Pt button working electrode and was found to be the same potential recorded for the back-side electrode at zero current.

Photoelectrochemical Deposition of Platinum

Electrodes were wetted with H₂O, etched for 15 s in HF(~6 M, aq), and then immediately immersed in an aqueous solution of 5 mM K₂PtCl₄ (99.9%, Alfa Aesar) and 200 mM LiCl. Using a three-electrode setup with a (KCl saturated) standard calomel reference electrode (SCE) and a Pt mesh counter electrode, the working electrode was held potentiostatically at -300 mV vs SCE while being illuminated by an ELH-type W-halogen lamp, with the light passing through a long-pass RG830 filter prior to striking the sample. The deposition was performed using a stirred solution and was terminated when 100 mC cm⁻² of cathodic charge had passed. The samples were then rinsed with H₂O and dried under a stream of N₂(g).

Electron-beam Evaporation

Immediately after etching samples with HF(~6 M, aq) or mechanically removing membrane-

embedded Si microwires from their growth substrate, samples were mounted onto a sample holder using Kapton tape affixed at the corners, placed into an evaporator (Temescal FC-1800 for Au (KNI) or Denton Explorer for all other metals) and positioned at an angle, set on planetary rotation, pumped down to $< 1 \times 10^{-5}$ Torr, and deposited metal until a desired planar equivalent registered on a calibrated quartz crystal.

Scanning Electron Microscopy with Energy Dispersive Spectroscopy

Imaging of Si microwire arrays during and after fabrication and processing, and when affixed as front-side and back-side electrodes, was performed on field-emission scanning-electron microscopes (Zeiss 1550VP and FEI Quanta 200F (Kavli Nanoscience Institute at Caltech (KNI))). The elemental composition of the front-side and back-side electrodes and samples was determined using an energy-dispersive spectrometer with a silicon drift detector (Oxford X-Max^N).

Electrochemistry

All reported current densities were referenced to the projected geometric area of the electrolyte contact to the electrode and/or membrane.

Free-standing Composite Membrane Fabrication

Nafion (~11 wt%, DMF) was exchanged from a Nafion solution (5 wt%, aq/alcohol) (Alfa Aesar) by heating at 55 °C for several days, and the resulting polymer was spin cast on (n⁺)p-type Si microwire arrays three times at 1000 RPM, each followed by drying in a vacuum oven at 60 °C for 40 min and then a 140 °C cure on a hotplate for 20 min. For n⁺p-type Si microwires, all four edges of the growth substrate wafer were mechanically removed and In–Ga eutectic was lightly scratched as ~10 spots, ~2 mm in diameter, on the back side of the wafer (~1.5 cm x 2 cm), followed by coating with Ag paint. Each sample was fashioned into a large electrode using Ag paint to affix the wafer onto a coiled tinned Cu wire that had been partially sealed into a glass tube using Hysol 1C epoxy and hardener. The exposed wire and silicon edges were coated in two coats of black nail polish (Sally Hansen, Black Out) (Figure S1a), each allowed to dry at room temperature for 60 min before Pt was deposited potentiostatically on the electrode (-100 mC cm^{-2}), as described above. The samples were rinsed with H₂O and then carefully removed from the tinned Cu wire using acetone and affixed to a glass slide using mounting wax (South Bay

Technology, Inc., Quickstick 135). Each partially Nafion-embedded Si–Pt microwire array was removed from its growth substrate by mechanical peeling using a Teflon-coated steel razor blade (for p-Si) or an 8” heavy-duty scraper blade (Better Tools, LLC, Part #20107) and a home-built microwire array peel-off tool, to ensure the microwire–membrane integrity, with no tears, of the composite membranes (for n⁺p-Si).^{S1} The peel-off tool contained a spring-loaded scraper blade that traveled along the surface of the wafer to sever the microwire–Nafion composite from the Si growth substrate. Pt was then evaporated onto the back side of the free-standing Nafion-embedded microwire array (5 nm planar equivalent) (Figure 1) followed by storage in a glove box under an inert Ar atmosphere.

Free-standing Composite Membrane Photoelectrochemical Evaluation (additional information)

Before assembling the composite membrane sample between the two glass cuvettes, the anode back side of the sample was wetted with HI to ensure that bubbles were not trapped at the surface. Approximately 20 composite membranes were evaluated. Before introducing the membranes into the H-cell, samples were qualitatively evaluated for their ability to split HI by immersing the membrane into the electrolyte, and visually monitoring, while under illumination, bubble formation and release from the microwire side of the composite membrane, as well as a darkening of the back side of the membrane due to I₃⁻ formation. In the H-cell, the anolyte was continuously stirred in the 1 mm path length cuvette which was vertically offset by ~0.5 cm from the bottom of the 10 mm path length cuvette, so that it could be probed using transmission-mode ultraviolet–visible electronic absorption spectroscopy. The 10 mm path length cuvette was equipped with a gas-tight sealable screw top with a silicone septum that contained 3 ports, each containing 1/16” Teflon tubing. One port served as an outlet to the mass spectrometer and was under slightly negative pressure, due to pull from the differential pump at the inlet of the mass spectrometer. Another port served as an inlet for inert carrier gas, and was slightly over-pressurized using ultra-high-purity Ar(g). The final port was open to allow the system pressure to equilibrate with ambient pressure and thereby prevent over-pressurization or under-pressurization, which ultimately ripped the membrane. Two traps were placed between the cuvette and the mass spectrometer: a dry-ice/isopropanol trap, followed by a second trap filled with Drierite pellets to scrub any additional acid or water prior to entering the mass spectrometer (Hiden Analytical, HPR20 with a 100 amu column). The molar decadic absorption coefficient of triiodide at its maximum (350 nm) is

$\sim 26,000 \text{ M}^{-1} \text{ cm}^{-1}$, and is $\sim 100 \text{ M}^{-1} \text{ cm}^{-1}$ at the probing wavelength (550 nm). These values were used to convert the sample absorbance to a concentration of I_3^- , and subsequently to the current that generated I_3^- , using the volume of the cell ($\sim 0.4 \text{ mL}$) and differentiation of the data over time. The catholyte consisted of $\sim 2.8 \text{ mL}$ of $\sim 7.6 \text{ M HI}$, while the anolyte consisted of $\sim 0.4 \text{ mL}$ of HI/I_3^- . The hydriodic acid was unstabilized (Sigma Aldrich, 7.6 M , aq, 99.99%, or Alfa Aesar, $7.3 - 7.7 \text{ M}$, aq, ACS grade); thus, prior to transferring hydriodic acid into each cuvette, adventitious I_3^- was electrochemically reduced in an H-cell that contained $\sim 7.6 \text{ M HI}$ in both compartments and a Nafion membrane separator. (The catholyte compartment was continuously bubbled with Ar(g) , and reduction occurred at a large carbon-cloth working electrode. Oxidation occurred at a Pt mesh or large carbon cloth counter electrode in the anolyte compartment.) The 1 mm path length cuvette had been exposed to air and was not purged further during the experiment, so the electrolyte inside this compartment contained adventitious I_3^- . The HI electrolyte in the 10 mm path length cuvette initially contained small amounts of adventitious H_2 from the electrochemical reduction of I_3^- . It was continually bubbled with Ar(g) during the experiments, and no decrease in the volume of the catholyte was observed during the course of the experiments. The custom acrylic sample holder had a port for a borescope (PCE Instruments UK Ltd., PCE-VE 310) to image and record the photoelectrochemical reactions (Figures S2d and S3).

Reference

- (S1) Tamboli, A. C.; Chen, C. T.; Warren, E. L.; Turner-Evans, D. B.; Kelzenberg, M. D.; Lewis, N. S.; Atwater, H. A. Wafer-Scale Growth of Silicon Microwire Arrays for Photovoltaics and Solar Fuel Generation. *IEEE Journal of Photovoltaics* **2012**, *2*, 294–297.