

Water Splitting with Silicon *p-i-n* Superlattices Suspended in Solution

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Photoelectrochemical (PEC) water-splitting to produce hydrogen was reported 50 years ago¹, yet artificial photosynthesis—the generation of chemical fuels (*e.g.* hydrogen) from solar energy—has yet to become a widespread technology. Electricity-generating solar cells based on rigid, planar Si photovoltaic (PV) devices, however, have become a ubiquitous electrical energy source economically competitive with fossil fuels. Analogous, economically viable PEC devices have not been realized, and standard Si p-type/n-type (*p-n*) junctions cannot be used for water splitting because the bandgap precludes generation of the needed photovoltage. An alternate paradigm, the particle suspension reactor (PSR), forgoes the rigid design in favor of individual PEC particles suspended in solution, a potentially low-cost option compared to planar systems². Here, we report Si-based PSRs by synthesizing high-photovoltage multijunction (MJ) Si nanowires (SiNWs) that are co-functionalized to

catalytically split water. By encoding a *p-i-n* superlattice within single SiNWs, tunable photovoltages exceeding 10 V were observed under 1-sun illumination. Spatioselective photoelectrodeposition of oxygen and hydrogen evolution co-catalysts enabled water splitting at infrared wavelengths up to ~1050 nm with the efficiency and spectral dependence of hydrogen generation dictated by photonic characteristics of the sub-wavelength diameter SiNWs. Unlike wider bandgap oxide and chalcogenide particles previously studied for PSRs³, MJ SiNWs bring the photonic advantages of a tunable, mesoscale geometry and the material advantages of Si—including small bandgap and economies of scale—to the PSR design, providing a new approach for water-splitting reactors.

In its simplest implementation, a water-splitting PSR would take the form of a clear bag filled with a photocatalytic particle slurry or solution exposed to daylight (Figure 1a), from which hydrogen and oxygen are siphoned^{2,4}. To operate efficiently, the particles for this reactor design must absorb visible light, produce the voltage required to split water (1.23 V plus kinetic overpotentials), exhibit stability in an aqueous environment, and be functionalized with an oxygen evolution catalyst (OEC) and hydrogen evolution catalyst (HEC). Although numerous PSRs operating under ultraviolet light have been reported^{3,5-8}, including one with a near unity quantum efficiency⁹, particles responsive to visible light are far less common and mainly consist of metal oxides¹⁰⁻¹⁵, oxysulfides¹⁶, nitrides¹⁷⁻²¹, and cadmium salts^{22,23}, with only a handful of reported bandgaps below 2 eV^{15,16}. Thus, all PSRs reported to date are incapable of absorbing red and infrared sunlight, limiting their potential energy conversion efficiency²⁴.

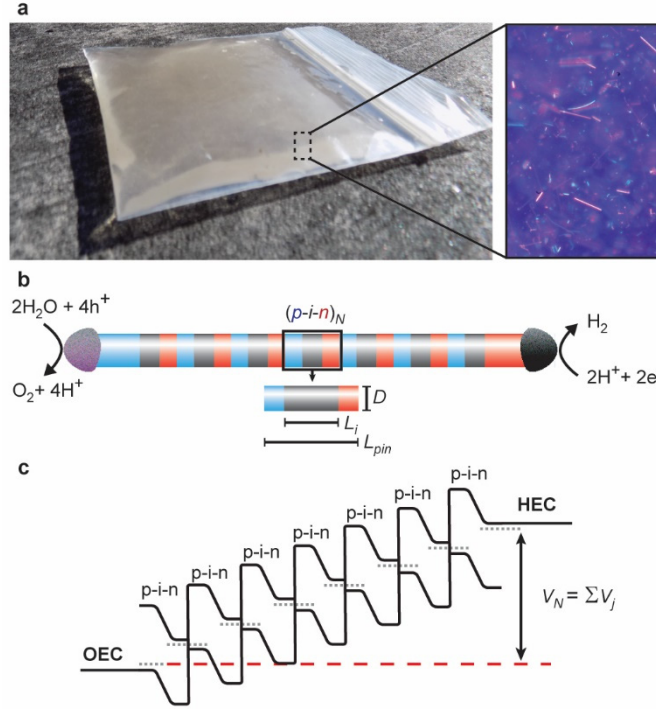


Figure 1 | Design of a PSR using co-functionalized SiNWs encoded with $p-i-n$ superlattices.

a, Illustrative example of the PSR, showing a photograph (left) of a clear plastic bag with suspended SiNWs and dark-field microscopy image (right) of SiNWs in the suspension. **b**, Schematic diagram of a single SiNW water splitting reactor showing the $p-i-n$ superlattice and net catalytic reactions at either end. Inset: illustration of a single junction defining the geometric parameters diameter (D), intrinsic segment length (L_i), and $p-i-n$ junction length (L_{pin}). **c**, Illustration of the band bending and net photovoltage (V_N) generated by summation of the photovoltage (V_j) from individual $p-i-n$ junctions in a superlattice, producing electrons and holes at the HEC and OEC functionalized ends, respectively, with the potential needed to split water.

For PV technology, Si is chosen for its close to ideal bandgap, earth abundance, non-toxicity, chemical stability, and economy of scale due to the microelectronics industry. However, its bandgap of 1.12 eV makes systems composed of a single $p-n$ junction unsuitable for direct

water splitting. Instead, a MJ configuration is needed—such as the planar, triple-junction amorphous Si/SiGe solar cells that have been used for water splitting²⁵—because they can sum the photovoltage of several p - n junctions to achieve the needed potential. To use Si in a PSR for water splitting thus requires the design of MJ particles. Si particles have been created by a variety of techniques, including spherical microcrystals crystallized from molten Si²⁶, nanocrystals synthesized by plasma²⁷ or colloidal techniques²⁸, and top-down fabrication and release of particles from silicon-on-insulator substrates²⁹⁻³¹, which can include the creation of p - n junctions by diffusion doping. Yet to our knowledge, MJ Si particles have only been reported once, in SiNWs grown by a vapor-liquid-solid (VLS) mechanism³².

NW-based optoelectronic systems have been studied extensively due to the advantageous photonic properties imparted by their sub-wavelength dimensions, such as enhanced optical cross sections, localized resonant modes, and light-trapping³³⁻³⁵. VLS-grown SiNWs with p - n or p -type/intrinsic/ n -type (p - i - n) single junctions encoded along their growth axis have been reported in several instances^{32,36-38}, and their theoretical performance has been analyzed^{39,40}. Under 1-sun illumination, the single junctions typically generate short-circuit current densities (J_{sc}) of 5-10 mA/cm² and open-circuit voltages (V_{oc}) of 0.2-0.4 V. To achieve MJ SiNWs, multiple p - i - n junctions must be grown sequentially (Figure 1b) and the n - p junction between the p - i - n units must behave as a tunnel junction, electrically connecting the p - i - n units in series via band-to-band tunneling of charge carriers in order to sum the voltage of individual units (Figure 1c). Despite the report more than 10 years ago of a SiNW with two p - i - n junctions, yielding a V_{oc} of ~0.4 V³², the challenging synthetic requirements for VLS growth of a p - i - n superlattice has barred further experimental development. Recently, we reported growth conditions that yield SiNWs with degenerate doping levels, sharp dopant transitions, no evident vapor-solid radial

overcoating, minimal gold (Au) loss⁴¹⁻⁴³, and tunnel junction behavior⁴⁴, providing the prerequisite synthetic requirements to yield SiNW *p-i-n* superlattices for usage as MJ particles in a PSR.

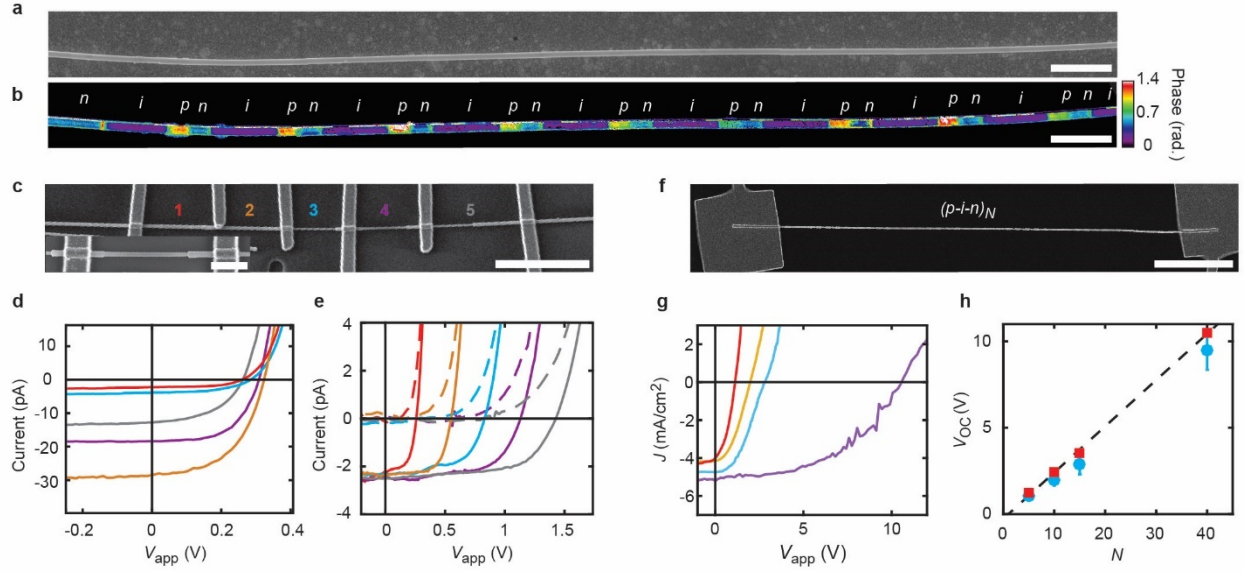


Figure 2 | Single MJ SiNW PV devices. **a**, Composite SEM image of an $N = 10$ *n-i-p* SiNW; scale bar, 2 μm . **b**, s-SNOM phase map of the SiNW shown in panel **a** with individual *p*, *i*, and *n* segments labeled; scale bar, 2 μm . **c**, SEM image of an etched $N = 5$ *n-i-p* SiNW with contacts defined for each junction labeled 1-5; scale bar, 5 μm . Inset: higher magnification SEM image showing junction 4; scale bar, 1 μm . **d**, I - V curves under 1-sun illumination of junction 1 (red), 2 (orange), 3 (cyan), 4 (violet), and 5 (gray). **e**, I - V curves from the same device as panel **d** measuring across junction 1 (red) and junctions 1 through 2 (orange), 3 (cyan), 4 (violet), and 5 (gray). Dashed and solid lines were collected in the dark and under 1-sun illumination, respectively. **f**, SEM image of an unetched $N = 15$ *p-i-n* SiNW with contacts on the *n*- and *p*-type terminals; scale bar, 10 μm . **g**, J - V curves for $N = 5$ (red), 10 (orange), 15 (cyan), and 40 (violet) SiNW devices under 1-sun illumination. **h**, Average (cyan circles) and champion (red squares)

V_{OC} as a function of N . Dashed line represents a linear fit to champion devices.

SiNWs ~ 150 - 200 nm in diameter were grown by a Au-catalyzed VLS process in a home-built chemical vapor deposition reactor (see details in Methods), a process that leaves the Au catalyst at the tip of the SiNW. During growth, the SiNWs were sequentially encoded with a variable number (N) of p - i - n or n - i - p units of variable total lengths L_{pin} and intrinsic segment lengths L_i . An example $N = 10$ n - i - p SiNW is shown by the scanning electron microscopy (SEM) image in Figure 2a, and the presence of the n - i - p superlattice was verified by infrared scattering-type scanning near-field optical microscopy (s-SNOM), which can directly map free carrier concentration along the length of a single SiNW^{39,45}. As indicated by the contrast in the s-SNOM image in Figure 2b, individual n - i - p units with average segment lengths of 0.74 ± 0.06 , 2.23 ± 0.08 , and 0.68 ± 0.05 μm , respectively, are clearly distinguishable along the length of the SiNW, verifying the fidelity and uniformity of the encoded structure. The PV performance of individual n - i - p units were characterized by fabricating metallic contacts to each junction of an $N = 5$ SiNW after selective wet-chemical etching to reveal the junction location, as shown by the SEM images in Figure 2c. Current-voltage (I - V) characteristics measured as a function of applied voltage (V_{app}) from each junction (labeled by junction index j) under 1-sun illumination are shown in Figure 2d with PV metrics (short-circuit current (I_{sc}), V_{OC} , fill factor (FF), series resistance (R_s), dark saturation current (I_0), ideality factor (n), and surface recombination velocity (S)) collected in Extended Data Table 1. Although the etching causes variations in I_{sc} and I_0 , the V_{OC} , FF , n , and S are comparable to one another and to single junctions reported in the literature^{32,39}, verifying the high quality of individual junctions. I - V curves measured across an increasing number of n - i - p units (Figure 2e) exhibit a V_{OC} that is additive and an I_{sc} that is, as expected,

limited by the lowest I_{SC} in the series.

The MJ performance of $p-i-n$ and $n-i-p$ superlattices were tested by fabricating single SiNW devices with electrical contacts on the n -type and p -type end segments (Figure 2f), enabling measurements with V_{app} applied across all synthetically encoded PV junctions and tunnel junctions. Prior to device fabrication, the SiNWs were hydrogen annealed to passivate surface defects³⁹, resulting in a large increase in I_{SC} and FF (Extended Data Figure 1). Figure 2g shows current density-voltage ($J-V$) curves under 1-sun illumination for champion SiNW devices with $N = 5, 10, 15$, and 40 , and L_i of $2.1, 2.1, 1.5$, and $0.2 \mu m$, and n -type/ p -type segments lengths of $1.3, 1.3, 1.3$, and $0.2 \mu m$, respectively. Note that the length of individual $p-i-n$ units was reduced for higher N to reduce the total length of the SiNWs and facilitate device fabrication, and $N = 5, 10$ and $N = 15, 40$ Si NWs were grown in $n-i-p$ and $p-i-n$ sequences, respectively. Current density (J) was defined as $J = I/(D \cdot L_{pin})$ using the projected area of a single $p-i-n$ segment, and all PV metrics are summarized in Extended Data Table 2.

As N increases, the value of J_{SC} is approximately constant while V_{OC} increases linearly, as shown in Figure 2g and h, highlighting the consistency of junctions within individual SiNWs and between the $n-i-p$ and $p-i-n$ growth polarities. A linear fit to champion devices yields a value of 0.27 V/junction , which is consistent with V_{OC} measurements on single junctions. Notably, a SiNW with $N = 40$ yielded a V_{OC} above 10 V , which is in substantial excess of the voltage needed for water splitting. R_s also increased linearly with N , and the increase ($\sim 10 \text{ M}\Omega/\text{junction}$) is consistent with the series resistance of an additional single junction and the effective resistance of a tunnel junction⁴⁴. Decreasing L_i for the higher N devices decreases I_{SC} , but I_o also decreases due to the lower surface area of the junction³⁹. With increasing illumination intensities, the SiNWs exhibited a linear increase in I_{SC} and logarithmic increase in V_{OC} (Extended Data Figure

2) as expected for PV devices behaving according to the ideal diode equation. Comparing the experimental I_{sc} to the theoretical I_{sc} based on optical simulations³⁹, we estimate the overall internal quantum efficiency (IQE) to be ~60% from each junction. This value agrees well with a spatially-dependent IQE of near unity in the intrinsic regions and near zero in the p - and n -type regions, as predicted by device simulations³⁹, and highlights the potential to improve overall performance in the future through minimization of the n -type and p -type segment lengths.

To split water, the MJ SiNWs require a HEC at the n -type end for proton reduction and an OEC at the p -type end for water oxidation, as illustrated schematically in Figure 1b. Moreover, for a PSR, the co-catalysts must be simultaneously deposited on millions to billions of SiNWs at once. Thus, we developed a bottom-up spatioselective photoelectrodeposition process utilizing the built-in junctions to electrochemically deposit a metal or metal oxide at the ends of the SiNWs, using Pt and cobalt oxide (CoO_x) materials as the HEC and OEC, respectively. Pt deposition was optimized on n -type terminated p - i - n superlattices by immersing in an aqueous solution containing 5 mM $[\text{PtCl}_6]^{2-}$ for 10 min under 5-sun illumination, which resulted in reduction to form Pt on the Au tip, as shown by the SEM image and scanning transmission electron microscopy (STEM) energy dispersive x-ray spectroscopy (EDS) elemental map in Figure 3a (for individual element maps, see Extended Data Figure 3a). CoO_x deposition was optimized on p -type terminated n - i - p superlattices by immersing in an aqueous solution of 5 mM Co^{2+} for 3 min under 5-sun illumination, resulting in oxidation to form CoO_x on the Au tip (Figure 3b and Extended Data Figure 3b). The deposition processes were then combined as a two-step sequence on p - i - n superlattices (Figure 3c) by first depositing Pt on the Au tip, releasing SiNWs from the silicon oxide growth substrate by sonication, and second depositing CoO_x as a conformal shell on the p -type base of SiNWs suspended in solution (see Methods for details).

This deposition order was chosen because Pt deposition on the *n*-type base of the *n-i-p* structures was relatively inconsistent (Extended Data Figure 4a). High-resolution transmission electron microscopy (HRTEM) images in Figure 3d and STEM EDS maps in Figure 3e confirm the spatioselectivity of the two processes, with EDS spectra showing no evidence of Pt at the *p*-type base (Figure 3f) or Co at the *n*-type tip (Figure 3g). Additional HRTEM imaging (Extended Data Figure 4b-c) indicates that the Pt is nanocrystalline while the CoO_x is amorphous.

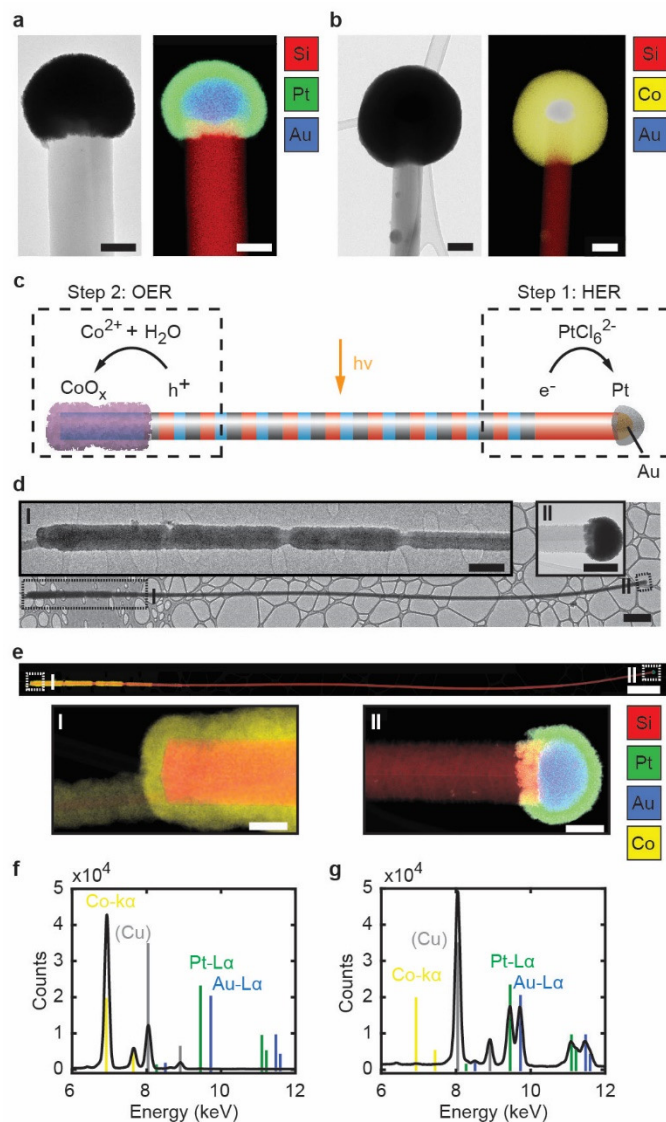


Figure 3 | Co-catalyst functionalization of MJ SiNWs by spatioselective

photoelectrodeposition. **a-b,** HRTEM image (left) and color-coded STEM EDS elemental map (right) for Pt deposited on a *p-i-n* superlattice (panel a) and CoO_x deposited on an *n-i-p* superlattice (panel b). **c,** Schematic representation of the oxidation and reduction of co-catalysts onto the MJ SiNWs. **d,** HRTEM image of an *N* = 15 *p-i-n* SiNW with Pt and CoO_x deposition; scale bar, 2 μm. Insets: higher magnification images of the *p*-type base (I) and *n*-type tip (II); scale bars, 600 nm (I) and 200 nm (II). **e,** Upper: Composite STEM EDS elemental map of the

SiNW shown in panel d; scale bar, 2 μm . Lower: higher magnification maps of the boxed regions labeled I and II; scale bars, 100 nm. **f-g**, EDS spectra (black lines) from the *p*-type base (panel f) and *n*-type tip (panel g) of the SiNW. Colored lines show the expected peak positions of Co (yellow), Pt (green), Au (blue), and Cu (gray). Cu signals originate from the TEM grid.

To test the PEC activity of co-functionalized MJ SiNWs, we fabricated single SiNW devices using a millimeter-scale two-electrode cell⁴⁶, as illustrated in Figure 4a. Separate devices were fabricated with either the HEC- or OEC-functionalized ends of 40-junction *p-i-n* SiNWs exposed to pH 7 water, with the other end of the SiNWs electrically connected to macroscopic Ir/IrO_x or Pt counter electrode, respectively. With zero externally applied bias and under chopped illumination with light emitting diodes (LEDs) of variable wavelength (455-650 nm), a photocathodic current (Figure 4b) and photoanodic current (Figure 4c) were observed for the SiNWs with the Pt and CoO_x ends exposed, respectively, which we attribute to the hydrogen and oxygen evolution reactions, respectively. Photocurrent was observed out to an illumination wavelength of 1050 nm for the photocathode and 940 nm for the photoanode (Extended Data Figure 5a-b); however, as expected from the wavelength-dependent absorption of Si, the photocurrent at these longer wavelengths is substantially smaller. No substantial photocurrent was generated from control electrodes (Extended Data Figure 5c-d).

Assuming an IQE of ~60% as deduced from the single-SiNW PV devices (Figure 2), a theoretical maximum wavelength-dependent external quantum efficiency (EQE) per junction of a single-SiNW PEC system was calculated (Figure 4d) by simulating the absorption efficiency of a single *p-i-n* segment, which shows strong photonic resonances (inset, Figure 4d)⁴⁷. The theoretical values correlate well with our experimentally determined EQE per junction for the

cathode (Figure 4d, yellow diamonds) and anode (Figure 4d, red circles), suggesting that the single-SiNW PEC reactors already achieve a quantum efficiency that is near unity in terms of photons absorbed per junction converted into solar fuel products. Such high efficiency has only previously been observed for SrTiO_3 ,⁹ a system fundamentally limited to only ultraviolet light absorption; thus, this result illustrates the immense potential for a MJ SiNW PSR design to enable efficient PSRs absorbing light across much of the solar spectrum.

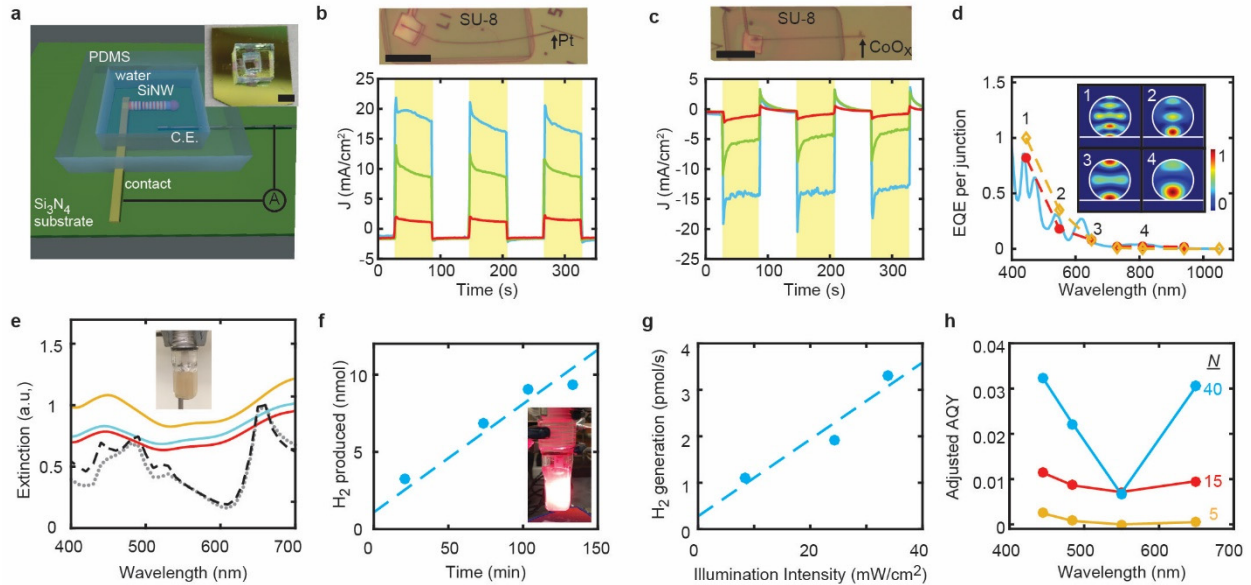


Figure 4 | Water splitting with OEC/HEC-functionalized MJ *p-i-n* SiNWs. **a**, Schematic rendering of the single-SiNW two-electrode PEC cell. Inset: photograph of a cell; scale bar, 3 mm. **b-c**, Optical microscopy images (upper; scale bars, 20 μm) and J vs. time (lower) under chopped illumination for $N = 40$ co-functionalized SiNWs with the *n*-type/Pt photocathode end exposed (panel b) and the *p*-type/ CoO_x photoanode end exposed (panel c). Measurements were done at zero V_{app} under illumination at 455 (cyan), 549 (green), and 650 (red). **d**, Experimental EQE per junction from single-NW PEC measurements for SiNW/ CoO_x (red circles) and

SiNW/Pt (orange diamonds) compared to simulated EQE spectrum (blue solid line) for $D = 200$ nm. Inset: normalized maps of absorption efficiency in the SiNW cross section under TM polarization at wavelengths of 455, 549, 650, and 810 nm labeled 1-4, respectively. **e.** Extinction spectra (solid lines) of suspensions of SiNWs with $N = 5$ (yellow), 15 (red), and 40 (cyan). The dashed and dotted lines are extinction and scattering spectra, respectively, from optical simulations. Inset: Photograph of the ~ 12 mL liquid cell used to evaluate SiNW-based PSRs. **f.** Total hydrogen generated as a function of time for a $N = 40$ PSR with 650 nm LED illumination at 34 mW/cm^2 . **g.** Hydrogen generation rate as a function of light intensity from a $N = 40$ PSR with 650 nm LED illumination. **h.** Adjusted AQY for hydrogen generation as a function of LED illumination wavelength for $N = 5$ (yellow), 15 (red), and 40 (cyan) PSRs.

Prototype PSRs were tested by suspending functionalized MJ SiNWs into aqueous pH 3 sulfuric acid solution to promote hydrogen evolution. PSRs with $N = 5$, 15, and 40 at concentrations of ~ 2000 , ~ 1000 , and ~ 600 SiNWs/ μL , respectively, were prepared and exhibited a cloudy appearance with extinction spectra showing several peaks and effective extinction coefficients above $\sim 1 \text{ cm}^{-1}$ (Figure 4e). Note that in a PSR, the SiNWs are free to rotate, resulting in variable angles of illumination. A simulated extinction spectrum (Figure 4e, dashed line), calculated by taking the weighted average of simulated extinction spectra for single SiNWs at various illumination angles assuming an isotropic distribution (see Methods for details), reproduces the general features of the PSR extinction spectra. Comparison to the simulated scattering spectrum (Figure 4e, dotted line) indicates that the PSR optical properties are dominated by the scattering rather than absorption characteristics of the SiNWs, as has also been observed for disordered SiNW fabric⁴⁸. In addition, the optical simulations indicate that the

subwavelength diameter of the SiNWs ensures approximately equal light absorption from each *p-i-n* unit nearly independent of illumination angle (Extended Data Figure 6), facilitating impedance matching between the junctions.

For measurement of hydrogen generation, suspensions were loaded into an ~12 mL cell (Figure 4e, inset), purged with argon gas, illuminated with LEDs of variable wavelengths, and periodically sampled for hydrogen analysis by gas chromatography (see Extended Data Table 3 for all PEC metrics). Note that SiNWs used in the PSRs were not hydrogen annealed because the high-temperature processing was not compatible with the catalyst deposition steps. For $N = 40$ SiNWs under 650 nm LED illumination, we observed clear hydrogen production over several hours with a steady increase in hydrogen with time (Figure 4f). Moreover, the hydrogen production rate increased approximately linearly with illumination intensity (Figure 4g). Note that no hydrogen was detected from control PSRs composed of MJ SiNWs without HEC and OEC catalysts. Suspensions were found to produce hydrogen for several days, after which performance decreased. Based on SEM images, the only apparent degradation of the SiNWs was dissolution of CoO_x catalyst, which is expected under pH 3 conditions⁴⁹. The relatively good stability of the SiNWs may be a result of the degenerate *n*- and *p*-type doping levels, which act as an etch stop in aqueous solution⁴², and the strong electric field in the intrinsic segments⁴⁰. The CoO_x catalyst is more stable in pure water and we observed an increase in hydrogen concentration over several days when using pH 7 water (Extended Data Figure 7a), but the generation rate was lower than in the acidic solution. Note that hydrogen production with 650 nm illumination is the longest wavelength ever to be reported for a PSR.

PSRs with $N = 5, 15$, and 40 were illuminated at four LED wavelengths, and the apparent quantum yield (AQY) and solar to hydrogen efficiency (STH) for hydrogen generation was

measured at each wavelength, with all metrics collected in Extended Data Table 3. To enable direct comparisons on the basis of photons absorbed per *p-i-n* junction between PSRs with different N and SiNW concentrations, an adjusted AQY (Figure 4h) was calculated by multiplying the AQY (%) by N and dividing by the product of L_i (μm) and optical density (O.D.). All suspensions produced hydrogen, and the AQY values tended to peak for illumination at 445 nm and 650 nm and dip at 485 and 550 nm, which was in approximate agreement with the extinction spectra of the samples (Figure 4d). This trend suggests that the overall sample absorption and hydrogen generation is correlated with the scattering response of the SiNW suspension, which increases the effective optical path length through the cell. The $N = 5$ PSRs produced the lowest adjusted AQY likely because a large fraction of the SiNWs did not generate the photovoltage needed for water splitting, and the $N = 40$ PSR was 10-20 times more efficient on a photon absorbed per junction basis at generating hydrogen than the $N = 5$ PSR. Additionally, in the presence of citric acid (a sacrificial electron donor), the AQY and STH from an $N = 40$ PSR increased substantially (Extended Data Figure 7b), suggesting that the OER reaction could be limiting the reaction rate and that further engineering of the OER co-catalyst and solution environment may be necessary for efficient fuel generation. Thus, the results show there is substantial opportunity in future PSR designs to optimize scattering characteristics, MJ design, and co-catalysts to improve performance.

In summary, we have demonstrated MJ SiNWs with *p-i-n* superlattices that can produce more than 10 V of photovoltage under 1-sun illumination, we have developed a process for *in situ* deposition of spatially-separated co-catalysts at the ends of the SiNWs, and we have demonstrated prototype water-splitting reactors responsive to light across visible and near IR wavelengths, with single-SiNW measurements demonstrate the potential for near-unity quantum

efficiencies. The PSR architecture developed herein is a highly tunable system—electronically, geometrically, photonically, and catalytically—with numerous opportunities for rational design to improve efficiency, *e.g.* improvements in the SiNW axial doping profile and surfaces to maximize *p-i-n* junction IQE and photovoltage^{39,40}, higher performance co-catalysts (*e.g.* Pt/Cr₂O₃ core/shell structures to prevent oxygen reduction⁹), SiNW morphological photonic design to enable optical bound states that boost infrared light absorption⁴⁷, *etc.* Furthermore, recent advances in the high-volume production of SiNWs could be leveraged for future scale-up⁵⁰. The long-term stability of the SiNWs will require study, and molecular functionalization of surfaces could be used to improve electrical properties⁵¹, prevent chemical degradation⁵², and stabilize the SiNWs in solution⁵³. Beyond water splitting, the ability to synthesize SiNWs with large, tunable photovoltages can enable a myriad of other applications, such as carbon dioxide reduction⁵⁴, nitrogen fixation⁵⁵, nanoscale propulsion⁵⁶, cellular signal transduction⁵⁷, and drug release⁵⁸.

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Author Contribution

T.S.T, D.J.H., S.R.L., S.R.B., S.E.M., and J.P.C. synthesized wires and made electrical devices. T.S.T., D.J.H., S.K., and J.-S.P. performed SiNW optical simulations. T.S.T and A.D.T. designed and performed the PSR experiments. E.T.R. and J.M.A. performed s-SNOM measurements. J.R.M. collected the STEM EDS spectra and elemental maps for the functionalized wires. T.S.T. and J.F.C. wrote the manuscript with input from all authors. J.F.C. conceived and supervised all aspects of the research.

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Methods

SiNW Synthesis

SiNWs were synthesized in a home-built chemical vapor deposition (CVD) reactor with a hot-walled tube furnace (Lindberg Blue M). Si/SiO₂ wafers were functionalized with poly-L-lysine (Sigma Aldrich), and Au nanoparticles (150 or 200 nm, BBI International) were deposited on the surface. The substrate was inserted into the CVD reactor and heated to 520 °C. SiNWs were grown at a reactor pressure of 20 Torr and a silane (SiH₄, Voltaix) partial pressure of 200 mTorr. Doping level was controlled by modulating the flow of precursor gases diborane (1000 ppm in H₂, Voltaix) and phosphine (1000 ppm in H₂, Voltaix) with mass-flow controllers (MKS Instruments, model P4B) to achieve an encoded doping level of 7.5×10^{20} and 5×10^{20} cm⁻³ for the *p*- and *n*-type segments, respectively. HCl (Matheson TriGas, 5N) gas was flowed at a 2:1 ratio with the SiH₄ to prevent vapor-solid overcoating and gold deposition on the NW sidewalls^{42,43}.

Single SiNW Devices

For PV measurements, NWs were mechanically dispersed onto Si wafers coated with 100 nm SiO₂ and 200 nm Si₃N₄ (Nova Electronic Materials) and pre-patterned with a marker pattern. SiNWs devices were annealed under 760 Torr forming gas (5% H₂ in N₂, Airgas) in a rapid thermal annealing system (ULVAC MILA-5000) by quickly heating to 600 °C and ramping down to 300 °C over 2 hours. For the etched devices, the native oxide was removed with buffered hydrofluoric acid (BHF, Transene BHF Improved) and the SiNWs were etched with a 20 wt. % solution of KOH (*aq*) for 60-120 seconds prior to the anneal. An electron-beam photoresist stack (MMA EL 9 and PMMA A2, Microchem) was spun onto the wires and contacts

were patterned to the wires via electron-beam lithography (Nanometer Pattern Generation System) using an FEI Helios 600 Nanolab dual-beam system. The native oxide on the contact area was etched using BHF and metal contacts (3 nm Ti, 300 nm Pd) were deposited immediately using an electron-beam evaporator (Kurt Lesker PVD 75) at a base pressure of $\sim 2 \times 10^{-8}$ Torr. Electrical measurements were taken using a Keithley 2636A SourceMeter connected to a home-built probe station consisting of Signatone micromanipulators (S725) and tungsten probe tips (SE-TL). A 1 kW Xe lamp solar simulator (Newport model 91191) with an AM1.5G filter was calibrated to 1-sun (100 mW/cm^2) using a reference Si photocell (Newport model 91150 V) and used to illuminate the SiNW devices. For measurements under increased illumination, the light from the lamp was concentrated over the device area using a lens. Device characteristics were calculated by fitting the dark I - V curves to a modified ideal diode equation that includes a series resistance R_s ⁵⁹.

For measurements in an electrochemical cell, materials and procedures were similar to PV devices. Co-functionalized MJ SiNWs from the same growth substrate were dropcast from a suspension in water onto a prefabricated marker patterns, and electron-beam lithography and electron-beam evaporation were used to deposit Ti/Pd contacts on one end of the wires (either n - or p -type). Directly after metal evaporation, SiO_x (75-100 nm) was deposited by electron-beam evaporation (Thermionics VE-100) on the metal contacts. A polymer (SU-8 2000.5, Microchem) was additionally patterned by electron-beam lithography over the metal contacts and the majority of the SiNW, leaving the NW tip exposed to solution. To create the liquid cell, a square polydimethylsiloxane (Dow SYLGARD 184) well with a thickness of 3 mm was cut using a clay punch (NS Creative Elements) to have outer dimensions of 6 x 6 mm and inner of 3 x 3 mm and was secured onto the chip. For photocathode measurements, an Ir wire was placed in a UV-

Ozone cleaner for 10 minutes to clean and oxidize the surface and was then inserted through the side of the PDMS wall. Using the home-built probe station, the MJ SiNW devices were connected to the counter electrode through the Keithley SourceMeter. Photocurrent at zero V_{app} was measured under illumination from an LED light source (Lumencor Spectra X Light Engine) at 445 ± 20 nm (44.6 mW/cm^2), 549 ± 10 nm (55.9 mW/cm^2), and 650 ± 13 nm (28.8 mW/cm^2). For longer wavelength illumination, single color LED light sources (ThorLabs) with collimation adapters were used at 730 ± 20 nm (236 mW/cm^2), 810 nm (380 mW/cm^2), 940 nm (506 mW/cm^2), and 1050 ± 20 nm (19 mW/cm^2). Similar measurements were done for the photoanode (*p*-type Si/CoO_x) but with a Pt wire counter electrode that was cleaned in BHF to remove any surface contaminants and oxide layer.

NW Functionalization

For Pt or CoO_x functionalization of the Au tip, MJ SiNWs, while still attached to the growth substrate, were etched in BHF and then immersed in a 5 mM H₂PtCl₆ (aq) or 5 mM Co(NO₃)₂ (aq) solution under 5-sun illumination for 10 mins. For co-functionalized PSR wires, Pt-functionalized wires were etched in BHF and removed from the substrate via sonication into a 0.3 mM Co(NO₃)₂ solution. The solution suspension was stirred under 5-sun illumination for 3 mins ($N = 15, 40$) or 10 mins ($N = 5$). Note that the CoO_x reaction was apparently slower for the $N = 5$ wires and required longer time periods to achieve a similar deposition volume. The suspensions were centrifuged for 20-30 minutes at 6000 rpm (Fisher Scientific accuSpin 1R) and dispersed in deionized H₂O.

Electron Microscopy

SEM was performed on a FEI Helios 600 Nanolab dual-beam system. For HRTEM and STEM imaging, NWs were transferred to lacey-carbon TEM grids (Ted-Pella no. 01895) by dipping the grid into a dilute suspension of functionalized wires. HRTEM and STEM-EDS was performed on a Tecnai Osiris HRTEM/STEM operating at 200 kV equipped with a SuperX™ quad EDS detection system. STEM-EDS maps were collected using Bruker Esprit software version 1.9 with a sub-nm probe having ~ 0.8 nA of beam current. The drift-corrected STEM-EDS maps were typically collected over a 5 min period.

Optical and Scanning Probe Microscopy

Optical bright-field and dark-field microscopy was performed on a Zeiss Axio Imager A.2m upright microscope. Near-field microscopy experiments were performed using a home-built infrared s-SNOM system based on a modified commercial AFM (Bruker Innova) as described previously⁴⁵. A vertically-polarized CO₂ laser (Access Lasers) at 10.6 μm wavelength was used as an excitation source. The near-field signal was demodulated at the third harmonic of the tapping frequency and used to construct an optical image simultaneously with the AFM topography. s-SNOM experiments were carried out using a homodyne interferometric scheme, utilizing a two-step procedure to calculate the near-field phase and amplitude⁶⁰. To allow for comparison of the near-field signal across samples, SiNWs were deposited onto Au-coated Si₃N₄ substrates and were normalized to the high-intensity, spectrally flat signal from the Au surface. Near-field spatial resolution was determined from near-field approach curves to be ~ 10 nm. Several scans ($2 \times 2 \mu\text{m}$, 512×512 pixels) were taken along the length of the wire to observe the doping profile. These images were then stitched together to provide a map of the multiple *n-i-p* junctions along the SiNW length. Doping assignments were determined by comparing the near-field phase and amplitude to the encoded doping profile. The *n*-type sections were shown to have

the highest near-field amplitude, with *p*-type sections having a lower amplitude but higher phase, and intrinsic Si having the lowest amplitude and phase. This agrees with previously established s-SNOM carrier sensitivity levels⁴⁵.

Particle Suspension Reactors

Co-functionalized MJ SiNWs were suspended in either a pH 3 H₂SO₄ (*aq*) solution, a pH 3 citric acid/monosodium citrate buffer solution, or in pH 7 water using a home-built quartz reactor fitted with a stainless-steel cap and Swagelok outlet/inlet valves. All solutions used water from a deionized water system (resistivity = 18 MΩ·cm). The solution was stirred and purged with argon gas for approximately one hour. The reactor was then closed and illuminated with an LED source (Lumencor Spectra X Light Engine) at wavelengths of 445 ± 20 , 485 ± 20 , 549 ± 10 , and 650 ± 13 nm. The fiber optic cable directing the illumination was mounted such that the diameter of the beam was the same width as the reactor sidewall (1.5 cm) and illuminating almost the entire area of the suspension. Headspace samples (~0.5 mL) were extracted from the outlet valve using a Luer-lok syringe and injected into a gas chromatograph (Varian 450). Concentration of H₂ gas was determined using a calibrated pulsed discharge helium ionization detector. Moles of H₂ were calculated using the volume of the reactor headspace plus the syringe, assuming ideal gas behavior. The reactor was purged for 20-30 minutes with argon in between trials. Extinction spectra of the suspensions were measured on a UV-Vis Spectrophotometer (Cary-5000, Agilent) using a cuvette with 1 cm path length. Previous experiments showed that extinction was approximately linearly related to pathlength, allowing an optical density for the solution to be calculated for the PSR. NW density in the PSRs was estimated by drop casting a known volume of the suspension and using SEM to count full-length NWs over a measured projected area for extrapolation of the total number of SiNWs in the volume.

Optical Simulations

All absorption, scattering, and extinction spectra were calculated with finite-element modelling in COMSOL Multiphysics version 5.4. For the EQE spectrum shown in Figure 4d, a 2D simulation consisting of a 200 nm diameter SiNW on a dielectric stack (200 nm Si₃N₄, 100 nm SiO₂ and 500 nm Si) and embedded in 1 μ m of SU-8 polymer. Absorption efficiency was calculated by dividing the absorbed power inside of the wire area by the incident power at each wavelength. Absorption mode profiles were generated by plotted by normalizing the data of Ohmic absorption losses within the SiNW cross section. For the absorption data shown in Extended Data Figure 6, a 3D simulation geometry consisting of a 32 μ m long Si cylinder divided axially into ten 3.2 μ m long segments (to represent an $N = 10$ MJ SiNW) was illuminated from a plane wave light source. The cylinder was surrounded by 200 nm of air with refractive index of one and a perfectly matched layer on all sides. The absorbed power in each segment was calculated for both TE and TM polarization from 400-1000 nm and the two were averaged to determine the unpolarized result. The spectrum was then multiplied by the appropriate factor to account for the solar irradiance spectrum and integrated to determine the photocurrent generation, assuming an IQE of unity. This model was run for illumination angles in 10° increments (0, 10, 20, 30, 40, 50, 60, 70, 80, and 90°) and interpolated to 1° increments. A weighted average of the photocurrent was calculated assuming a three-dimensional isotropic distribution of the SiNW orientation in solution. Photocurrent for a bulk, planar $N = 10$ Si PV device, with each junction of a thickness equivalent to the length of junctions in the SiNW, was calculated analytically by solving for the photon generation rate from known absorption coefficients and then integrating over each 3.2 μ m segment assuming zero reflection from the

surface. Scattering was calculated by integrating the Poynting vectors over the NW surface, and extinction spectra were calculated by summing the scattering and absorption spectra.

Extended Data for Water Splitting with Silicon *p-i-n* Superlattices Suspended in Solution

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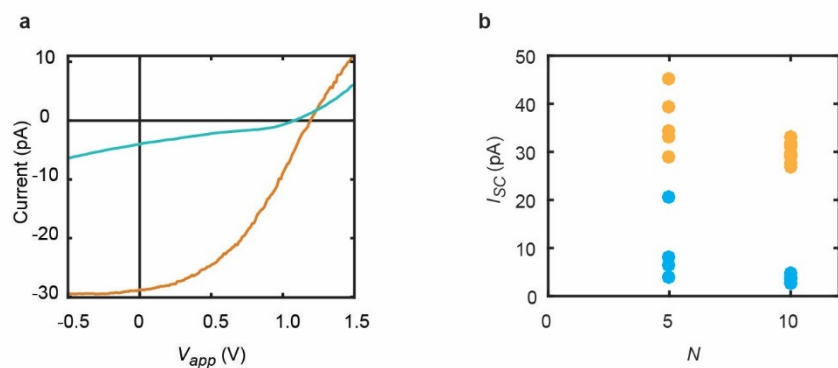
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Extended Data Table 1 | PV metrics for individual *n-i-p* junctions in a wet-chemically etched $N = 5$ single SiNW

junction index (<i>j</i>)	L_i (μm)	D_i (nm) ^a	I_{SC} (pA)	V_{OC} (V)	FF	R_s ($\text{G}\Omega$)	I_o (fA)	n	S (cm/s) ^b
1	2.1	180	2.2	0.25	0.58	18	15	2.0	1.04E+03
2	2.1	163	28.4	0.32	0.53	2.3	32	2.0	2.46E+03
3	2.1	93	3.9	0.28	0.52	14	8.3	1.9	1.12E+03
4	2.1	120	18.3	0.30	0.60	23	58	2.1	6.11E+03
5	2.1	114	12.6	0.25	0.50	4.1	18.5	2.1	2.03E+03

^adiameter of etched intrinsic segment

^bapproximated via equation 2 in ref. 34



Extended Data Figure 1 | Effect of hydrogen anneal on PV performance. a, I - V curves for $N = 5$ $n-i-p$ SiNW PV devices with an anneal (orange) and with no anneal (cyan) under 1-sun illumination. **b,** I_{sc} for $N = 5$ and 10 $n-i-p$ PV devices with an anneal (orange) and without an anneal (cyan).

Extended Data Table 2 | Single MJ SiNW PV metrics

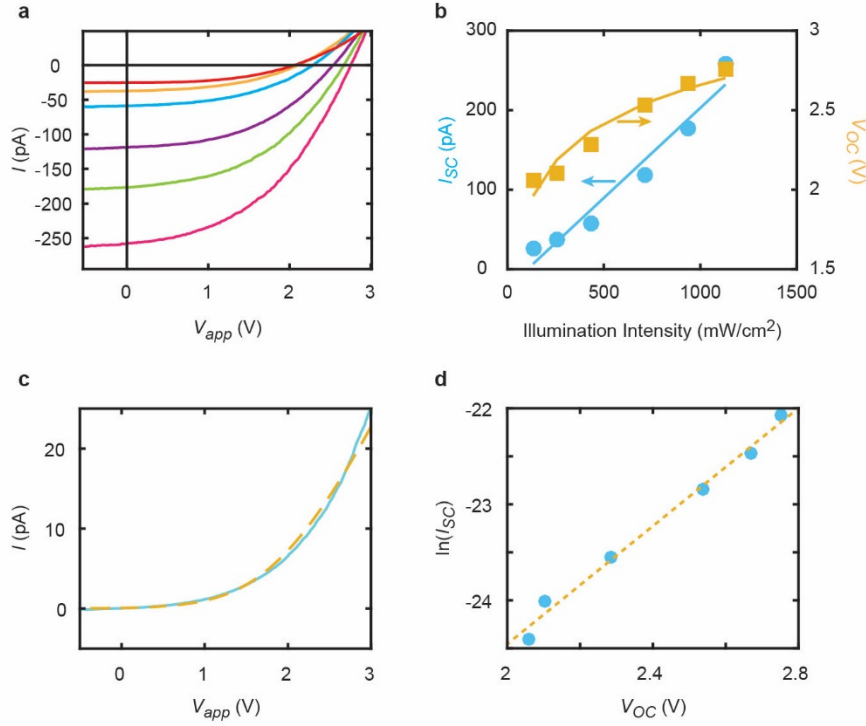
N	Growth Polarity	D^a (nm)	L_i (μm)	V_{oc} (V)	V_{oc}/N (V/junc.)	I_{sc} (pA)	FF	R_s/N ($G\Omega/\text{junc}$)	I_o (fA)	n/N^b	S (cm/s) ^c
5	$n-i-p$	200	2.1	1.23	0.25	23.9	0.37	2.04	184	1.68	1.15E+04
				1.06	0.21	21.7	0.31	17.5	77	1.09	4.82E+03
				0.98	0.20	19.4	0.39	3.43	66	1.28	4.11E+03
				0.89	0.18	14.4	0.54	4.86	423	1.08	2.65E+04
				0.89	0.18	21.1	0.41	9.12	41	0.83	2.55E+03
				Average: ^d	1.01	0.20	20.1	0.40	7.39	158	1.19
10	$n-i-p$	200	2.1	2.43	0.24	13.2	0.43	14.3	145	1.76	9.10E+03
				2.35	0.24	12.1	0.44	7.45	367	2.37	2.30E+04
				2.27	0.23	14.9	0.49	4.16	319	1.65	2.00E+04
				2.21	0.22	16.0	0.42	16.6	469	1.87	2.94E+04
				2.18	0.22	18.7	0.36	15.5	60	1.66	3.73E+03
				2.18	0.22	25.0	0.39	10.3	274	1.72	1.72E+04
				2.16	0.22	11.8	0.42	9.56	159	1.64	9.98E+03
				2.12	0.21	31.7	0.42	6.39	223	1.29	1.39E+04
				2.07	0.21	20.7	0.31	13.0	76	1.11	4.77E+03
				2.03	0.20	27.0	0.36	5.61	879	2.11	5.50E+04
				2.00	0.20	33.1	0.36	2.67	259	1.61	1.62E+04
				2.00	0.20	12.9	0.55	2.28	491	1.64	3.08E+04
				1.92	0.19	24.4	0.33	6.16	294	1.53	1.84E+04
				1.89	0.19	16.1	0.37	14.0	348	1.64	2.18E+04
				1.80	0.18	18.3	0.48	5.79	55	0.83	3.42E+03
				1.79	0.18	6.3	0.37	21.3	113	0.97	7.11E+03
				1.74	0.17	24.9	0.44	3.32	451	1.19	2.83E+04
				1.68	0.17	29.9	0.37	4.71	1750	1.57	1.10E+05
				1.62	0.16	16.5	0.42	0.52	2330	1.80	1.46E+05
				1.52	0.15	19.3	0.27	1.63	170	0.93	1.06E+04
				1.48	0.15	40.0	0.44	0.46	207	0.85	1.30E+04
				1.31	0.13	5.5	0.32	13.5	566	1.90	3.55E+04
				Average: ^d	1.94	0.20	19.9	0.40	8.15	455	1.53
15	$p-i-n$	200	1.5	3.49	0.23	5.0	0.56	16.3	79	2.00	6.89E+03
				3.19	0.21	13.8	0.35	16.5	51	1.74	4.49E+03
				3.02	0.20	6.1	0.49	11.5	116	1.47	1.01E+04
				2.81	0.19	22.5	0.4	17.2	5.67	1.08	4.97E+02
				2.6	0.17	8.2	0.35	24.4	0.56	1.02	4.06E+01
				1.94	0.13	5.8	0.46	15.0	48	1.05	4.20E+03
				Average: ^d	2.84	0.19	10.2	0.44	16.8	50.0	1.39
40	$p-i-n$	150	0.2	10.5	0.26	2.2	0.49	19.9	5.62	1.56	4.93E+03
				10.2	0.26	2.0	0.85	53.4	1.80	1.19	1.58E+03
				10.1	0.25	1.1	0.67	29.6	5.74	2.03	5.03E+03
				9.62	0.24	1.6	0.47	62.0	1.22	1.26	1.07E+03
				8.4	0.21	4.4	0.52	11.4	45	1.06	3.98E+04
				7.81	0.20	1.4	0.53	35.7	9.68	1.41	8.49E+03
				Average: ^d	9.44	0.24	2.1	0.59	35.3	11.5	1.42

^a approximate diameter of catalyst used

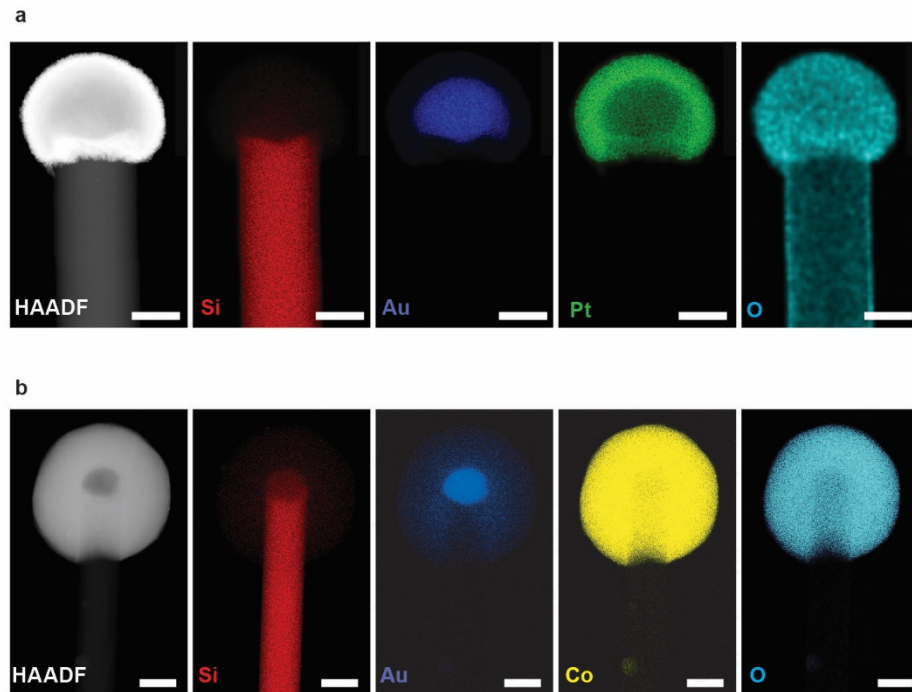
^b n also increases linearly with N_i as per the ideal diode equation

^c approximated via equation 2 in ref. 39

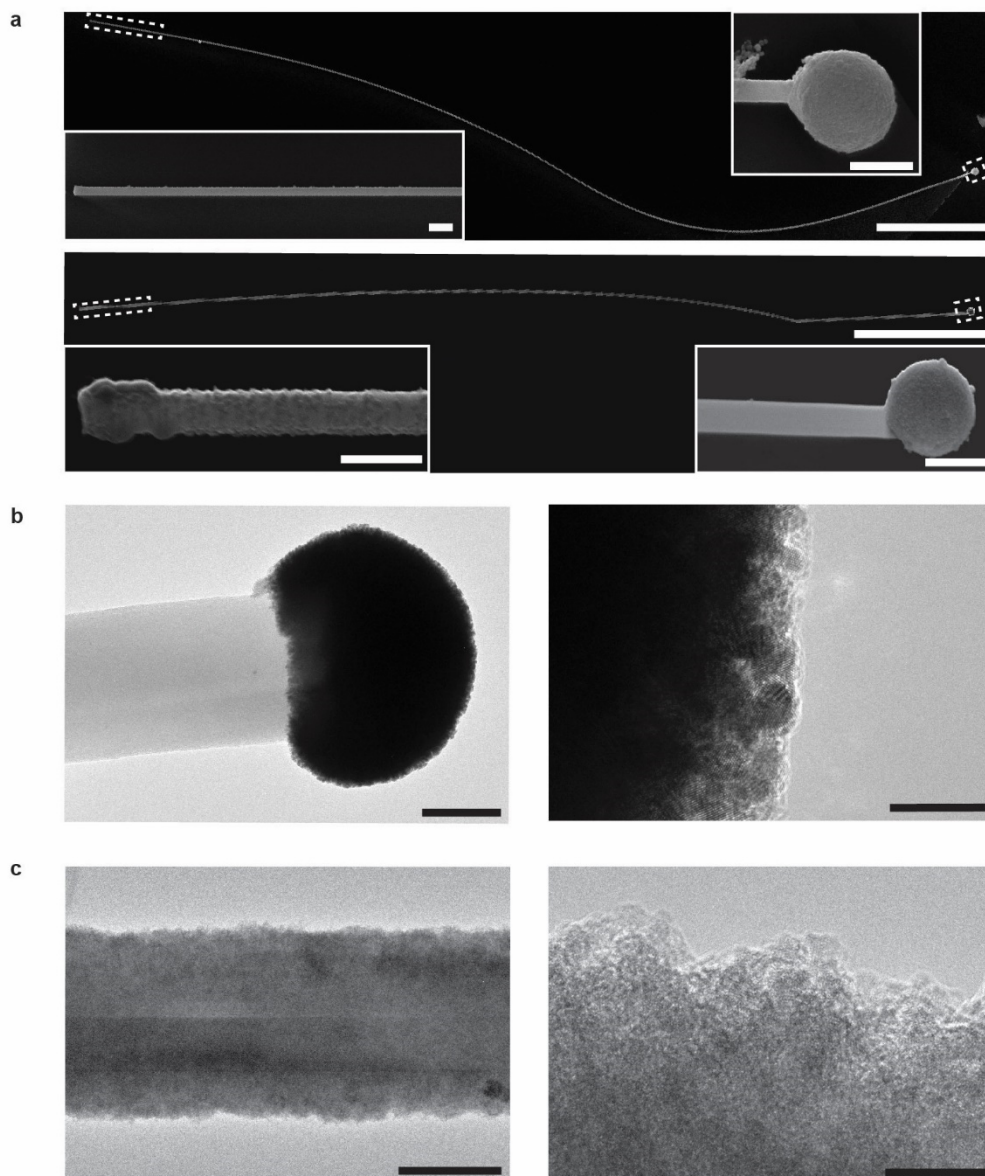
^d trends in the average values with changing *p-i-n* geometry generally follow the trends predicted in ref. 39, where increases in L_i tend to increase both I_{sc} and I_o with relatively minor effect on V_{oc}/N



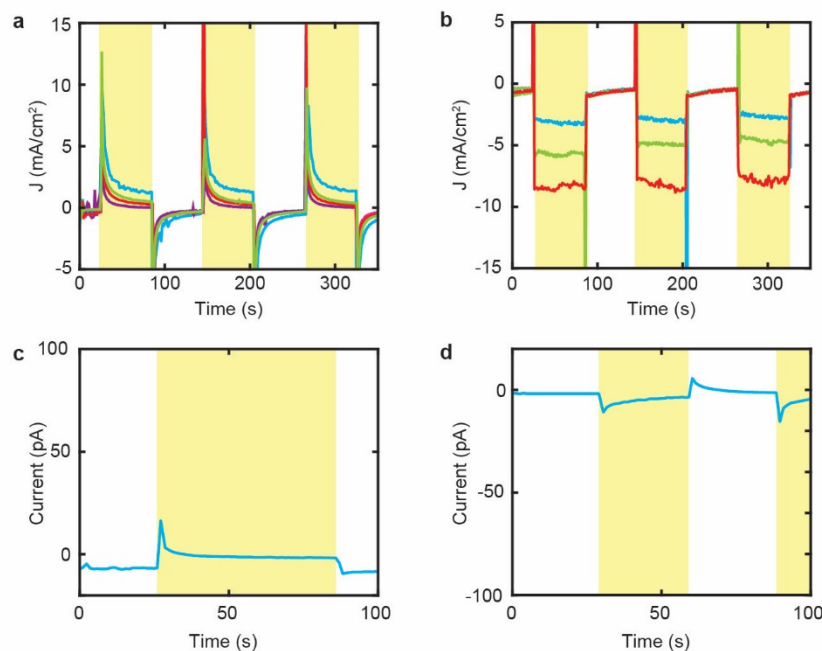
Extended Data Figure 2 | Single $N = 10$ n - i - p SiNW PV device under multi-sun illumination. **a**, The I - V curves of a $N = 10$ SiNW under 1.3 sun (red), 2.5-sun (orange), 4.3-sun (cyan), 7.2-sun (purple), 9.4-sun (green), and 11.3-sun (magenta) illumination. **b**, The dependence of I_{sc} (cyan) and V_{oc} (orange) on the illumination intensity for the SiNW shown in panel a. Solid lines show the linear fit (cyan) and logarithmic fit (orange) for the I_{sc} and V_{oc} trends, respectively. **c**, Dark I - V curve (cyan) of the same SiNW with a fit to the ideal diode equation modified to include R_s (yellow, dashed), yielding a normalized ideality factor (n/N), I_0 , and R_s of 1.53, 234 fA, and 36 $\text{G}\Omega$, respectively. **d**, Plot of $\ln(I_{sc})$ vs. V_{oc} from the multi-sun illumination data shown in panels a-b. Dashed line represents a fit to the ideal diode equation, yielding a normalized ideality factor and I_0 of 1.27 and 51 fA respectively.



Extended Data Figure 3 | STEM EDS of photoelectrochemically deposited co-catalysts. a-b, STEM high-angle annular dark field (HAADF) images (far left) and color-coded EDS maps (right) of individual elements for the MJ SiNWs shown in main text Figure 3a (panel a) and main text Figure 3b (panel b); scale bars, 100 nm for panel a and 200 nm for panel b. The apparent oxygen signal from the Pt shell in panel a is an artifact arising from a strong background x-ray signal, as no oxygen peaks are present in the EDS spectra (not shown) integrated over the Pt shell only.



Extended Data Figure 4 | Electron microscopy images of $N = 15$ SiNWs co-functionalized with Pt and CoO_x co-catalysts. **a**, SEM images of two co-functionalized $n-i-p$ SiNWs; scale bars, 5 μm . Insets: higher magnification images of the dashed boxed regions showing the n -type bases with Pt (left) and p -type tips with CoO_x (right); scale bars, 200 nm. Pt deposition was only evident on the n -type base of a fraction of the SiNWs, and the amount of deposited material was small compared to CoO_x deposition on the p -type base of $p-i-n$ SiNWs. **b**, TEM images of the Pt-functionalized n -type tip of a $p-i-n$ SiNW at low magnification (left) and higher magnification (right), showing the polycrystalline nature of the deposited Pt nanoparticles; scale bars, 100 nm (left) and 10 nm (right). **c**, TEM images of the CoO_x functionalized p -type base of the same $p-i-n$ SiNW shown in panel b at low magnification (left) and higher magnification (right), showing the amorphous nature of the deposited CoO_x ; scale bars, 200 nm (left) and 10 nm (right).



Extended Data Figure 5 | Photoelectrochemical response of single SiNW devices. a-b, Chopped photocurrent density ($J = I/(D \cdot L_{pin})$) vs. time for $N = 40$ co-functionalized SiNWs with the n -type/Pt photocathode end exposed (panel a) and the p -type/ CoO_x photoanode end exposed (panel b). Measurements were done at zero V_{app} under illumination at 730 (cyan), 810 (green), and 940 (red). Panel a also shows the response of the photocathode under 1050 nm illumination (violet). **c-d,** Two-electrode photocurrent measurements in the PEC cell in pH 7 water under chopped 445 nm LED illumination (shaded area denotes when the LED was on) and zero V_{app} for control electrodes (Pd/SiO_x/SU-8) identical to the electrodes used for electrical contact to the SiNWs. Measurements in panel a and c used an Ir/IrO_x wire counter electrode and measurements in panel b and d used a Pt wire counter electrode.

Extended Data Table 3 | Photoelectrochemical Metrics for MJ SiNW PSRs

<i>N</i>	PSR O.D. @450 nm	<i>L_i</i> (μm)	LED wavelength (nm)	LED power (mW)	H ₂ generation rate (nmol/hr)	AQY ^a (%)	STH efficiency (%) at LED wavelength ^b
5 ^c	3.7	1.5	445 ± 34	78	13.7	0.0026	1.2e-3
			485 ± 20	63	3.64	0.0008	3.8e-4
			549 ± 15	100	B.D.L ^e	-	-
			650 ± 13	59	3.01	0.0005	3.4e-4
15 ^c	2.7	1.5	445 ± 34	78	17.4	0.0033	1.5e-3
			485 ± 20	63	11.5	0.0025	1.2e-3
			549 ± 15	100	17.2	0.0021	1.1e-3
			650 ± 13	59	16.1	0.0028	1.8e-3
40 ^c	2.9	1	445 ± 34	86	14.6	0.0025	1.1e-3
			485 ± 20	72	9.13	0.0017	8.4e-4
			549 ± 15	105	4.63	0.0005	2.9e-4
			650 ± 13	60	14.1	0.0024	1.5e-3
40 ^d	2.9	1	445 ± 34	75	49.7	0.0099	4.4e-3
			485 ± 20	60	21.5	0.0049	2.4e-3
			549 ± 15	92	10.2	0.0013	7.3e-4
			650 ± 13	53	15.3	0.0031	1.9e-3

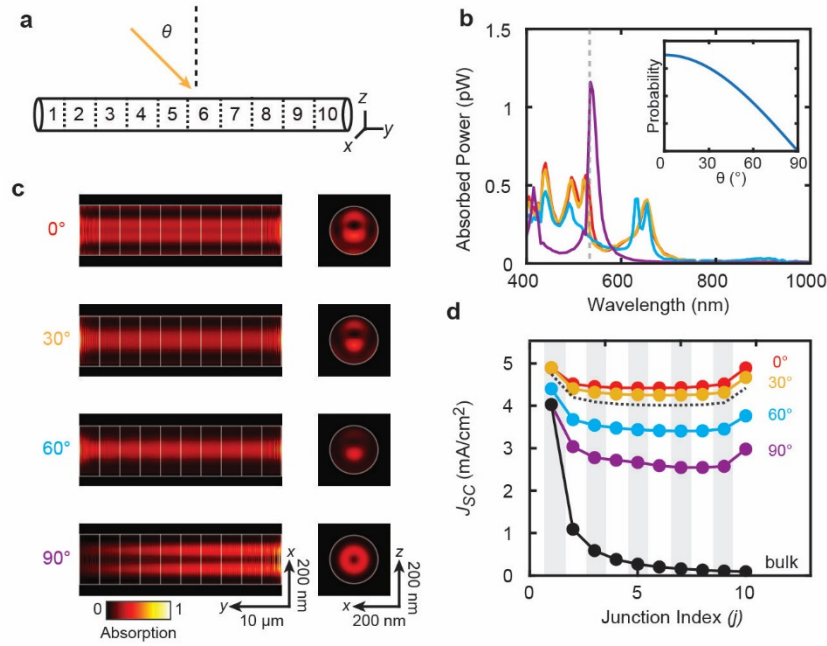
^a AQY = 2*R*/*I*; *R* = rate of H₂ production, *I* = incident photon flux

^b Solar to hydrogen (STH) efficiency calculated for illumination at the given LED wavelength and calculated as STH = (*G*·237 kJ/mol)/*P*_{LED} = 2*G*·*F*·(1.23 V)/*P*_{LED}, where *G* is the H₂ generation rate in units of mol/s, *F* is Faraday's constant, *P*_{LED} is the LED power in units of W, and 1.23 V is the thermodynamic potential for water splitting. The factor of 2 accounts for the fact that 2 electrons are needed to generate one H₂ molecule.

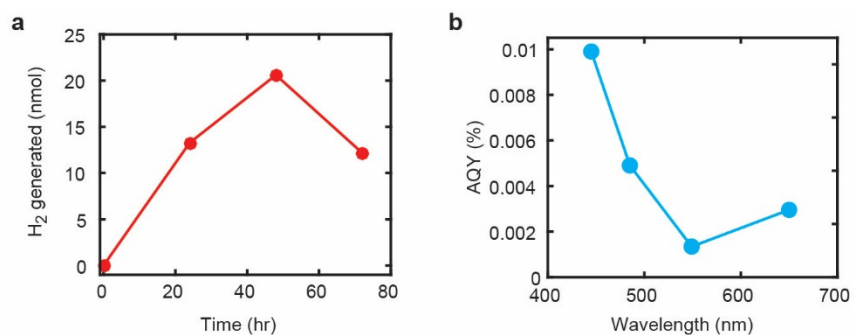
^c Data collected in pH 3 sulfuric acid solution

^d Data collected in pH 3 citric acid buffer solution

^e B.D.L. = below detection limit



Extended Data Figure 6 | Simulated absorption and calculated photocurrent from a SiNW. **a**, Simulated geometry of a 32 μm long SiNW divided into 10 junctions, labeled by junction index j , where the illumination angle, θ , is defined versus the surface normal. **b**, Absorbed power spectrum for $j = 5$ under 1-sun illumination at an incident angle of 0 (red), 30 (yellow), 60 (cyan), and 90° (violet), demonstrating the angular dependence of the SiNW absorption. Inset: Relative probability of each possible illumination angle assuming a three-dimensional isotropic distribution. **c**, Normalized axial (left) and radial (right) absorption profiles at 550 nm (dashed line in panel b) at incident angles of 0, 30, 60, and 90°. **d**, J_{sc} for each junction at various angles of illumination determined by appropriately integrating the photon absorption spectra within each segment, assuming the AM1.5G solar spectrum and an IQE of unity. End scattering effects tend to increase absorption in the first and last junction by $\sim 10\%$, but the intermediate junctions show the same J_{sc} within $\sim 15\%$, even for illumination coaxial with the SiNW. This is in sharp contrast the expected photocurrent of a bulk $N = 10$ solar panel with the same junction thickness (black dots), calculated analytically assuming known absorption coefficients and neglecting surface reflections. The grey dashed line shows the weighted average expected J_{sc} assuming a three-dimensional isotropic distribution of SiNWs.



Extended Data Figure 7 | Hydrogen generation in PSRs in pH 7 water and pH 3 citric acid buffer solution. a, Total hydrogen gas produced by an $N = 15$ PSR over the course of several days in deionized water (pH 7) under 650 nm illumination. Values are corrected for hydrogen removed during sampling process. The apparent decrease in H₂ generation after two days is likely due to a stop in H₂ generation combined with leakage from the cell. **b,** Quantum yield of an $N = 40$ PSR in an aqueous citric acid buffer solution (pH 3) under various wavelengths of LED illumination.