In Operando Deconvolution of Photovoltaic and Electrocatalytic Performance in ALD TiO$_2$ Protected Water Splitting Photocathodes

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ABSTRACT

In this work, we demonstrate that buried junction photocathodes featuring an ALD TiO$_2$ protective overlayer can be readily characterized using a variation of the dual working electrode (DWE) technique, where the second working electrode (WE2) is spatially isolated from the hydrogen-evolving active area. The measurement of the surface potential during operation enables the deconvolution of the photovoltaic and electrocatalytic performance of these photocathodes in operando, by reconstructing J-$\Delta$V curves (reminiscent of photovoltaic J-V curves) from the 3-electrode water splitting data. Our method provides a clearer understanding of photocathode degradation mechanism during stability tests, including loss of the catalyst from the surface, which is only possible in our isolated WE2 configuration. Two buried junction photocathodes are investigated in this work: a pn$^+$-Si/TiO$_2$ photocathode as a well behaved model system, and an emerging material system based on Cu$_2$O/Ga$_2$O$_3$ to prove the general applicability of the technique.

TOC GRAPHICS
Photoelectrochemical (PEC) water splitting has been recognized as a promising avenue for harvesting renewable hydrogen fuel from inexhaustible solar energy and water.\textsuperscript{1-4} One approach to achieve larger open-circuit voltages ($V_{oc}$) is using so-called “buried junctions”, which can be modeled as a series combination of a p–n junction photoabsorber, a protective layer, and surface catalyst (pn/cat).\textsuperscript{5,6} In such a situation, the $V_{oc}$ is decoupled from the semiconductor-electrolyte interface and the increased band bending of the p-n junction can significantly enhance electron-hole pair separation.\textsuperscript{7}

The efficiency of a pn/cat photocathode is largely determined by the intrinsic properties of the buried p–n junction.\textsuperscript{8} The semiconductor-catalyst and catalyst-electrolyte interfaces also play a critical role in the overall performance of the photodeodes. Issues such as charge transport in the protective layer, the nature of the semiconductor-catalyst contact (Ohmic or Schottky-type), as well as the chemical reactions occurring at the catalyst-electrolyte interface are intertwined.\textsuperscript{9,10} Therefore, it is highly desirable to develop an experimental technique that can not only evaluate the PEC performance but also simultaneously provide an understanding of these different interfaces during PEC operation.

The dual working electrode (DWE) technique was first reported in the 1970s. Photoanodes coated with thin gold films showed a photovoltaic effect, representing early examples of \textit{in situ} measurements of the surface potential.\textsuperscript{11-13} Recently, the Boettcher group has used the DWE technique to study a photoanode-catalyst interface.\textsuperscript{14} However, the second working electrode in all of the previous works has either been a transparent conducting oxide (TCO) or a thin metal film that covers the entire active area.\textsuperscript{15,16} For
systems that do not employ TCOs as part of the buried junction structure, it has thus far not been possible to carry out DWE studies without introducing a metallic film, which influences the measurement through partial light absorption and by affecting the catalyst binding to the photoelectrode surface. It is therefore essential and advisable to measure the device in the same configuration as would be in the actual PEC cell for unambiguous interpretation of the results.

Here, we demonstrate that ALD TiO$_2$, a common protective layer for water splitting photocathodes, enables the surface potential to be measured at a position that is remote from the active area, due to the high doping and conductivity of the film.$^{17,18}$ A pn$^+$-Si photocathode with 100 nm-thick ALD-TiO$_2$ protective layer was chosen as a model system for the development of the DWE technique. A schematic diagram of the DWE setup is depicted in Fig. 1a. WE1 is used for controlling the back contact potential (V1) of the photocathode. WE2 is connected to the photocathode surface and kept at open circuit during PEC measurements to directly probe the surface potential (or in other words to probe the energy level of surface-accumulated electrons) in relation to the reference electrode (V2). To avoid direct contact of WE2 and the active area, WE2 was contacted a small distance away from the illuminated area and separated by a thin coating of opaque epoxy, as shown in Fig. 1b. When illuminated, a photovoltage is created across the pn$^+$-Si homojunction. Considering that both the n$^+$-Si/TiO$_2$ and TiO$_2$/Pt are ohmic contacts,$^{17,19}$ the measured potentials of V1 and V2 directly give the energetic positions of the quasi-Fermi level of holes and electrons, respectively. The difference between V1 and V2, denoted $\Delta V$, is the output voltage of the pn$^+$ Si junction. It is worth noting that as the photoelectrons diffuse away from the illuminated area (as shown in Fig. 1b), the electrons cannot enter the electrolyte and will ultimately recombine. This leads to a lower electron density than in
the illuminated area and a slightly reduced $V_{oc}$ is recorded. The small drop in the measured surface potential is robust and reproducible, and does not complicate the analysis herein.

After the Pt catalyst deposition, the conventional current density-back contact potential ($J$-$V1$) curve of the $p^+\text{Si/TiO}_2/$Pt(ed) photocathode was obtained in 0.5 M H$_2$SO$_4$ with a linear sweep from positive to negative potential (Fig. 1c). Under one sun illumination, the $p^+\text{Si/TiO}_2/$Pt(ed) photocathode exhibits an onset potential for water reduction of ~0.5 $V_{RHE}$. As $V1$ becomes more negative, the photocurrent density increases and eventually saturates to 25 mA cm$^{-2}$ at $V1 = -0.2$ $V_{RHE}$. WE2 enables the *in situ* measurement of surface potential $V2$ during the sweep of $V1$. Supplementary Fig. S3 presents $V2$ and $\Delta V$ values as a function of $V1$ with and without illumination.

A hidden $J$-$\Delta V$ curve, analogous to the current-voltage characteristic of a PV cell, can then be extracted and is plotted in Fig. 1c. The $V_{oc}$ and $J_{sc}$ are 475 mV and 24.6 mA cm$^{-2}$, respectively (the characteristics are also listed in Supplementary Table S1). A significant loss of fill factor is observed when comparing the $J$-$V1$ and $J$-$\Delta V$ curves, which derives from the additional series resistances in a PEC cell *versus* a PV cell, namely the TiO$_2$/catalyst junction resistance, the overpotential of the catalyst required for driving a chemical reaction, and the solution resistance.$^{20}$ In essence, the $J$-$\Delta V$ curve shows the best possible fill factor that can be achieved by the $J$-$V1$ curve. In practice, a real PEC $J$-$V1$ curve will always have a smaller fill factor due to the catalyst overpotential as well as the series resistances mentioned above. Moreover, because the solution resistance does not change in the strongly acidic media, the difference in fill factor between $J$-$V1$ and $J$-$\Delta V$ curves represents only a change in the electron transfer kinetics through the TiO$_2$/Pt/electrolyte interface.
In order to more clearly visualize the effect of the surface potential on the current, a stepwise chronoamperometry measurement was carried out whereby the potential of V1 was stepped every 30 s and both V2 and the photocurrent were recorded (Fig. 1d). When V1 is positive of \(~0.5\) V\textsubscript{RHE}, V2 remains at a constant distance (constant \(\Delta V\), see also Supplementary Fig. S3) and nearly zero photocurrent is recorded. Substantial cathodic photocurrents appear at \(V1 = 0.4\) V\textsubscript{RHE}, where V2 is more negative than 0 V\textsubscript{RHE} (with \(\Delta V\) now starting to shrink). After the onset potential, although V2 continues to move negatively with each step, \(\Delta V\) shrinks further as the photocurrent increases. Ultimately, both V2 and the photocurrent become constant, even as V1 becomes more negative, eventually entering a reverse bias-type regime. Supplementary Fig. S4 depicts band energy diagrams under several conditions of applied bias, and Supplementary Fig. S5 gives a detailed discussion of the relationship between photovoltage and the onset potential.

A critical issue for photoelectrodes is the long-term stability. In order to characterize the degradation mechanism in the Si photocathode, we performed a 2 h stability test by holding V1 at 0 V\textsubscript{RHE}, a typical value for these types of test in the literature.\(^8\) Fig. 2a shows the J-V1 and J-\(\Delta V\) curves before and after the 2 h stability test. Compared with the initial J-V1 scan, the scan after the 2 h shows similar onset potential and slightly decreased saturation photocurrent, but a remarkably poorer fill factor. As the J-\(\Delta V\) curves remain the same, it is immediately apparent that the problem relates to the catalyst and not to the buried junction. Fig. 2b depicts how the surface potential V2 and photocurrent density change over time under a static back contact potential of 0 V\textsubscript{RHE}. Over 2 h, the photocurrent density drops from \(~23\) to \(~20\) mA cm\(^{-2}\), while V2 steadily shifts to more
negative values. Fig. 2c clearly shows the negative shift of the surface potential following the stability test, which indicates that higher overpotential is needed in order to achieve a similar current density. A poor contact between the surface and the catalyst (TiO$_2$/catalyst) as well as worsening kinetics at the catalyst/electrolyte interface (e.g. surface poisoning) will result in a higher overpotential for the catalytic interface.$^{21}$ Pt was then re-deposited onto the electrode surface (Fig. 2c,d). Due to the fact that the fill factor is completely restored upon re-platinization, we can confirm that neither a degradation in the p–n junction of the silicon nor resistive losses through e.g. formation of a silicon oxide layer are responsible for the change in the J-V1 curve. The degradation likely results from desorption of the Pt nanoparticles, as has been previously observed for electrodeposited platinum on ALD TiO$_2$.\cite{22} When the ALD TiO$_2$ was replaced by a thin metallic Ti film, the Pt catalyst binding was much more robust over a 2 h stability measurement (Supplementary Fig. S7).

For the pn$^+$-Si photocathodes described above, the Pt catalyst was electrodeposited onto either the TiO$_2$ or Ti metal surface as nanoparticles with a size range of ~10-30 nm (Supplementary Fig. S8a). This non-continuous catalyst morphology may be unfavorable for efficient extraction of the surface electrons, resulting in a poor fill factor of the J-V1 curve.\cite{23} Therefore, we investigated a nominally 2 nm-thick Pt film with nearly full coverage on the TiO$_2$ layer by sputter coating (denoted pn$^+$Si/TiO$_2$/Pt(sp)). The Pt deposited in this way makes the surface slightly rough (Supplementary Fig. S8b). Fig. 3a compares the J-V1 curves of pn$^+$Si/TiO$_2$/Pt(sp) and pn$^+$Si/TiO$_2$/Pt(ed) photocathodes under one sun illumination. Sputtered Pt exhibits a similar onset potential and improved fill factor, but much reduced photocurrent densities due to the optical transmission loss.
through the 2 nm-thick Pt film (Supplementary Fig S9). For better comparison between the sputtered and electrodeposited samples, we also measured the J-V1 curve of the pn⁺Si/TiO₂/Pt(sp) at an increased light intensity to achieve a similar photocurrent density, plotted in green. The green curve exhibits an earlier onset potential despite having the same \( V_{oc} \) as the Pt(ed) curve, suggesting a better catalytic activity of sputtered Pt over electrodeposited Pt. Support for this hypothesis is shown by comparing their individual catalytic activities towards H₂ generation when deposited on FTO slides (Fig S10). Additionally, pn⁺Si/TiO₂/Pt(sp) always shows an enhancement in the fill factor the in J-V1 curves, reflecting the smaller TiO₂/Pt/electrolyte interfacial resistance for the TiO₂/Pt(sp) as compared to the TiO₂/Pt(ed). In the case of a conformal Pt film, electron transfer is more probable as the catalyst surface area is increased, which is also indicated by the much more positive V2 value in pn⁺Si/TiO₂/Pt(sp), shown in Supplementary Fig. S11. For example, to reach the same saturation photocurrent, a ~130 mV overpotential is required for pn⁺Si/TiO₂/Pt(sp) but ~200 mV for pn⁺Si/TiO₂/Pt(ed).

What we have already hypothesized by the performance of the different Pt on FTO is confirmed by the determination of the J-ΔV curves. At similar saturation photocurrents the J-ΔV of pn⁺Si/TiO₂/Pt(sp) is essentially identical with the pn⁺Si/TiO₂/Pt(ed) (see the green and red dashed curves) while the J-V1 curve shows a clearly higher FF for the device with sputtered Pt.

Thus far, we have developed the DWE technique with a model pn⁺Si/TiO₂/Pt(ed) photocathode, with which we can gain a deeper insight into the PEC process and the photocathode stability. Next, we applied this technique to the emerging material ALD TiO₂-protected Cu₂O to demonstrate the generality of the technique.²²,²⁴ An n-type Ga₂O₃
was used as a buffer layer between the \( \text{Cu}_2\text{O} \) and \( \text{TiO}_2 \) overlayer because this interlayer ensures a positively shifted onset potential, compared to that of \( \text{n-Al:ZnO} \) (AZO) (Supplementary Fig. S12).\textsuperscript{25,26} Fig. 4a schematically depicts the multilayer structure of the \( \text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3/\text{TiO}_2 \) photocathode. In a similar fashion as for the silicon photocathodes described previously, a second working electrode was introduced to probe the surface potential \( V_2 \), prior to deposition of the Pt catalyst by sputtering.

PEC measurements were performed in a pH 5 phosphate/sulfate solution. Fig. 4b displays the \( J-V_1 \) and \( J-\Delta V \) curves. A positive onset potential of \( \sim 0.9 \ \text{V}_{RHE} \) is observed in the \( J-V_1 \) curve, and at \( V_1 = 0 \ \text{V}_{RHE} \), the photocurrent density is 3.9 mA cm\(^{-2}\). The onset potential is much more positive than that from both \( \text{Cu}_2\text{O}/\text{ZnO} \) and \( \text{Cu}_2\text{O}/\text{AZO} \) photocathodes, reflecting the larger photovoltage generated by the \( \text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3 \) junction. In the case of the \( J-\Delta V \) curve, the \( V_{oc} \), \( J_{sc} \) and fill factor are 836 mV, 4.0 mA cm\(^{-2}\) and 36.1\%, respectively. Compared with reported \( \text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3 \) solar cells in the literature, the \( V_{oc} \) and fill factor values are comparable, but the \( J_{sc} \) is lower due to light absorption by the Pt catalyst.\textsuperscript{26,27} Still, resistance at the \( \text{TiO}_2/\text{Pt/electrolyte} \) interfaces contribute to the fill factor loss between the \( J-V_1 \) and \( J-\Delta V \) curves. The fill factor loss is not very significant. As the \( J-\Delta V \) is basically mirroring the \( J-V_1 \) curve, this indicates that the buried \( \text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3 \) junction is responsible for the shape of the \( J-V_1 \) curve of \( \text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3/\text{TiO}_2/\text{Pt(sp)} \) and not the catalytic activity of the Pt catalyst. When using an electrodeposited Pt the PEC system exhibits a lower fill factor, showing that the \( \text{TiO}_2/\text{Pt/electrolyte} \) resistance indeed can also limit \( J-V_1 \) performance, as shown in Supplementary Fig. S15. We further carried out a stepwise test on the

Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/Pt(sp) photocathode under illumination. Results and discussion are provided in Supplementary Fig. S16 and S17 and confirm our statements above.

To study the stability of the Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/Pt(sp) photocathode, a 2 h chronoamperometric measurement was performed under illumination at V1 = 0 V$_{RHE}$. Fig. 4b shows the comparison of the J-V1 curves before and after a 2 h stability test. The onset potential shows a negative shift of nearly 120 mV, although the photocurrent density remains similar. Fig. 4b also provides the initial J-$\Delta$V curve and the one after the 2 h stability test. An obvious decrease in V$_{oc}$ is evident, from 836 mV to 743 mV, while the J$_{sc}$ shows a slight increase from 4.0 to 4.1 mA cm$^{-2}$ (Supplementary Table S1). Compared with the pn$^+$-Si photocathode, the Cu$_2$O/Ga$_2$O$_3$ photocathode shows a much faster degradation of the photovoltaic performance. For the silicon system, J-$\Delta$V remained constant while the J-V1 changed (Fig. 2). In the Cu$_2$O/Ga$_2$O$_3$ case, J-$\Delta$V has changed while J-V1 remains similar (retains a similar photocurrent and fill factor). We thus attribute the loss of performance in this system to the Cu$_2$O/Ga$_2$O$_3$ heterojunction, which could be due to slight photocorrosion that increases recombination in the system, or due to intrinsic instability of the Cu$_2$O/Ga$_2$O$_3$ junction.

In conclusion, we have developed a new configuration of the DWE technique that is a universal method to systematically investigate independently the photovoltaic and electrocatalytic properties of catalyst-modified buried junction photocathodes. By means of surface potential measurements, the intrinsic properties of the buried p–n junction were studied, and the hidden J–$V$ curve of a photovoltaic cell was extracted. Additionally, the fill factor loss between J-V1 and J-$\Delta$V curves was identified as a parameter that characterizes the TiO$_2$/Pt/electrolyte interface, where the morphology of the catalyst plays...
an important role. Furthermore, the PEC performance degradation mechanism was investigated and discussed. We have demonstrated that the stability of underlying p–n junctions in buried junction photocathodes can be characterized in operando. As new material combinations are synthesized for PEC measurements, the DWE electrode technique enables a rapid diagnosis of the cause of degradation in these systems, while also obtaining the PV characteristics of these newly developed junctions without the need to construct separate PV cells.

Supporting Information. Experimental methods, SEM images, Faradaic efficiencies, V2/ΔV-V1 curves, etc.

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Notes

The authors declare no competing financial interest.

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Figure 1  Schematic illustration of (a) the DWE configuration used during PEC measurements with a pn⁺Si/TiO₂/Pt photocathode and (b) the structure of the sensing electrode WE2, located a small distance (~1 mm) away from the illuminated area, separated by a thin coating of opaque epoxy (not to scale). For simplicity, the band benders at the interfaces of the highly doped n⁺-Si and TiO₂ have been omitted. (c) The J-V1 and J-ΔV curves of pn⁺Si/TiO₂/Pt(ed), collected by a LSV scan toward negative potential with a scan rate of 10 mV s⁻¹ in 0.5 M H₂SO₄, ΔV = V1 - V2. (d) V2 and J values of pn⁺Si/TiO₂/Pt(ed) with stepwise controlled V1 under illumination. Each V1 step lasts 30 s. Pt(ed) indicates that the Pt was deposited by electrodeposition.
Figure 2 (a) J-V1 (solid) and J-ΔV curves (dashed) of pn$^{-}$Si/TiO$_2$/Pt(ed) before and after a 2 h stability test, collected by a LSV scan with a scan rate of 50 mV s$^{-1}$ towards negative potential in 0.5 M H$_2$SO$_4$. (b) Changes in V2 and J during a 2 h stability test. V1 is held at 0 V$_{RHE}$. (c) V2-V1 curves of pn$^{+}$Si/TiO$_2$/Pt(ed) before and after a 2 h stability test, and after Pt catalyst re-deposition. (d) J-ΔV curves (dashed) of pn$^{+}$Si/TiO$_2$/Pt(ed) and the corresponding J-V1 curves (solid). All data are collected under simulated one sun illumination.
Figure 3  (a) Comparison of J-V1 curves between pn’Si/TiO$_2$/Pt(ed) and pn’Si/TiO$_2$/Pt(sp), collected by a LSV scan with a scan rate of 10 mV s$^{-1}$ towards negative potential in 0.5 M H$_2$SO$_4$. (b) J-$\Delta$V curves (dashed) of pn’Si/TiO$_2$/Pt(ed) and pn’Si/TiO$_2$/Pt(sp), combined with their J-V1 curves (solid). All data are collected under illumination. For comparison, the performance of pn’Si/TiO$_2$/Pt(sp) with similar photocurrent densities as pn’Si/TiO$_2$/Pt(ed), by increasing the light intensity, is
Figure 4 (a) Schematic structure of a Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/Pt(sp) photocathode. The thickness of Ga$_2$O$_3$ and TiO$_2$ ALD-layers are 20 and 100 nm, respectively. WE1 controls the back contact potential V1 and WE2 measures the surface potential V2. (b) J-ΔV curves (dashed) of Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/Pt(sp) before and after 2 h stability test, overlaid with the corresponding J-V1 curves (solid).
Supporting Information

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Experimental Methods

**Si wafer cleaning.** (111)-oriented Si wafers (thickness ~0.5 mm) used for DWE fabrication were purchased from PrimeWafers. The p-Si substrate was lightly boron-doped (~2×10^{16} cm\(^{-3}\)) and a 2 µm-thick n-type surface layer (polished) was doped with phosphorus (~2×10^{19} cm\(^{-3}\)). These wafers were cut into 2.5 × 1 cm\(^2\) pieces and sonicated sequentially in acetone, ethanol and MilliQ water (18 MΩ) for 10 minutes each. Next, a two-step deep cleaning was accomplished by using a 5:1:1 mixture of H\(_2\)O:NH\(_4\)OH:H\(_2\)O\(_2\), followed by a 5:1:1 mixture of H\(_2\)O:HCl:H\(_2\)O\(_2\), both at 50 °C for 10 minutes, in order to completely remove organic and inorganic contaminants. The native oxide layer was etched away by dipping the wafer pieces in 2% HF for 30 s. The samples were then rinsed with deionized water and dried under a stream of nitrogen, and then placed immediately into the ALD chamber for deposition of TiO\(_2\) onto the n\(^{+}\)-Si surface.

**Cu\(_2\)O plate preparation.** A Cu\(_2\)O plate was prepared via oxidation of a high purity Cu plate (99.9999%), using a method adapted from the literature.\(^1\) The Cu plate (0.1 mm thick) was first cut into small pieces (~2 × 2 cm\(^2\)) and heated from room temperature to 1050 °C (ramp: 17 °C per min) and kept at this temperature for 1 h under Ar flow (1 L min\(^{-1}\)). Next, air was introduced into the furnace and held for 3 h. The gas environment was then switched back to Ar for another 3 h of annealing at the same temperature. After cooling down to room-temperature under Ar, the as-prepared Cu\(_2\)O plate was dark red when held up to the light.
Atomic layer deposition of TiO$_2$ and Ga$_2$O$_3$. TiO$_2$ on Si wafer and Ga$_2$O$_3$-TiO$_2$ on Cu$_2$O plate were deposited by atomic layer deposition (ALD) using a Picosun R200 tool. Before the deposition, the sample was rinsed with deionized water and dried under a stream of N$_2$. The samples were then placed inside the ALD chamber, which was already heated to 120 °C. Tetrakis(dimethylamino)titanium (Sigma-Aldrich) and H$_2$O were used as the precursor for Ti and O, respectively. The Ti precursor was heated to 85 °C and a 1.6 s pulse was used (with software boost function), followed by a 6.0 s N$_2$ purge. H$_2$O was held at room temperature and a 0.1 s pulse was used, followed by a 6.0 s N$_2$ purge. To reach 100 nm of thickness for TiO$_2$, 1860 cycles were used. Measurement of the thickness of ALD-TiO$_2$ deposited on a piece of Si witness wafer was carried out by ellipsometry (alpha-SE, J.A. Woolam Co.), and fitted with a model for transparent films. The cross sectional SEM image (Supplementary Fig. S1) shows that the ALD-TiO$_2$ protective layer is conformably coated on the Si wafer.

For the Ga$_2$O$_3$ layer, bis(µ-dimethylamino)tetrakis-(dimethylamino)digallium (STREM, 98%) was used as Ga precursor. The ALD chamber temperature was kept at 160 °C during deposition. The Ga precursor was held at 150 °C and a 2.5 s pulse was used (with software boost function), followed by a 7.0 s N$_2$ purge. The H$_2$O was held at room temperature, and a 0.1 s pulse was used, followed by a 4.0 s N$_2$ purge time. To deposit a 20 nm-thick Ga$_2$O$_3$ thin film, 250 cycles were used. In order to avoid ALD growth on the back side of the sample (potentially leading to shunting problems), teflon tape was used to cover
the back side of the Si wafers and Cu$_2$O plates during the ALD process. Supplementary Fig. S13 present the Cu$_2$O/Ga$_2$O$_3$/TiO$_2$ multilayered structure.

**Fabrication of Si-based DWE.** After ALD TiO$_2$ deposition, the working electrode 1 (WE1) contact was made to the back side of the p-type silicon by scratching the wafer, applying Ga–In eutectic (Aldrich) and attaching copper foil (Aldrich). A layer of epoxy resin (Loctite Epoxide-resin EA 9461) was then used to cover and glue the electrode to a glass microscope slide, with a certain portion of the TiO$_2$ surface left uncovered for use as the electrochemical active area. For making the front contact, a 20 nm-thick Au layer was sputtered (Safematic CCU-010) onto the epoxy as well as a small part of the exposed TiO$_2$. A copper wire was connected to the Au layer with Ag paint (Ted Pella, Inc.) on top of the epoxy, as a connection for the second working electrode (WE2). Finally, the front contact was protected from the electrolyte by masking it with a second epoxy layer. Supplementary Fig. S2 shows an optical photograph and the structure scheme of an as-fabricated pn$^-$Si/TiO$_2$ DWE.

**Fabrication of Cu$_2$O-based DWE.** After the deposition of the Ga$_2$O$_3$-TiO$_2$ overlayer, a 100 nm-thick Au layer was then sputtered onto the back side of the Cu$_2$O plate (the front side was protected with teflon tape), followed by connecting an Ag wire with Ag paint as WE1. Epoxy resin was then used to cover the whole back side of the electrode to provide protection and enhance the stiffness of the Cu$_2$O plate. WE2 was connected to the ALD-TiO$_2$ surface using the same method as for the Si-based DWE, described above.
**Platinum catalyst deposition.** For some samples, Pt catalyst was deposited onto the as-prepared DWE via galvanostatic electrodeposition from a 1 mM H₂PtCl₆ aqueous solution, denoted as Pt(ed). A constant current of -0.85 µA cm⁻² was applied to the back contact (WE1) for 15 min. For other samples, nominally 2 nm-thick Pt catalyst was deposited by sputter coating, denoted as Pt(sp).

**Characterization.** The morphologies of electrodeposited Pt and sputtered 2 nm-thick Pt film, and the cross-sectional scanning electron microscopy (SEM) images of pn⁺Si/TiO₂ and Cu₂O/Ga₂O₃ photoelectrodes were obtained with a Zeiss Supra 50 VP scanning electron microscope. The polycrystalline structure of the Cu₂O plate is revealed by the X-ray diffraction (XRD) pattern (Supplementary Fig. S14), using a Rigaku Smartlab diffractometer with Cu Kα radiation. UV-VIS spectra of the Pt(ed) and Pt(sp) on FTO slides were recorded with a Shimadzu UV-3600Plus UV/Vis/NIR spectrometer equipped with an integrating sphere.

**Photoelectrochemical Measurements.** Photoelectrochemical measurements were performed in a four-electrode configuration using a BioLogic SP-300 bipotentiostat. The reference electrode was Ag/AgCl (0.197 V vs. NHE) and a Pt wire served as the counter electrode. All electrode potentials were converted into RHE scale: at room temperature, \( V_{\text{RHE}} = V_{\text{NHE}} + 0.059 \times \text{pH} = V_{\text{Ag}/\text{AgCl}} + 0.059 \times \text{pH} + 0.197. \) Before the measurements, the electrolyte was sparged with N₂ for at least 10 min to remove dissolved oxygen. Simulated one sun illumination (100 mW cm⁻²) was provided by a 150 W Xe-lamp with AM 1.5 G filter from LOT Oriel, and the intensity was
calibrated with a standardized silicon diode from PV Measurements (USA). 0.5 M H₂SO₄ and 0.1 M pH 5 phosphate solution (containing 0.5 M Na₂SO₄) were used for Si-based and Cu₂O-based DWE experiments, respectively. Linear sweep voltammograms (LSVs) were collected by sweeping the back contact potential (V₁). V₁ stepwise measurements were performed by potential step chronoamperometry (CA). Each V₁ potential step had a duration of 30 s. The stability tests of the samples were performed for 2 h with V₁ held at 0 V₉HE under one sun illumination. During all measurements, the second working electrode was kept at open circuit to record the surface potential (V₂) against the reference electrode.

**Faradaic efficiencies.** The Faradaic efficiencies of the photocathodes were measured in a gas-tight three-compartment cell in a three-electrode configuration, with an Ag/AgCl reference electrode and a Pt wire counter electrode. The photocathodes were covered with epoxy to fix the active area to ~0.08 cm². The measurement was performed in the same electrolyte as in the PEC measurements (described above). The electrolyte was stirred and constantly sparged with Ar gas at a rate of 20 ml/min. The gas outlet from the cell was connected to a 450-GC Gas Chromatograph Bruker Daltonics GmbH for gas analysis. One LSV scan was first performed for choosing a suitable V₁ potential for the Faradaic efficiency tests. During the measurement, the exposed area of the photocathode was illuminated with a white-light LED. The intensity of the light was calibrated to reach a similar photocurrent density as obtained under simulated one sun illumination, as described above.
**Supplementary Figure S1** Cross-sectional SEM image of the pn$^+$-Si wafer with 100 nm-thick ALD-TiO$_2$ protective layer.
Supplementary Figure S2 (a) Photograph and (b) structure scheme of a pn’Si/TiO₂ DWE device.

The 100 nm-thick ALD-TiO₂ overlayer gives a dark green color on the Si wafer due to optical effects. WE1 is a piece of Cu foil attached to the back side of the p-Si via Ga–In eutectic. WE2 is a conductive cable directly connected to the TiO₂ layer via a 20 nm-thick Au layer and Ag paint. The electrode is protected by epoxy. The ruler is in centimeters.
Supplementary Figure S3 V2 and ΔV as a function as linearly swept V1 in dark (dashed) and light (solid) conditions.

When V1 is more positive than 0 $V_{RHE}$, V2 is similar to V1, thus ΔV is 0, indicating that no voltage difference is generated under dark conditions in this potential region. When V1 is scanned to more negative potentials than 0 $V_{RHE}$, V2 stays mainly unchanged with a value slightly more negative than 0 $V_{RHE}$, contributing to the tiny dark current. This region of very negative V1 corresponds to a reverse bias across the p–n Si homojunction, as is evident from the ΔV-V1 curve.

Under illumination, ΔV maintains a constant value of 475 mV until V1 reaches ~0.47 $V_{RHE}$. In this positive potential region, ΔV equals the output $V_{oc}$ as there is no current flow across the interface. The potential where ΔV begins to shrink indicates the real onset potential of hydrogen production, which appears in this case at ~0.47 $V_{RHE}$. As the photocurrent increases while sweeping the potential negatively, ΔV decreases until a saturation photocurrent density is obtained, and then continues to shrink as the photocurrent remains saturated.
**Supplementary Table S1** J-V parameters extracted from the J-ΔV behavior of the water splitting photocathodes. We expect the pn\(^+\)-Si junction samples from the same wafer to generate the same \(V_{oc}\). The small \(V_{oc}\) variation among pn\(^-\)Si/TiO\(_2\)/Pt(ed), pn\(^+\)Si/Ti/Pt(ed), pn\(^-\)Si/TiO\(_2\)/Pt(sp) is likely due to the different light intensity as a result of light absorption by the catalyst and overlayers, or perhaps passivation and recombination at the Si/overlayer interface (through pinholes). The power conversion efficiency (\(\eta\)) is given for completeness, and is defined as:

\[
\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}}
\]

where \(P_{in}\) of one sun illumination is the incident illumination power density (100 mW cm\(^{-2}\)). For the pn\(^+\)Si/TiO\(_2\)/Pt(sp) sample, an increased light intensity (\(P_{in} = \sim 137\) mW cm\(^{-2}\)) was also used.
Supplementary Figure S4 Schematic band energy diagrams of a pn$^+$-Si/TiO$_2$ photocathode during a LSV scan by controlling V1 (under illumination). The potentials of the y-axis are $V_{RHE}$, and $E(H^+/H_2)$ is at 0 $V_{RHE}$. The Pt catalyst at the TiO$_2$ surface is not depicted in the schemes. Due to the high carrier doping density in both n$^+$-Si and TiO$_2$, the electron (quasi)-Fermi levels are located very close to the conduction band edge, and the space charge region widths are very short, ensuring that Ohmic contacts are formed at both the n$^+$-Si/TiO$_2$ and TiO$_2$/Pt interfaces.

A pn/cat electrode can be seen as a PV cell with one of the current collectors replaced by the electrolyte solution, where under certain conditions of V1, current can flow due to a chemical redox reaction at the surface. Schematically illustrated above, at very positive V1, such as 0.8 or 0.6 $V_{RHE}$, the electron quasi-fermi level (V2) is still much more positive than $E(H^+/H_2)$. Photoexcited electrons cannot be transferred into solution since the potential of the photoexcited electrons is still not high enough to drive proton reduction. In this region of V1 (before the onset of hydrogen generation), $\Delta V$ values remain constant and equal to $V_{oc}$. The flat band potential of TiO$_2$ itself is located near $E(H^+/H_2)$. As soon as V2 is slightly more negative than 0 $V_{RHE}$,
hydrogen evolution is thermodynamically allowed, and electrons flow into the electrolyte by reducing protons into hydrogen gas. The V1 potential at this point is defined as the onset potential. As V1 becomes more negative, the $\Delta V$ value shrinks as the photocurrent corresponding to hydrogen generation increases. When V1 catches up to V2, $\Delta V$ is 0 and the buried p–n junction is at the short-circuit condition. Finally, as soon as the photocurrent becomes saturated due to the photon flux and recombination, V2 reaches a steady value independent of V1. The reverse bias across the p–n junction becomes stronger as V1 level continues to move to more negative potential.

Supplementary Figure S5 Zoom-in view of J-V1 (solid) and J-$\Delta$V (dashed) curves of a pn'-Si/TiO$_2$/Pt(ed) photocathode with a scan rate of 10 mV s$^{-1}$.

The $V_{oc}$ appears at a more negative potential than the onset of photocurrent under certain sweeping conditions, as shown in Supplementary Fig. S5. This means that V2 is more positive than 0 V$_{RHE}$ while current is flowing. In order to confirm that these small photocurrents
correspond to hydrogen evolution and not to e.g. proton intercalation, we carried out faradaic efficiency measurements (See Supplementary Fig. S6). Hydrogen was indeed observed at very small cathodic photocurrent densities, such as -0.08 mA cm\(^{-2}\), at potentials more positive than we would expect from the J-\(\Delta V\) analysis. This phenomenon likely arises from the fact that the slightly lower electron density than in the illuminated area and consequently an actually slightly reduced \(V_{\text{oc}}\) is detected compared to the illuminated area (as shown in Fig. 1b). Thus, the onset potential appears earlier than the \(V_{\text{oc}}\) in Supplementary Fig. S5. This \(V_{\text{oc}}\) loss is highly dependent on the distance between the Au contact and the illumination area, represented by \(d\) in this scheme. For all the samples we measured, \(d\) is \(-1\) mm. When intentionally lengthening \(d\), \(V_{\text{oc}}\) further decreases, yielding \(-75\) mV loss at \(d = 3\) mm. From our experience with more than fifty samples, the offset between the measured \(V_{\text{oc}}\) and the apparent onset from the J-V1 curves is typically a few tens of mV with a platinum catalyst.
Supplementary Figure S6 (a) J-V1 curve of a pn⁺Si/TiO₂/Pt(ed) photocathode for faradaic efficiency measurements. (b)-(c) Comparison of calculated (by photocurrent) and measured H₂ (by GC) under current control, due to the variation of potential with illumination intensity. Note that when the photocurrents are very small, precise measurement of the amount of H₂ by GC is difficult, resulting in seemingly >100% faradaic efficiency for the very small values.
Supplementary Figure S7 J-V1 (solid) and J-ΔV (dashed) curves of pn⁺Si/Ti/Pt(ed) before and after 2 h stability test.

A $V_{oc}$ of 448 mV and a $J_{sc}$ of 23.5 mA cm$^{-2}$ are obtained from the initial J-ΔV curve, slightly smaller than that of the pn⁺Si/TiO$_2$/Pt(ed) photocathode, which may be due to the antireflective property of TiO$_2$ layer. The initial J-V1 curve exhibits a large fill factor loss relative to the J-ΔV curve. The similarities of the J-ΔV parameters of this sample with those of the ALD-protected sample indicates that the 100 nm-thick TiO$_2$ layer is highly conductive and does not contribute to a loss of fill factor in the J-V1 curve. After the 2 h stability test, the saturated photocurrent, $V_{oc}$ and fill factor of the J-ΔV curves remained the same (see Supplementary Table S1), showing that the pn⁺-Si junction is well protected by the thin Ti layer during the 2 h test.
Supplementary Figure S8 Plan view SEM images of (a) pn⁺Si/TiO₂/pt(ed) and (b) pn⁻Si/TiO₂/pt(sp) photocathode.
Supplementary Figure S9 Spectral transmission and reflectance curves for a Pt(ed) (solid) and Pt(sp) (dashed) deposited on FTO slides.
Supplementary Figure S10 J-V curves of Pt(ed) and Pt(sp) deposited on FTO slides in 0.5 M H$_2$SO$_4$. 
Supplementary Figure S11 V2-V1 curves of a pn$^+$Si/TiO$_2$/Pt(ed) and a pn$^+$Si/TiO$_2$/Pt(sp) photocathodes (under one sun illumination). For comparison, the performance of pn$^+$Si/TiO$_2$/Pt(sp) with similar photocurrent densities as pn$^+$Si/TiO$_2$/Pt(ed), by increasing the light intensity, is also displayed (the green curve).
**Supplementary Figure S12** Schematic band alignment of the Cu$_2$O/Ga$_2$O$_3$ and Cu$_2$O/AZO heterojunctions. Cu$_2$O/Ga$_2$O$_3$ exhibits a small conduction band offset ($\Delta E_{CB}$) of ~0.19 eV. This value is much smaller than the counterpart of Cu$_2$O/AZO (~1 eV). Therefore, compared with AZO, Ga$_2$O$_3$ shows an improved conduction-band offset with Cu$_2$O, enabling a larger photovoltage and the ability to shift the onset potential positively.
Supplementary Figure S13 Cross-sectional SEM image of Cu$_2$O/Ga$_2$O$_3$/TiO$_2$ electrode. The thickness of Ga$_2$O$_3$ and TiO$_2$ are 20 nm and 100 nm, respectively.
Supplementary Figure S14 The XRD pattern of the synthesized Cu$_2$O plate. Identification of the diffraction peaks is referred to the standard Cu$_2$O data (JCPDS No. 05–0667).
Supplementary Figure S 15  J-V1 curves of a Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/Pt(sp) and a Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/Pt(ed) photocathodes (under one sun illumination).
Supplementary Figure S16 V2 and J values of the Cu2O/Ga2O3/TiO2/Pt(sp) photocathode under stepwise controlled V1 under one sun illumination. Each V1 step lasts 30 s.

When V1 is more positive than 0.8 V\text{RHE}, V2 is more positive than 0 V\text{RHE} but accompanied by a small photocurrent density. In this region, ΔV is determined as ~800 mV. When V1 is more negative than 0.8 V\text{RHE}, the photocurrent increases and ΔV shrinks dramatically, following the same trend as with the pn+\text{}/Si photocathode. Eventually the photocurrent reaches a plateau and V2 likewise saturates, even as the V1 potential moves steadily more negative.
Supplementary Figure S17 J-V1 curve of a Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/Pt(sp) photocathode for faradaic efficiency measurements. (b) Comparison of calculated (by photocurrent) and measured (by GC) H$_2$ under current control, due to the variation of potential with illumination intensity. Note that when the photocurrents are very small, precise measurement of the amount of H$_2$ by GC is difficult, resulting in seemingly >100% faradaic efficiency for the very small values.

As seen also with the silicon-based photocathode, the onset potential occurs earlier than the $V_{oc}$ (Fig. 4b). Again, faradaic efficiency measurements were carried out at very small photocurrent densities, (e.g. -0.024 mA cm$^{-2}$), which confirmed that these currents do indeed correspond to hydrogen evolution. The rationale for the discrepancy between the apparent onset and the measured $V_{oc}$ is the same as for the silicon-based photocathode, discussed in Supplementary Fig. S7.
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