Light-induced water oxidation at silicon electrodes functionalized with a cobalt oxygen-evolving catalyst

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Contributed by Daniel G. Nocera, April 30, 2011 (sent for review March 30, 2011)

Integrating a silicon solar cell with a recently developed cobalt-based water-splitting catalyst (Co-Pi) yields a robust, monolithic, photo-assisted anode for the solar fuels process of water splitting to O2 at neutral pH. Deposition of the Co-Pi catalyst on the Indium Tin Oxide (ITO)-passivated p-side of a np-Si junction enables the majority of the voltage generated by the solar cell to be utilized for driving the water-splitting reaction. Operation under neutral pH conditions fosters enhanced stability of the anode as compared to operation under alkaline conditions (pH 14) for which long-term stability is much more problematic. This demonstration of a simple, robust construct for photo-assisted water splitting is an important step towards the development of inexpensive direct solar-to-fuel energy conversion technologies.

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Author contributions: J.J.H.P., M.T.W., Y.S., and D.G.N. performed research; J.J.H.P. contributed new reagents/analytic tools; J.J.H.P., M.T.W., and Y.S. analyzed data; J.J.H.P. and D.G.N. wrote the paper.

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The realization of Si-based, direct solar-to-fuel devices hinges on overcoming the inherent photoelectrochemical instability of Si in the presence of the highly oxidizing conditions of water splitting (32, 33). We now show that Si surfaces can be effectively protected from photoinstability at neutral pH with thin layers of Indium Tin Oxide (ITO) and that the passivated np-Si junction can function as efficient photoassisted anodes for the water oxidation reaction, where a photon/u equation of the Co-Pi catalyst is a structural relative of PSII OEC. PSII OEC has been the creation of a cobalt-phosphate (Co-Pi) catalyst. The predominate structure of Co-Pi (21) where the fourth Mn atom is linked via a μ-oxo-bridge. The predominate structure of Co-Pi in ca. nanometer thin films is a Co3O4-Co (4 = alkali metal ion) biscubane that is the head-to-tail dimer of PSII OEC.

The Co-Pi catalyst may be interfaced to semiconducting metal-oxides to enhance the efficiency of photoelectrochemical water splitting. In particular, Co-Pi has been deposited onto Fe3O3 (22–24), and WO3 thin films (25) and on ZnO rods (26) to effect a several hundred-millivolt reduction in the onset potential for water oxidation relative to the unfunctionalized photoanode. For Fe2O3 (23) and WO3 (25) films, this promising reduction of the onset potential has been achieved at neutral pH. While these metal-oxide semiconductors benefit from high photoelectrochemical stability, their band-gaps and losses associated with bulk and interfacial transport place limits on the theoretical efficiency of overall water splitting (27). Among nonoxides, silicon (Si) is a preferred semiconductor material because it absorbs a significant part of the solar spectrum, is earth-abundant, has low losses associated with bulk and interfacial carrier transport, and hence it is widely used in photovoltaic applications. The integration of np-Si junctions with water splitting has the potential to significantly reduce current costs of solar energy conversion by potentially reducing the balance of system costs attendant to separate devices for solar capture/conversion and storage (28–30). Such an approach is particularly well suited for small-scale solar-to-fuel devices, which have enormous potential for decentralized power generation and storage, particularly in developing economies (31).

Results and Discussion

A schematic representation of the illuminated Co-Pi-functionalized np-Si electrode and its energy diagrams in dark and under illumination (for water oxidation at 1 mA/cm2) are given in

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H2O O 2

An interfacial SiO which is an effective barrier for charge transfer. Therefore, a junction, followed by a rapid thermal annealing step in N by depositing a 1 (a potential of 1.3 V vs. NHE at the ITO|CoPi interface) for the dark (black line) and illuminated with a Xe lamp (green line, intensity ∼100 mW/cm²). In some of the samples, a p+ layer was incorporated by depositing a 1 μm film of Si-doped (1%) Al on the p-side of the junction, followed by a rapid thermal annealing step in N2 at 900°C (34). An interfacial SiO2 (~1.5 nm) layer was intentionally deposited on the p-side of the junction to provide a smooth transition from the Si substrate to the overlying passivating layer (35) so that recombination caused by high interface state densities due to mismatch in lattice constants, expansion coefficients, and other geometric factors is minimized. Because water molecules can penetrate into the Co-Pi film (3, 11), the catalyst cannot be directly deposited on the p-side of the np-Si junction, since Si at the interface would quickly oxidize into a thick SiO2 layer (35), which is an effective barrier for charge transfer. Therefore, a 50-nm film of ITO was deposited on the p-side of the Si junction as a protective barrier layer. Samples were annealed (400°C, N2, 30 min) to enhance the conducting properties of the ITO (36). A patterned metal front contact (Ti/Pd/Ag, 20/20/100 nm thickness, respectively) was deposited on the n-side of the sample. Top of this contact, a 10-μm layer of photoresist (AZ Electronic Materials, AZ-9260) was spin-cast to prevent the metal and n-Si surfaces from contacting water when the sample was immersed in the electrolyte. Finally, the Co-Pi film was grown on top of the ITO layer by means of electrodeposition (SI Appendix: Fig. S1). In a typical photoelectrochemical experiment (vide infra), a sample of Co-Pi-functionalized np-Si is immersed in an aqueous 0.1 M potassium phosphate (KPi) electrolyte and illuminated from the n-side. Absorption of light by the photoresist is negligible, as can be concluded from the absorption spectrum of the photoresist (SI Appendix: Fig. S2).

Fig. 2 shows a comparison of the cyclic voltammograms (CV) of npSi|ITO|Co-Pi and np+Si|ITO|Co-Pi anodes. In both cases, a film of the Co-Pi catalyst (250 nanomole Co) was electrodeposited (see SI Appendix). In principle, the Co-Pi catalytic activity can be increased by using thicker films (>7500 nanomoles), but transport limitations within thick films cause deviations in the current-voltage behavior (3). The sample was immersed in a 0.1 M KPi electrolyte at pH 7. Under these conditions, the Nernstian potential for water oxidation is 0.82 V vs. a normal hydrogen electrode (NHE). When applying the potential through the ITO thin film in the dark (Fig. 2, blue trace), the onset for water oxidation occurs at 1.2 V vs. NHE, implying an overpotential of ∼0.4 V. This value is in agreement with the required overpotential for Co-Pi on commercial ITO electrodes (3, 4). The significant currents in this electrode configuration, in which the photovoltaic (PV) component is shorted, indicate that the sputtered ITO film has a sufficiently low sheet resistance (170 Ω/sq, as determined in a four-point probe measurement). The onset for water oxidation remains located at 1.2 V, but the observed dark currents are much lower (Fig. 2, black trace) when the potential is applied through the metal contacts, such that current must flow through the PV component. Under reverse-bias conditions for the np-Si junction (e.g., positive applied potentials), the dark anodic current is determined by the leakage current across the np-Si junction, which should be negligible for a highly quality np-Si junction. The low but nonnegligible dark
current from our np-Si junctions (Fig. 2) reveals that the solar cell is partially shunted.

When illuminating the structure from the n-side with 100 mW/cm² light from a Xe lamp (AM1.5 illumination), the potential onset for water oxidation is decreased significantly for both the npSi|ITO|Co-Pi and the np⁺Si|ITO|Co-Pi sample (Fig. 2). Clearly, photogenerated holes in the Si are injected into the ITO film, after which they participate in the water oxidation reaction at the Co-Pi catalyst. As can be seen in SI Appendix: Fig. S4, incorporation of the Co-Pi catalyst results in a much lower onset potential for water oxidation (both in light and dark) compared to Si|ITO electrodes without Co-Pi, illustrating the benefit of functionalizing passivated np-Si junctions with the Co-Pi catalyst.

The current increases much faster with potential for the np⁺Si|ITO|Co-Pi sample than for the npSi|ITO|Co-Pi sample even though photocatalysts carriers presumably encounter the same, negligible series resistance in the bulk of either device (under illumination). These disparate CV characteristics can be explained by considering the non-Ohmic nature of the pSi|ITO interface compared to that of the p⁺Si|ITO interface. When p⁺Si is brought in contact with ITO, equilibration of the Fermi levels is achieved by exchange of charge carriers across the interface. Because the work function of ITO [4.4–4.7 eV (37, 38)] is smaller than that of p-Si [5.0–5.2 eV (39)], electrons will flow from the ITO into the p⁺-Si, creating a negatively charged space-charge layer in the Si with associated downward band bending (Fig. 2, inset). The negative charge acquired accumulates mainly at fixed acceptor impurity atoms. In the relatively lightly doped p⁺-Si, the space-charge region can extend far into the p⁺-Si (up to ~1 μm) and the resulting downward band bending acts as a Schottky barrier for hole transport. In the highly doped p⁻-layer, in contrast, the space-charge region extends only a few nanometers into the p⁻-layer because of the high number of dopant atoms that can accept the electrons from the ITO (Fig. 2, inset). Hence, the space-charge region in the p⁻-layer is thin enough for holes to tunnel across the p⁻-Si|ITO interface, which behaves as an Ohmic contact.

A prefeature prior to the catalytic wave is observed in the CVs of Fig. 2 for anodes in the dark and under illumination. This prefeature is attributed to oxidation of Co³⁺ centers in the Co-Pi film to Co⁴⁺ and, partially, Co⁵⁺ centers (3, 40, 41); these redox conversion processes give rise to transient currents. Upon prolonged electrolysis at the “prefeature potential,” the current decreases to zero, indicating that negligible residual water oxidation catalysis takes place at the prefeature potential.

The energy band diagrams corresponding to steady-state operation in dark and under illumination at 1 mA/cm² current are given in Fig. 1 B and C, respectively, for an np⁺Si|ITO|Co-Pi anode. Previous reports (3, 4, 10) as well as steady-state data obtained here (vide infra) establish that ~1.3 V vs. NHE is required to maintain a 1 mA/cm² current density for water oxidation on a 2D surface, thus pinning the potential at the ITO|Co-Pi solution interface at ~1.3 V. Because the rectifying characteristics of the np-Si junction impede anodic current flow, a larger reverse-bias of ~1.6 V vs. NHE must be applied to the anode in the dark to enable 1 mA/cm² of anodic current to tunnel across the buried np-Si junction (Fig. 1B). In contrast, a much lower potential of 0.8 V vs. NHE is needed to attain a 1 mA/cm² current density under illumination (Fig. 1C). This reduction of the required applied potential originates both from the photovoltage generated by the solar cell (0.5 V) and from the lower impedance of the np-Si junction under illumination because excited photocarriers can move freely through the conduction and valence bands. The foregoing discussion highlights a key distinction between this construct and a conventional photo- electrochemical anode. In the latter, photovoltage generation and current rectification occur at the solution/semiconductor interface. The driving force for water oxidation is therefore dictated by the energy of the band edge relative to the thermodynamic potential for water oxidation. In the construct of Fig. 1, the photovoltage generation and current rectification occur at the buried np-Si junction. Thus, it is the intersection of the i-V curve of the PV component with the i-V curve of the Co-Pi electrochemical component that dictates the (photo)potential and (photo) current available for water splitting (42).

Further insight in the presence of non-Ohmic interfaces within the Si|ITO|Co-Pi structures is provided by examining the Tafel behavior (43). For the native catalyst on ITO, a Tafel slope near 59 mV/decade is characteristic of an O₂ evolution mechanism involving a reversible one-electron transfer prior to a chemical turnover-limiting step (3). For the experiments described here, mechanistic information about the Co-Pi catalyst from the Tafel plot is convoluted by the electrical properties of the PV and ITO components of the anode. Accordingly, the Tafel data is examined solely as a measure of the steady-state activity of the photo-assisted anode as a function of applied potential. For the npSi|ITO|Co-Pi in Fig. 3A, the slope of the Tafel plot is 285 mV/decade when measured in the dark and 275 mV/decade when measured under 100 mW/cm² illumination. We attribute the large values of the Tafel slopes to the non-Ohmic contact at the pSi|ITO interface. For the np⁺Si|ITO|Co-Pi (Fig. 3B) in the dark, the slope of the Tafel plot is also large (220 mV/decade), which is consistent with the high impedance for anodic current across the reverse-biased np-Si junction in the dark. Under 100 mW/cm² illumination, however, the Tafel slope is reduced significantly to a value of 106 mV/decade indicative of greater carrier mobility through the Si conduction and valence bands and the more attractive Ohmic nature of the p⁺Si|ITO interface. When applying the potential through the ITO film both for npSi|ITO|Co-Pi and for np⁺Si|ITO|Co-Pi samples, the Tafel slope is found to be 110 mV/decade. That this value is higher than the 59 mV/decade that was observed for Co-Pi on ITO electrodes (3, 10) implies hindered conduction across the sputtered 50 nm ITO film. The Tafel data in Fig. 3 underlines the importance of establishing an Ohmic contact at the pSi|ITO interface. Although the onset potential for water oxidation is significantly reduced when illuminating the np⁺Si|ITO|Co-Pi sample, excessive overpotentials are nevertheless required to attain significant anodic currents, as evidenced from the higher Tafel slopes of Fig. 3A.

The reduction of the onset for water oxidation for the np⁺Si|ITO|Co-Pi sample can be accurately determined from the Tafel data in Fig. 3B. At low current densities (where the Tafel behavior is linear), the potential required for a given current density is reduced by ~0.52 V when the anode is subject to 100 mW/cm² illumination (~AM 1.5). Given the fact that the V oc of the np⁺Si|ITO solar cell is 0.57 V under AM 1.5 illumination...
(SI Appendix: Fig. S3), we conclude that most of the generated photopotential in the solar cell is utilized to reduce the onset potential for water oxidation.

The magnitude of the external potential required to attain a given current density is well described by the intrinsic properties of the solar cell, as is demonstrated in Fig. 4. In particular, the photovoltage, and, therefore, the necessary bias voltage, scales logarithmically with the light intensity in parallel with a corresponding increase in \( V_{oc} \) for the isolated solar cell (44). Fig. 4A shows the potential required to drive water oxidation at a constant current of 20 \( \mu \text{A}/\text{cm}^2 \) through a \( \text{npp}^-\text{Si|ITO|Co-Pi} \) photoanode as a function of the illumination intensity. The onset potential for water oxidation shifts to lower values for higher illumination intensities in line with the expected increase in \( V_{oc} \). Fig. 4A also shows the results of the same galvanostatic experiment for an \( \text{npp|ITO|Co-Pi} \) photoanode. Again, the onset potential for water oxidation is reduced for increasing illumination intensities. In the dark, a potential of 1.20 V is required to attain a current of 20 \( \mu \text{A}/\text{cm}^2 \) for the \( \text{npp}^-\text{Si|ITO|Co-Pi} \) sample whereas the required potential is 1.29 V for the \( \text{npp|ITO|Co-Pi} \) sample. This discrepancy is ascribed to the non-Ohmic nature of the \( \text{pSi|ITO} \) interface, thus leading to a higher overpotential to attain a given anodic current.

Fig. 4B shows the incident-photon-to-current-efficiency (IPCE) as a function of wavelength for a \( \text{npp}^-\text{Si|ITO} \) solar cell (measured in air), a \( \text{npp}^-\text{Si|ITO|Co-Pi} \) sample, and a \( \text{npp|ITO|Co-Pi} \) sample. The shape of these three data traces is very similar, implying that most of the anodic current originates from absorption of 600–900 nm photons. As in a regular Si solar cell, there are significant losses in the visible region (400–600 nm) and above 1,000 nm because of recombination in the emitter layer and recombination at the back surface, respectively (44). Additionally, light trapping was not optimized for the solar cells, leading to additional losses across the entire spectrum. Fig. 4B once more clearly illustrates the necessity of a good Ohmic contact at the \( \text{pSi|ITO} \) interface as carrier collection is very inefficient when this interface is non-Ohmic.

The Faradaic efficiency of the Co-Pi-sensitized \( \text{npp-Si} \) was measured with a fluorescence-based \( \text{O}_2 \) sensor. SI Appendix: Fig. S5 shows that, after initiating electrolysis at 0.9 V vs. NHE, the percentage of \( \text{O}_2 \) detected in the headspace increased in accordance with attributing all current to result from the \( 4e^- \) oxidation of water to produce \( \text{O}_2 \). The \( \text{O}_2 \) detection experiment in SI Appendix: Fig. S5 demonstrates that the photocurrent in the \( \text{npp-Si|ITO|Co-Pi} \) samples is stable minimally over a period of 12 h in 0.1 M KPi electrolyte and that the Faradaic efficiency for \( \text{O}_2 \) production remains unity. Long-term stability of the device benefits from operation at pH 7. ITO is chemically unstable in acidic media (45) and the conductivity of ITO decreases upon anodization in basic electrolytes (46). That the functionalized electrode described here can operate at pH 7 is a distinct advantage over water-splitting concepts in more extreme pH conditions.

The foregoing results are obtained on Co-Pi-functionalized single-junction Si cells, for which the open circuit voltage \( (V_{oc}) \) falls in the expected 0.5–0.7 V range (44). Because this voltage is too low to supply the entire thermodynamic potential of 1.23 V, an applied external voltage was required. To perform water splitting without an external voltage bias, the Co-Pi catalyst must be integrated with a Si-based tandem cell of sufficient \( V_{oc} \) (47, 48) or alternatively, with two or more single-junction Si cells connected in series to provide a sufficient photopotential for water oxidation. In line with the latter possibility, a \( \text{npp}^-\text{Si|ITO|Co-Pi} \) photoanode was connected in series to an additional \( \text{npp}^-\text{Si|ITO} \) ITO cell via alligator clips that were interconnected with copper wires. Good contact between the clips and the metal|ITO substrate was achieved by means of silver paint. Fig. 5 shows the CVs for a single \( \text{npp}^-\text{Si|ITO|Co-Pi} \) sample immersed in a 0.1 M KPi electrolyte in dark and under illumination with a Xe lamp (dark blue line, intensity \( \sim100 \text{ mW/cm}^2 \)). Similar as in Fig. 2, illumination leads to a decrease of the potential onset for water oxidation by 0.5 V. Upon connecting the second solar cell in series with the \( \text{npp}^-\text{Si|ITO|Co-Pi} \) photoanode, the potential onset was further reduced by another 0.5 V.

The solar conversion efficiency for \( \text{O}_2 \) production was determined from:

\[
\eta(%) = \frac{100(E_{\text{Nernst}} - E_{\text{appl}})i}{P_{\text{ill}}A}
\]

where \( E_{\text{Nernst}} \) is the Nernstian potential for water oxidation relative to NHE, \( E_{\text{appl}} \) is the applied potential relative to NHE, \( i \) is the current at a given applied potential, \( P_{\text{ill}} \) is the power density of the incident light, and \( A \) is the illuminated area. Eq. 1 deviates slightly from previous equations of this type (49) because our values of \( E_{\text{appl}} \) are derived from measurements made relative to a reference electrode. Thus, the efficiency metric \( \eta \) reflects an
upper limit value expected for solar-to-hydrogen efficiency that ignores overpotential losses at the cathode and Ohmic resistive losses in the cell. We prefer to use Eq. 1 because it isolates the performance of the Co-Pi|Si photoanode. For a single $\text{npp}\ ^1\text{Si}\{\text{ITO}\}\{\text{Co-Pi}\}$ cell, the maximum measured value of $\eta$ was 0.015% (measured over a potential range of $\sim$300 mV from the onset potential under illumination). This low value of $\eta$ arises because in a single cell configuration, only 0.5 V photopotential is available; the remaining potential is applied externally. Along this line, connecting a second solar cell in series leads to an increase in maximum efficiency to 0.25% since an additional 0.5 V is now derived from the photopotential, thereby reducing the externally applied potential. Higher values of $\eta$ may be obtained by connecting a third solar cell in series, which will omit the need for applying an external potential and thus permit efficiencies in excess of the highest reported efficiency for a metal-oxide CoPi system ($\sim$0.25%) (23). We note that Si absorbs a larger fraction of incident solar irradiance than metal-oxide semiconductors due to its lower band gap, thus utilizing near-infrared photons that are not absorbed in metal-oxide semiconductors. Hence, our results are consistent with theoretical predictions (27) that multi-photon water-splitting configurations (in which the required potential is generated by sequential absorption of multiple photons) are more efficient than single-photon water splitting. The foregoing discussion highlights that the value of $\eta$ as defined in Eq. 1, when determined for a single half reaction of water splitting, can be an ambiguous metric, particularly when comparing light absorbers of disparate bandgaps (e.g., Si vs. Fe$_2$O$_3$).

An alternative efficiency metric, which is particularly relevant for the optimization of the electrochemical interface, is the percent of the maximum power generated by the photovoltaic component that is utilized to drive the electrochemical half reaction. This can be calculated as follows:

$$\eta(\%) = \frac{100 \cdot \Delta V \cdot i}{P_{\text{np}} \cdot \eta_{\text{PV}}} \quad [2]$$

in which $\eta_{\text{PV}}$ is the peak solar-to-electrical power conversion efficiency, determined from the I-V curve of an identically prepared solar cell (SI Appendix: Fig. S3), and $\Delta V$ is the potential difference between the light and the dark (connected to ITO) Tafel plots in Fig. 3. Using Eq. 2, the efficiency is 5.6% for a single npp$^1$Si[ITO]{Co-Pi} electrode at an applied potential of 0.8 V vs. NHE. SI Appendix: Fig. S6 gives a comparison of the two calculation methods for $\eta$. In this report, we used relatively low loading of Co-Pi films ($\sim$250 nanomoles Co), resulting in a lower activity and an impedance mismatch between the power supplied by the photovoltaic and the power utilized to drive the electrochemical half reaction. Improvements in efficiency per Eq. 2 are expected for deposition of thicker catalyst films, because the activity of the Co-Pi film has been shown to increase monotonically with catalyst loading on a planar electrode (3, 11). We have previously shown that it is possible to increase anode activity to 100 mA/cm$^2$ with a 3D catalyst support (11). Thus thicker Co-Pi films or thin Co-Pi films on a roughened (i.e., high surface area) Si surface will be better matched to the typical current densities obtained from crystalline Si solar cells at their maximum power point ($\sim$35 mA/cm$^2$) (44).

The Co-Pi-functionalized Si photoanode presented here embodies a promising approach for photovoltaic-photoelectrochemical water splitting that relies on operation at or near neutral pH. Photoelectrochemical water splitting (50) using single-junction concepts based on single-photon absorption have been widely investigated subsequent to the initial report by Fujishima and Honda of water splitting on TiO$_2$ photoanodes (51). The drawback of the single-photon approach is the requirement of large bandgap materials (which absorb only a small fraction of solar light) to generate sufficient photovoltage for water splitting. As a result, the maximum achievable solar-to-hydrogen efficiency is limited to $\sim$7% for single-photon water splitting (27, 42). Multi-photon photoelectrochemical water splitting is more promising because higher efficiencies may be achieved (27, 42). In a multi-photon device architecture, the required potential for water oxidation is generated by sequential absorption of low-energy photons in a tandem solar cell. The most efficient photoelectrochemical tandem device for water splitting reported to date is 16.5% (hydrogen production efficiency) (52, 53). This device comprises a GaInP$_2$/GaAs tandem cell and platinum catalysts to produce hydrogen and oxygen, immersed in a strongly basic electrolyte (53). Although highly efficient, high costs are associated with the GaInP$_2$/GaAs tandem cell and the catalysts and device stability is poor (52). Though less efficient (2.5–8% hydrogen production efficiency), Si-based tandem cell concepts (33, 53–56) have promise of lower cost. These tandem cells typically consist of a stack of amorphous Si and Si-Ge alloys that are operated in basic electrolyte (pH $>$ 13). The p-side of these tandem cells is usually passivated with ITO, which cannot be annealed because high-temperature treatment is detrimental to the amorphous Si in the tandem cell. Accordingly, the ITO offers only marginal protection of the Si from the extreme conditions of a caustic solution (36), thus resulting in decreased overall device performance (33). Higher efficiencies (up to 7.8%) (33, 53, 54) have been reported for tandem amorphous Si cells in which the oxygen evolving catalyst was not directly deposited on the solar cell, but connected to it through wires. The complexity of the fabrication of the latter PV-PEC devices however presents challenges for large-scale utilization. To this end, the Co-Pi-functionalized Si photoanode presented here provides distinct advantages because it can be operated under benign conditions. At pH = 7, a wide range of materials may be employed as a protective barrier layer of Si materials such as Fluorine-doped Tin Oxide (FTO) and ITO, which exhibit much better long-term stability at neutral pH relative to strongly acidic or alkaline conditions (57, 58). Moreover, the use of crystalline Si gives latitude in sample processing at higher temperatures; namely ITO can be annealed at temperatures approaching 400 °C to furnish a robust thin layer, especially in a neutral pH electrolyte environment. The envisioned approach to connect three crystalline Si cells in series affords flexibility in achieving impedance matching as compared to a tandem cell concept, in which impedance matching has to be realized between the electrochemical load and the photovoltaic element and between the three light-absorbing elements within the solar cell. In the “series approach,” impedance matching is only required between the photovoltaic element and the electrochemical load.

In conclusion, we demonstrated the successful integration of the water-splitting Co-Pi catalyst with a crystalline Si solar cell. That most of the voltage of the solar cell can be utilized to lower the onset potential for oxidation is a promising result. The device presented here serves as a proof of principle that photoelectrochemical water splitting may be achieved with crystalline Si photoanodes and inexpensive catalysts at neutral pH, thus pointing the way to the development of inexpensive integrated devices for the direct solar-to-fuel conversion based on water splitting.

**Materials and Methods**

Boron-doped p-type silicon was used as a starting material and np-Si junction was created by phosphorous diffusion. The metallic contacts and the passivating layers were deposited on the np-Si wafer by sputtering methods. Details of the sample fabrication are provided in SI Appendix. Standard electrochemical techniques were used to electrodeposit the Co-Pi on Si-junction cells. The current-voltage (Tafel) behavior of the Co-Pi catalyst deposited on silicon in the region of water oxidation was measured over a 200 mV range in 10–30 mV increments. Because the onset potential for water oxidation is a function of the illumination intensity (Fig. 4A), the Tafel plot shows the potential (corrected for the solution resistance) vs. the log of the current.
density. This approach is justified because we are primarily interested in Tafel slope, which does not change when using the absolute potential instead of the overpotential. Photoelectrochemistry measurements were done in a one-compartment cell with a flat fused silica surface; the light source was a Xe lamp equipped with a filter to modify the spectral distribution of the light in order to match the solar spectrum. Faradaic efficiencies were measured fluorescence-based O₂ sensor techniques. More detailed descriptions of the electrochemical methods employed in these studies, IPCE, and other photoelectrochemical measurement methods are provided as SI Appendix. In addition, the SI Appendix provides additional data for CVs, Current-Voltage (IV) curves of solar cells, absorption spectra, and a comparison between two methods for calculating conversion efficiencies.

Supporting Information

Light-induced Water Oxidation at Silicon Electrodes Functionalized with a Cobalt Oxygen Evolving Catalyst

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Experimental Methods

Materials. Boron-doped $p$-type silicon was used as a starting material (3'' diameter, thickness 0.3 mm). The resistivity of the wafers was 3 $\Omega$ cm, corresponding to a dopant concentration of about $5 \times 10^{15}$ cm$^{-3}$, as determined in a four point probe setup (Cascade Microtech Inc., CPS Probe station). An $np$-Si junction was created by phosphorous diffusion in an oven containing a phosphoryl chloride (POCl$_3$)/N$_2$ atmosphere at 822 °C for 20 min, followed by a 20 min anneal in an O$_2$/N$_2$ atmosphere, also at 822 °C. In our oven configuration, phosphorous diffusion occurred on both sides of the silicon wafers, resulting in an $npn$-wafer. As a result of the high-temperature treatment, the surface of the $npn$-wafers was covered with a glassy PO$_x$ surface layer. To selectively remove one of these $n$-layers, we spin-coated photoresist (Shipley 1822, 2-$\mu$m thickness) on one side of the wafer and removed the PO$_x$ layer from the wafer side that was not coated with photoresist by dipping in a HF solution (5 wt %). Subsequently, we removed the exposed $n$-type silicon by dry-etching with a sulfur-based reactive ion etch to a depth of at least 5 $\mu$m. Finally, we removed the PO$_x$ on $n$-type of the wafer (that was originally covered with the photoresist) by dipping in HF-solution (~ 10 wt %).

Sample Fabrication. The metallic contacts and the passivating layers were deposited on the $np$-Si wafer using an AJA International sputtering system (Orion 5). Our AJA system is equipped with three 300 W Guns, two of which are RF for either conductive or dielectric materials and one of which is DC for conductive materials only. Thin films of the metal contact (Ti/Pd/Ag) and SiO$_2$ were deposited in an inert Ar environment, ITO was reactively sputtered in mixture of Ar and O$_2$ (Ar/O$_2$ flowrate ratio was 11/1). The overall pressure was $\sim 4 \times 10^{-6}$ bar in all cases. The deposition rate of the films was measured using a quartz crystal monitor (QCM) in a preliminary 'conditioning' run. After all thin films had been deposited the 3'' wafers were cut in a suitable size for the electrochemistry measurements (1 $\times$ 2 cm$^2$ pieces).

Electrochemical Methods. All electrochemical experiments were performed using a CH Instruments 760C potentiostat and a Ag/AgCl reference electrode (BASi, MF-2052). The
Ag/AgCl electrode potentials were converted to the NHE scale using \( E(\text{NHE}) = E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V} \). Pt mesh (Alfa Aesar) was always used as the auxiliary electrode. Unless otherwise stated, the electrolyte was 0.1 M potassium phosphate at pH 7.0 (KPi electrolyte) and the measurements were performed at ambient temperature in air-saturated solutions.

**Electrodeposition of Co-Pi films.** Thin Co-Pi films were electrodeposited in a two-compartment electrochemical cell with a glass frit junction of fine porosity. The auxiliary compartment was charged with 40 mL of 0.1 M KPi electrolyte and the working compartment was charged with 40 mL of solution obtained by combining 20 mL of 0.2 M KPi electrolyte and 20 mL of 1 mM Co\(^{2+}\) solution. The working electrode was a 1 \( \times \) 2 cm\(^2\) piece of ITO-passivated np-Si, fabricated as described above. Typically, a 1 cm\(^2\) area of the electrode was exposed to the solution. Electrolysis was carried out at 1.10 V versus NHE without stirring and without iR compensation, while the reference electrode was positioned 2–3 mm from the surface of the p-side of the working electrode.

**Photoelectrochemistry.** Photoelectrochemistry measurements were done in a one-compartment cell with a flat fused silica surface, allowing for a more accurate determination of the reflection of incident light at the surface of the cell. The light source was a Xenon lamp (Oriel, model 66021) and right after the lamp, the light was directed through a cooled water bath to filter out the infrared light, preventing heating of the electrolyte in the electrochemical cell. An Oriel 81094 filter was positioned right after the water bath to modify the spectral distribution of the Xenon lamp in order to match the solar spectrum. The light was focused by a positive lens to a surface area of 1.0 cm\(^2\) at the sample position. For the intensity-dependence studies (Figure 4a), the output of the Xe lamp was attenuated with a series of neutral density filters.

**IPCE Measurements.** The IPCE measurements were done in a setup of PV Measurements Inc. (Model QEX7). The wavelength was scanned in the 350 – 1100 nm range with 25 nm steps. Photon power densities were determined using a calibrated Si photodiode. The dark current originated from the total immersed surface area of 1 cm\(^2\), whereas photocurrents originated just from the illuminated area (4 \( \times \) 4 mm\(^2\)). Both light and dark measurements were
obtained at a potential of 1.25 V vs. NHE. Typical monochromatic illumination intensities in the IPCE measurements were 1.0 mW/cm².

**Determination of Faradaic Efficiency.** The Faradaic efficiency of the Co-Pi-functionalized np-Si was measured with a fluorescence-based O₂ sensor (Ocean Optics, FOXY-OR125-G). Electrolysis was performed in 0.1 M KPi electrolyte in a gas-tight electrochemical cell under an N₂ atmosphere with the sensor placed in the headspace. The working electrode was illuminated with a Xe lamp at an intensity of ~500 mW/cm². Right after the lamp, a water bath was placed to prevent that the electrolyte in the electrochemical cell would heat up due to the infrared photons from the lamp spectrum. After initiating electrolysis at 0.9 V versus NHE, we recorded the percentage of O₂ was detected in the headspace together with the amount of current that passed through the electrode during ~12 hr.

**Tafel Plot Data Collection.** The current-voltage (Tafel) behavior of the Co-Pi catalyst deposited on silicon in the region of water oxidation was measured over a 200 mV range in 10 – 30 mV increments. Electrolysis was conducted at each potential in a 0.1 M KPi electrolyte (no Co²⁺ present) until the current density (i) reached a steady state value. Prior to data collection, the solution resistance was measured with a clean silicon sample onto which no Co-Pi was deposited using the iR test function. Also, a current of 1 mA/cm² was applied during several hours before the Tafel plot data was collected. We determined the Tafel behavior in the dark and at various light intensities. Normally in Tafel plot analysis, the potential values are converted to overpotential values (η) by correcting for ohmic potential losses and subtracting the thermodynamic potential for water oxidation under the experimental conditions. However, since the onset potential for water oxidation is a function of the illumination intensity (Figure 4a), we decided to plot the potential (corrected for the solution resistance) versus the log of the current density. This approach is justified since we are primarily interested in slope of the Tafel data (being a measure of the steady-state activity of the photoassisted anode as a function of applied
potential) (1,2) and this slope does not change when using the absolute potential instead of the overpotential.


Figure S1. Typical CV curve for an npSi-ITO structure immersed in 0.1 M KPi electrolyte containing 0.5 mM Co\(^{2+}\). The oxidation wave starting at 1.08 V is associated with the oxidation of Co\(^{2+}\) leading to the formation of the CoPi film. The strong catalytic wave at 1.2 V is due to water CoPi-catalyzed water oxidation, convoluted with CoPi formation. The thickness of the electrodeposited CoPi film could be estimated by performing the electrodeposition under controlled potential electrolysis at 1.10 V vs. NHE. At this potential, negligible water oxidation catalysis occurs. Thus, the charge passed at 1.10 V during a deposition is a direct measure of Co\(^{2+}\) oxidation and therefore provides an upper limit for the number of Co ions incorporated into the film.
Figure S2. Absorption spectra of 10 µm thick photo-resist that was used to protect the metal front contacts from exposure to the electrolyte.
Figure S3. IV curves for an npSi-ITO solar cell in the dark (▬▬, teal) and light (▬▬, dark blue) (AM 1.5 illumination) and an npp⁺Si-ITO solar cell in the dark (▬ — —, gray) and light (▬ — —, black) (AM 1.5 illumination). The npSi-ITO cell has poor solar cell performance ($I_{sc} = 0.67 \text{ mA/cm}^2$, $V_{oc} = 0.52 \text{ V}$) owing to the non-Ohmic contact between the p-silicon and the ITO. In the presence of the p⁺ layer, the performance of the solar cell improves dramatically ($I_{sc} = 26.70 \text{ mA/cm}^2$, $V_{oc} = 0.57 \text{ V}$), which is a result of the much better Ohmic contact at the p⁺Si-ITO interface. The fill factor of the npp⁺Si-ITO is far from optimal (0.47) but good enough for the purpose of our electrochemical experiments since the anodic currents were limited to ~3-4 mA/cm² at maximum.
Figure S4. CV curves of an $npp^+$Si-ITO electrode in the dark (▬, dark blue) and light (▬, light blue) (AM 1.5 illumination). After electrodeposition of a 30 nm Co-Pi layer on the ITO, the onset potential for water oxidation is strongly reduced both in dark (▬, burgundy red) and in light (▬, red). The samples were immersed in a 0.1 M KPi electrolyte in and the scan rate was 2.5 mV/s.
Fig. S5. O₂ production measured by a fluorescent sensor (green line, ▶️) and the theoretical amount of produced O₂ (red line, 🔴), obtained from the I-t curve, assuming a Faradaic efficiency of 100%.
Figure S6. Conversion efficiencies as a function of applied voltage for a single $npp^+\text{Si-ITO-Co-Pi}$ electrode. Figure S6a corresponds to the solar to fuel conversion efficiency according to the following formula:

$$\eta(\%) = \frac{100 \cdot (E_{\text{Nernst}} - E_{\text{appl}}) \cdot i}{P_{hv} \cdot A}$$ \hspace{1cm} (S1)$$

Figure S6b corresponds to a definition of efficiency in which the power used to drive the electrochemical load, given by the voltage saved by application of the solar cell ($\Delta V$) times the corresponding current density ($i$), is divided by maximum power generated by the PV:

$$\eta(\%) = \frac{100 \cdot \Delta V \cdot i}{P_{hv} \cdot A \cdot \eta_{PV}}$$ \hspace{1cm} (S2)$$
Figure S7. Conversion efficiencies as a function of applied voltage for an $npp^+$Si-ITO-Co-Pi electrode connected in series with an $npp^+$Si-ITO solar cell. The efficiency was calculated following equation S1 (see previous page).