Interfacial Connections between Organic Perovskite/n$^+$ Silicon/Catalyst that Allow Integration of Solar Cell and Catalyst for Hydrogen Evolution from Water

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The rapidly increasing solar conversion efficiency (PCE) of hybrid organic–inorganic perovskite (HOIP) thin-film semiconductors has triggered interest in their use for direct solar-driven water splitting to produce hydrogen. However, application of these low-cost, electronic-structure-tunable HOIP tandem photoabsorbers has been hindered by the instability of the photovoltaic-catalyst-electrolyte (PV+E) interfaces. Here, photolytic water splitting is demonstrated using an integrated configuration consisting of an HOIP/n$^+$silicon single junction photoabsorber and a platinum (Pt) thin film catalyst. An extended electrochemical (EC) lifetime in alkaline media is achieved using titanium nitride on both sides of the Si support to eliminate formation of insulating silicon oxide, and as an effective diffusion barrier to allow high-temperature annealing of the catalyst/TiO$_2$-protected-n$^+$silicon interface necessary to retard electrolytic corrosion. Halide composition is examined in the (FA$_{1-x}$Cs$_x$)PbI$_3$ system with a bandgap suitable for tandem operation. A fill factor of 72.5% is achieved using a Spiro-OMeTAD-hole-transport-layer (HTL)-based HOIP/n$^+$Si solar cell, and a high photocurrent density of $-15.9$ mA cm$^{-2}$ (at 0 V vs reversible hydrogen electrode) is attained for the HOIP/n$^+$Si/Pt photocathode in 1 m NaOH under simulated 1-sun illumination. While this thin-film design creates stable interfaces, the intrinsic photo- and electro-degradation of the HOIP photoabsorber remains the main obstacle for future HOIP/Si tandem PEC devices.

1. Introduction

Hydrogen produced from water electrolysis is a renewable energy carrier that has many uses in chemical manufacturing, fertilizer production and transportation powered by fuel cell technology$^{[1,2]}$. Photovoltaically driven water-splitting using integrated semiconductor-electrodes comprised of anode (oxygen evolution reaction (OER)) and cathode (hydrogen evolution reaction (HER)) catalysts offers a direct route for solar-to-hydrogen (STH) conversion. These photoelectrochemical devices (PEC) are under active investigation in number of laboratories$^{[3–7]}$. No commercial PEC devices currently exist owing to costly manufacturing, rare materials, and challenges in long-term stability$^{[8]}$. Herein, we address the latter two criteria. The rapidly increasing power conversion efficiency (PCE) of the potentially low-cost hybrid organic–inorganic perovskite (HOIP) thin-film solar cells has made HOIPs promising as electronic-structure-tunable...
photoabsorbers. However, their instability in water and especially electrolytes has greatly limited their application to photoelectrolysis. HOIP semiconductors have received intense attention due to their facile solution-process manufacturing, low-cost materials, tunable bandgap, and excellent optoelectronic properties. To date, their PCE has increased to a certified 25.7%.[10] These exceptional properties also make HOIPs attractive as a wide-band top junction in a tandem solar cell that uses a lower-bandgap bottom junction such as crystalline silicon (Si).[11–18] A higher PCE is theoretically achievable in a tandem device by using a suitable bandgap combination with appropriate band alignments that achieve good current matching in series connected junctions, overcoming the Shockley–Queisser efficiency limit of 33.7% for a single-junction solar cell. However, the PCE of recently reported HOIP/Si tandems remains well below the theoretical efficiency limit.[18,19]

For a solar cell, the theoretical output current, \( J \), under an applied bias, \( V \), is given by the well-established relation given in Equation (1).[20] Under illumination, it is composed of the light generated (maximum) photocurrent density, \( J_0 \), minus the dark current density due to recombination, and minus the current density resulting from series and shunt resistances, \( R_s \) and \( R_{sh} \), respectively:

\[
J = J_0 \left[ \exp \left( \frac{q(V + J R_s)}{n k T} \right) - 1 \right] - \frac{V + J R_s}{R_{sh}} \quad \text{(1)}
\]

where \( J_0 \) is the reverse diode (maximum) saturation current density, \( n \), the ideality factor of the diode, \( kT \), the Boltzmann thermal energy, and \( q \), the elementary charge. The ideality factor depends on the dominant recombination mechanism of light-induced charges in solar cells and is typically in the range of \( 1 < n < 2 \). In the ideal case, \( n = 1 \).[21,22] The two extreme cases correspond to \( n = 1 \) direct band-to-band bulk recombination of free carriers (radiative 2nd order, e.g., bimolecular), and \( n = 2 \) trap-assisted interfacial recombination via non-radiative 1st order (mono-molecular) processes. Recombination at the interfaces between the HOIP and the electron- or hole-transport layers (ETL, HTL) is found to be dominant in n-i-p type HOIP solar cells under 1 sun illumination.[21,22] Thus, the low PCE of HOIP/Si tandem solar cells is mainly due to the lower fill factor (FF), the ratio of the maximum power to the product of open circuit voltage, \( V_{oc} \), and short circuit voltage, \( I_{sc} \), and the lower \( V_{oc} \) than ideality, caused by the inefficiency of charge separation/extraction, charge recombination, and high ratio of \( R_s/R_{sh} \) in solar cells.[23] Recent improvements in the interfacial conductivity have produced a FF of >84% enabling a PCE of 29.15% for a HOIP/Si tandem solar cell.[24]

Although the integrated PEC configuration is favored by techno-economic analyses,[8] the non-integrated photovoltaic-electrolytic (PV+EC) configuration has advantages for unstable interfaces. For example, a HOIP/Si tandem PV cell in air, which is wire-coupled to both cathode and anode catalysts immersed in electrolyte, has achieved a STH efficiency of 20% over an operational time of \( \geq 15 \) h under simulated 1-sun illumination.[23–26] Here, we focus on improving the HOIP/Si/catalyst interfaces by reducing corrosion in liquid electrolyte and increasing their series conductivity using a thin film of titanium nitride (TiN) (Scheme 1). This high-density (5.4 g cm\(^{-3}\)) 3D-conductor suppresses formation of insulating silicon oxide (SiO\(_2\)) allowing improved charge transfer to HOIPs and serving as an effective diffusion barrier to allow the higher temperature anneals needed for creating optimal devices. Also, quasimetals TiN has been proved to be electron conductive and hole-blocking on Si.[27]

Both interfaces (TiN/n\(_i\)/Si/TiN) are used in combination with a titanium oxide (TiO\(_2\)) layer for two purposes: on the HOIP side as an electron transport layer (ETL), and on the catalyst side as an electron conducting and hole-blocking on Si.[28]

To improve the environmental stability of HOIPs against humidity,[28] the use of mixed-cations such as methylammonio (MA), formamidinium (FA) and cesium (Cs) have been examined.[29,30] In this study, we used a lead halide ABX\(_3\)-type perovskite and mixtures of FA and Cs, where A and B are cations and X is anion: (FA\(_{0.83}\)Cs\(_{0.17}\))PbI\(_3\). For protection, we isolated the HOIP thin film under a quartz window for light transmission and encapsulated the resulting sandwich with epoxy (Scheme 1). The fabrication details are given in Supporting Information.

2. Results and Discussion

2.1. Characterization of TiN Connection Layer/Diffusion Barrier

We systematically varied the thickness of TiN deposited by thermal evaporation of Ti in N\(_2\) atmosphere from 3 to 5 nm in steps of 1 nm on top of hydrofluoric acid (HF)-etched n\(_i\)/Si. The TiN film thickness was measured by atomic force microscopy (AFM) (Figure 1a,b; Figure S1, Supporting Information). The surface root mean roughness, \( R_q \), of the TiN films has a constant value of 0.5 nm regardless of the film thickness, and is slightly rougher than the n\(_i\)/Si substrate (0.5 versus 0.2 nm in \( R_q \), Figure 1c). X-ray photoelectron spectroscopy (XPS) (Figure 1d–f) reveals three chemical states of Ti assigned as TiO\(_2\), TiON, and TiN.[31] The oxygen originates from three species: titanium oxide, oxynitride, and hydroxide adsorbed to the film surface (Figure 1f).[32] Rutherford backscattering spectroscopy (RBS) was carried out on the TiN films for quantitative analysis of atomic composition (Figure 1g; Figure S3 and Table S1, Supporting Information). The areal density of the measured oxygen without excluding surface hydroxides is \( 1.8 \times 10^{16} \) atoms cm\(^{-2}\), which does not change with the film thickness. This indicates that the detected oxygen likely originates from surface hydroxide groups adsorbed to the HF-etched n\(_i\)/Si and TiN/n\(_i\)/Si before and after the TiN depositions during sample transfer. The simulated N/Ti atomic ratio is 0.79, 0.76, and 0.78 for the 3, 4, and 5 nm thick TiN films, respectively (Figure 1h); the variation is small and the difference from a 1:1 stoichiometry may result from a lower N\(_2\) pressure than needed for formation of stoichiometric TiN during the depositions.
equivalent thickness of the TiN films is calculated to be 2.2, 3.0, and 3.6 nm, respectively.

The transmittance of the TiN films was investigated as a function of film thickness (Figure 1i). At 550 nm the transmittance of the 3, 4, and 5 nm thick films is on par with that of TiN films fabricated by pulse laser deposition (PLD) with the same thickness.[34] The 4 nm thick TiN film was selected for more detailed study.

2.2. Characterization of TiO₂ ETL and Protection Layer

Planar or mesoporous n-type TiO₂ is typically used as an ETL in HOIP-based solar cells,[35] owing to its favorable conductivity attributed to oxygen vacancies.[36] A TiO₂ layer was used also as it forms a stable protection layer in alkaline electrolytes at pH 14 under bias as low as −1.4 V (standard hydrogen electrode), the onset potential for formation of Ti₂O₃.[37] We deposited 15 nm thickness of TiO₂ by thermal evaporation of Ti in O₂ atmosphere on 4 nmTiN/n⁺ silicon. The as-deposited film has the same roughness as the underlying TiN film on the polished n⁺Si side (Figure S4, Supporting Information). XPS reveals that it is composed of a dominant TiO₂ oxide along with a small amount of suboxides (Ti₂O₃ and TiO) (Figure 2d). To fully oxidize the film, annealing in air at 300 °C for 30 min was successful in fully converting the film to TiO₂ (Figure 2d), without loss of film morphology and roughness, as confirmed by AFM (Figure 2a; Figure S4, Supporting Information). XPS depth profiling of the resulting interface was conducted to determine the spatial segregation of the TiO₂/TiN/n⁺Si layers (Figure 2b). The Ti2p and N1s peaks assigned to TiN were localized in between the TiO₂ and Si layers without changing their binding energies after annealing (Figure S5a,b, Supporting Information). The Si2p spectra as a function of sputtering time (Figure 2c) confirmed no SiOₓ at the TiN/Si interface. Note that Ti2p peaks that can be assigned to metallic Ti or TiNₓ (x < 0.3) with a low N content were observed within the Si side of TiN/Si interface, indicating a slight diffusion of Ti and/or N into Si. This is consistent with the reported depth profiling of TiN on Si sputtered at 300 °C.[38] Overall, our profile data demonstrate that the TiN layer successfully blocked inter-diffusion between TiO₂ and Si during annealing.

Because the HOIP thin films were fabricated by spin-coating on the TiO₂ ETL, this surface needs to be highly hydrophilic to enhance adherence to the HOIP precursor solution. The surface hydrophilicity was evaluated by measuring the contact angle of a droplet of the precursor solution on the TiO₂ surface. The as-deposited TiO₂ surface is relatively hydrophobic (32° contact angle), while after annealing it is slightly reduced (23° contact angle). We found it necessary to create an even higher
hydrophilicity TiO$_2$ surface to maximize wetting and improve performance. Reactive Ion Etching (RIE) with an oxygen plasma was used to treat the as-deposited TiO$_2$ surface, resulting in a 0° contact angle.

The O1s XPS spectra demonstrate that the oxygen speciation includes both titanium oxides and hydroxides in the as-deposited films (Figure 2d,e). Quantitative fits of these spectra before and after the RIE treatments were carried out to estimate the O/Ti atomic ratio based on the Ti2p$_{3/2}$ and O1s peaks (blue- and pink-colored peaks in Figure 2d,e), respectively (see calculation details in Supporting Information). The relative surface densities of titanium hydroxides were calculated based on the O1s peak area (light-blue-colored peaks in Figure 2e).

The O/Ti atomic ratio in the layer increased from 1.69 for the as-deposited state to 1.90 and 1.92 after air annealing and RIE treatment, respectively (Figure 2f). However, both air annealing and RIE treatment reduced the amount of surface hydroxide groups, although RIE created a higher OH surface density and was responsible for the improved hydrophilicity. Note that the TiO$_2$ film after either of the oxygenation methods has a lower O/Ti atomic ratio as compared to the stoichiometry of TiO$_2$, implying the existence of oxygen vacancies. This outcome is responsible for the favorable n-type conductivity. The simulation of the channeling RBS spectrum (Figure S6, Supporting Information) suggests that the annealed TiO$_2$ film without excluding surface hydroxides has an average composition, within error, of TiO$_{2.4}$ and contains $1.81 \times 10^{17}$ atoms cm$^{-2}$, which corresponds to a thickness of 20.0 nm using the known bulk density of anatase TiO$_2$ (3.78 g cm$^{-3}$). The spatial thickness was determined from cross-sectional images of the films by transmission electron microscopy (TEM), as described below.

Figure 1. Morphology, roughness, chemical analysis and optical properties of TiN films deposited by thermal evaporation. a,b) AFM images of HF-etched n$^+$Si and 4 nm thick TiN film coated n$^+$Si, respectively. c) Mean square surface roughness of HF-etched n$^+$Si and 3, 4, and 5 nm thick TiN films coated n$^+$Si substrates. d) Ti2p, e) N1s, and f) O1s XPS spectra of 4 nm thick TiN film coated n$^+$Si, respectively. g) RBS channeling spectrum (120 degree in channeling angle) of 4 nm thick TiN film coated n$^+$Si. h) The N/Ti atomic ratio of and the oxygen areal density of the TiN films as a function of thickness calculated based on the simulation of the RBS spectra. i) Transmittance spectra of the TiN films with different thicknesses deposited on quartz substrates as well as the bare quartz substrate.
2.3. PV Performance of HOIP/n+Si Solar Cells

We chose the mixed A-site cation system FA1-xCsxPbI3 and a 17% Cs composition for its established performance and stability in PV devices.[39,40] We can use the composition (FA 0.83Cs0.17)PbI3 (1.55 eV bandgap) to produce the single-junction n-i-p device with PCE >20%.[40] Accordingly, we selected this composition of HOIPs for fabricating the HOIP/n+Si PEC device in this study.

A typical UV–vis absorption spectrum of (FA0.83Cs0.17)PbI3 is shown in Figure 3a.

X-ray diffraction (XRD) reveals that this material is composed of a major phase of cubic perovskite[40] and a minor phase of PbI2 (P3m1, JCPDS-73-0591)[41] (Figure S12, Supporting Information). Helium ion microscopy (HIM) confirms this observation: there are mainly two phases with different contrast (Figure 3b). The major dark domains are attributed...
to the perovskite phase, while the smaller bright domains are the PbI$_2$ phase.\cite{42} The bright contrast indicates the insulating nature of PbI$_2$.\cite{17} The presence of PbI$_2$ phases at perovskite boundaries is due to the release of organic species during the annealing process. A small excess of PbI$_2$ phases has proved to passivate charge carrier trapping sites at perovskite boundaries.\cite{43} The surface of the HOIP thin film prepared on 15 nmTiO$_2$/4 nmTiN/n$^+$Si is variable below 60 nm. It is much rougher than the annealed TiO$_2$ surface underneath it (22.1 vs 0.5 nm in Rq, Figure 3c; Figure S4, Supporting Information). This is likely due to the crystallite particles of the HOIP.

To fabricate a functional solar cell, the thickness of each layer on top of the TiO$_2$/TiN/n$^+$Si substrate was controlled (Figure 3d): \( \approx \)380 nm HOIPs, \( \approx \)250 nm spiro-OMeTAD as a HTL, \( \approx \)15 nm MoO$_x$ as a buffer layer, and \( \approx \)250 nm transparent indium zinc oxide (IZO) as a conducting contact layer. The best device under simulated AM 1.5G light illumination from the IZO side achieved 13.5% PCE with a \( J_{sc} \) of 17.6 mA cm$^{-2}$, \( V_{oc} \) of 1.06 V, and \( FF \) of 72.0% with negligible hysteresis based on the \( J-V \) curves (Figure 3e and Table 1). The calculated current density based upon the external quantum efficiency (EQE) (Figure 3f) is 16.2 mA cm$^{-2}$, which is consistent with the \( J_{sc} \) obtained from the \( J-V \) curve. The device exhibited good stability: 85% of the initial PCE was maintained even after 600 h of continuous illumination in air (Figure 3g). For comparison, the PV parameters of the same n-i-p HOIP solar cell on
Table 1. The PV parameters of the HOIP/n°Si and HOIP/FTO solar cells.

<table>
<thead>
<tr>
<th>Solar cells</th>
<th>Jsc [mA/cm²]</th>
<th>Voc [V]</th>
<th>FFexp (%)</th>
<th>PCE (%)</th>
<th>FFid (%)</th>
<th>FFexp/FFid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOIP/n°Si (under 1-sun illumination from the IZO side)</td>
<td>17.6</td>
<td>1.06</td>
<td>72.5</td>
<td>13.5</td>
<td>88.7</td>
<td>81.7</td>
</tr>
<tr>
<td>HOIP/FTO (under 1-sun illumination from the glass substrate side)</td>
<td>23.2</td>
<td>1.14</td>
<td>76.0</td>
<td>20.1</td>
<td>89.3</td>
<td>85.1</td>
</tr>
</tbody>
</table>

FFexp is the experimentally measured fill factor, while FFid is the ideal FF factor, which is calculated using Equation (2) with the assumption of n = 1 for ideal bulk band-to-band radiative recombination without compromising Voc.

2.4. Effectiveness of the TiN Film on Minimizing the Series Resistance and Improving the FF

To assess the effectiveness of the use of the TiN film on minimizing the series resistance and improving the FF, we calculated the ratio of the experimental FF (FFexp) to the ideal FF (FFid) for both the HOIP/n°Si and HOIP/FTO solar cells using Equation (2). This commonly used empirical expression applies when the shunt resistant, Rs, is infinite and series resistance, Rs, is negligible (Rs = 0):

\[
\text{FF} = \frac{\text{voc} - \ln(\text{voc} + 0.72)}{\text{voc} + 1}
\]

where Voc is defined as a “normalized Voc”:

\[
\text{voc} = \frac{q}{nkT} \cdot V_{oc}
\]

n is the ideality factor, k, Boltzmann’s constant and kT/q = 0.02586 V at 300 K. The corresponding FFexp/FFid ratios are 81.7% and 85.1% for the HOIP/n°Si and HOIP/FTO solar cells, respectively. For both cases, FFexp is lower than FFid, which is attributed to the inefficiency of hole extraction from the HOIP to the HTL as indicated by the significant FF improvement when using a more hole-selective HTL. The FF of the benchmark HOIP/FTO solar cell here is comparable to the reported spiro-OMeTAD-HTL-based HOIP/FTO solar cell. The 4% lower FFexp/FFid ratio of the HOIP/n°Si may be due to the residual insulating SiOx on the n°Si substrate.

2.5. Evaluation of the TiO2 Layer as an ETL

To evaluate the TiO2 layer as an ETL, we compared the time-resolved photoluminescence (TRPL) kinetics of the HOIP thin films prepared on two substrates: HF-etched n°Si and 15 nmTiO2/4 nmTiN/n°Si. Addition of the TiO2/TiN layers decreased the carrier lifetime in the HOIP thin film by 64% from 58 ± 5 to 21 ± 4 ns (Figure 3h,i), indicating that the TiO2 layer does facilitate the extraction of light-induced electrons from the photoabsorber. This explains the high FF of the HOIP/n°Si solar cells in this study.

2.6. EC Durability Improvement of Pt/TiO2/TiN/n°Si Interfaces

To evaluate the performance of the Pt thin film for HER, we carried out electrochemical (EC) measurements on the Pt/TiO2/TiN/n°Si electrodes. For details of EC measurements, see Supporting Information. To improve the adhesion of the Pt on TiO2, we conducted vacuum annealing (~1 × 10⁶ torr, 300 °C for 30 min). The cross-sectional image of the annealed device (18 nmPt/15 nmTiO2/4 nmTiN/n°Si) was observed by high-resolution transmission electron microscopy (HRTEM) along the [011] direction of the face-centered cubic (FCC) Si (Fd3m space group, JCPDS-77-2108). The thickness of the Pt film measured on the high angle annular dark field (HAADF) image (Figure 4a) is ~18.2 nm, which is consistent with the RBS result (17.8 nm, Figure S9, Supporting Information). The measured TiO2 and TiN layers are 14.6 and 4.2 nm, respectively (Figure 4b,c). The fast Fourier transformation (FFT) image processing (Figure 4a, inset; Figure S13, Supporting Information) reveals that the Pt film was partially crystallized after the vacuum annealing. This treatment produced the room-temperature stable FCC phase (Fd3m space group, JCPDS-04-0802). Further analysis of the FFT image (Figure 4b, inset) of the TiO2 film shows that it is also crystallized after the air annealing. This treatment produces the room-temperature stable tetragonal anatase phase (I41/amd space group, JCPDS-71-1167). The (011) planes of the TiO2 anatase phase, with a spacing of ~3.4 Å, can be clearly seen. Their normal has an angle of 59° with respect to the normal to the TiN film. The diffuse weakly oscillating pattern in the FFT image (Figure 4d) indicates that the TiN thin film is amorphous, which is confirmed by the randomly distributed atomic pattern in Figure S14 (Supporting Information).

Figure 4g and Figure S15 (Supporting Information) show representative chronopotentiometric (CP) analysis of the as-deposited and annealed Pt thin films at ~10 mA cm⁻² current density in 1 M NaOH over 48 h. The as-deposited Pt on TiO2/TiN/n°Si exhibits poor adhesion indicated by the continuous increase in the overpotential needed to maintain the HER current, which increased by ~418 mV over 48 h. Using an unpolished Si substrate led to much poorer adhesion of as-deposited Pt (an increase of the overpotential by ~565 mV over 11.8 h, Figure S15, Supporting Information), likely due to uneven deposition of Pt/TiO2/TiN layers on Si. By contrast, the stability of the Pt/TiO2 interface was significantly enhanced by vacuum annealing regardless of which Si surface was used to make the interface. The corresponding annealed Pt films deposited on the TiO2/TiN layer require ~0.264 and ~0.286 V versus RHE, when coated on the polished and unpolished faces of the n°Si substrate. Under alkaline conditions, there is an initial decrease in activity beginning at ~8 h. After the break-in period, no further significant change in activity was observed for 48 h.
indicating a stable Pt/TiO$_2$ interface. XPS analysis of the Pt/TiO$_2$/TiN/n$^+$Si electrode surface before and after the CP tests for 8 and 24 h reveals that Pt remained intact without formation of PtO during the CP test, but surface copper contamination was detected after the CP test for 8 h, which is likely to cause the initial activity decrease (see Figure S16, Supporting Information). Also, no platinum leakage into the electrolyte was detected by inductively coupled plasma optical emission spectrometry (ICP-OES) after the CP test until 24 h, confirming the good HER stability of the vacuum-annealed Pt film (see Table S2, Supporting Information).

Figure 4h shows a representative kinetic analysis using IR-corrected cyclic voltammetry (CV) of annealed Pt thin films on 15 nmTiO$_2$/TiN/(polished or unpolished)n$^+$Si. The corresponding HER overpotential...
at $j = -10 \text{ mA cm}^{-2}$ gave values of 0.135 and 0.122 V versus RHE, respectively. The lower overpotential of the latter is due to its higher surface roughness factor derived from the electrochemical surface area (ECSA) measurements (Figure S19, Supporting Information). The Faradaic efficiency (FE) for H$_2$ production is 97 ± 3% and was determined after 1 h of the CP measurement (Figure S21, Supporting Information). The Tafel slope derived from the average of the first CV cycles gave values of 56 and 64 mV dec$^{-1}$, while the exchange current density, $j_0$, gave values of $3.5 \times 10^{-4}$ and $4.4 \times 10^{-4}$ A cm$^{-2}$, respectively (Figure S20, Supporting Information). The HER activity of Pt is orientation-dependent with Tafel slopes of 55, 75, and 140–150 mV dec$^{-1}$ for (100), (110), and (111) faces, respectively, at low overpotentials in 0.1 M KOH solution. The measured Tafel values here suggest that the low index (100) and (110) faces are likely dominant on the annealed Pt thin film, and the Volmer–Heyrovsky mechanism is the likely rate-determining step for the HER.

The obtained exchange current densities, $j_0$, are on par with the literature values in alkali ($j_0 = 1.0–6.9 \times 10^{-4}$ A cm$^{-2}$). We estimated the turnover frequency (TOF) using the method of Kibsgaard et al., which yields a TOF of 0.52 and 0.43 H$_2$ per site per second for the annealed Pt thin films. The corresponding EC performances were summarized in Table 2.

### 2.7. PEC Performance of HOIP/n$^+$Si/Pt Photocathode

After evaluating the PV and EC performance of the components, we fabricated the integrated device with HOIP on the polished surface of the n$^+$Si substrate and the Pt/TiO$_2$/TiN layers on the opposite surface of the n$^+$Si substrate. The resulting PEC device formed by integrating the HOIP/n$^+$Si with the thin film catalyst is comprised of IZO/MoO$_x$/Spiro-OMeTAD/HOIP/TiO$_2$/TiN/(polished)n$^+$Si/(unpolished)/TiN/TiO$_2$/Pt, as illustrated in Scheme 1. The reverse orientation of the Si photoabsorber was prepared for comparison, with the Pt/TiO$_2$/TiN layers fabricated on the polished side of n$p$Si. The non-IR corrected $J–V$ curves measured in 1 M NaOH under 1-sun simulated illumination for the representative PEC devices are shown in Figure 4i. The PEC device achieved a photocurrent density measured at 0 V versus RHE ($j_0$) of and a saturated photocurrent density ($J_{sat}$) of −15.9 and −16.6 mA cm$^{-2}$, respectively.

To examine sources of loss arising from the PEC configuration, we compared how the $j_0$ and $J_{sat}$ photocurrent densities of the integrated HOIP/n$^+$Si/Pt device change versus a PV+E configuration. The latter was prepared by removing the Pt/TiO$_2$/TiN layers of the former via scoring and wiring the underlying Si substrate to a multi-layer electrode comprised of vacuum-annealed Pt/TiO$_2$/TiN/n$^+$Si (see fabrication details in Supporting Information and schematic illustration in Figure S23, Supporting Information). For LSV measurements, the resulting HOIP/n$^+$Si photocathode was placed in air under 1-sun simulated illumination, while the vacuum-annealed Pt/TiO$_2$/TiN/n$^+$Si electrode was immersed in 1 M NaOH electrolyte. The corresponding $j_0$ and $J_{sat}$ photocurrent densities are −16.6 and −170 mA cm$^{-2}$, respectively, which are slightly higher (+4% and 2%, respectively) and shifted positive (+57 mA V$^{-1}$ at a photocurrent density of −5 mA cm$^{-2}$) of the $J–V$ curve compared to the PEC configuration (Figure 4i). This is attributed to the larger incident light intensity without the quartz window/ electrolyte in the PV+E configuration. The resulting $j_0$ and $J_{sat}$ photocurrent densities of the integrated HOIP/n$^+$Si/Pt PEC configuration suffer minor optical losses compared to the PV+E configuration. The corresponding PEC performances were summarized in Table 3. Accordingly, a tandem PEC configuration using these materials and fabrication methods has the potential to achieve a STH efficiency of >19.6% with the assistance of a Si n-i-p junction to drive the two water splitting reactions without bias. Next, we turn attention to interfacial charge recombination.

### Table 2. The EC parameters of vacuum-annealed 18 nm thick Pt film on 15 nmTiO$_2$/4 nmTiN/(polished or unpolished)n$^+$Si substrates.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel slope [mV dec$^{-1}$]</th>
<th>$j_0$ [A cm$^{-2}$]</th>
<th>$J_{sat}$ (mV)</th>
<th>$J_{sat}$ [mA cm$^{-2}$]</th>
<th>Faradaic efficiency (%)</th>
<th>TOF at $j = 100$ mV [H$_2$, s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum-annealed Pt/TiO$_2$/TiN/ (polished)n$^+$Si</td>
<td>56</td>
<td>$3.5 \times 10^{-4}$</td>
<td>0.135</td>
<td>6.7</td>
<td>97 ± 3</td>
<td>0.52</td>
</tr>
<tr>
<td>Vacuum-annealed Pt/TiO$_2$/TiN/ (unpolished)n$^+$Si</td>
<td>64</td>
<td>$4.4 \times 10^{-4}$</td>
<td>0.122</td>
<td>7.4</td>
<td>N/A</td>
<td>0.43</td>
</tr>
</tbody>
</table>

### Table 3. Parameters of the devices for the solar-driven HER in 1 M NaOH under 1-sun illumination.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$E$ at $j = -5$ mA cm$^{-2}$ [V vs RHE]</th>
<th>$J_{sat}$ [mA cm$^{-2}$]</th>
<th>$J_{sat}$ [mA cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/TiO$_2$/TiN/(polished)n$^+$Si (PEC)</td>
<td>0.209</td>
<td>−6.7</td>
<td>−7.0</td>
</tr>
<tr>
<td>IZO/MoO$_x$/Spiro-OMeTAD/HOIP/TiO$_2$/TiN/(polished)n$^+$Si/(unpolished)/TiN/TiO$_2$/Pt (PEC)</td>
<td>0.631</td>
<td>−15.9</td>
<td>−16.6</td>
</tr>
<tr>
<td>IZO/MoO$_x$/Spiro-OMeTAD/HOIP/TiO$_2$/TiN/(polished)n$^+$Si wired to air-annealed TiO$_2$/TiN/(unpolished)n$^+$Si (PV+E)</td>
<td>−0.197</td>
<td>−2.0</td>
<td>N/A</td>
</tr>
<tr>
<td>IZO/MoO$_x$/Spiro-OMeTAD/HOIP/TiO$_2$/TiN/(polished)n$^+$Si wired to vacuum-annealed Pt/TiO$_2$/TiN/(unpolished)n$^+$Si (PV+E)</td>
<td>0.688</td>
<td>−16.6</td>
<td>−17.0</td>
</tr>
</tbody>
</table>

2.8. Photocurrent Response

Hysteresis in the photocurrent response is observed using both the PEC and PV+E configurations when the photoabsorber is HOIP, but not when n+Si is the photoabsorber, as shown in Figure 4j. This response indicates that there is significant recombination of light-induced carriers occurring within the HOIP/n+Si photoabsorber under light illumination (e.g., within the IZO/MoOx/Spiro-OMeTAD/HOIP/TiO2/TiN/n+Si). By contrast, the Pt/TiO2/TiN/n+PSi PEC device exhibits no observable hysteresis under light illumination, suggesting that no significant charge recombination occurs between the Pt/TiO2/TiN/Si interfaces nor the Si/Ag-paint/Cu-wire contacts. This further localizes the observed hysteresis effect within the IZO/MoOx/Spiro-OMeTAD/HOIP interfaces. Recombination of light-induced carriers within HOIP solar cells has been widely investigated by the photovoltaic community. The upright growth of the HOIP film on the TiO2/TiN/n+Si substrate led to evaporation of organic cations and halides, exposing undercoordinated Pb2+, I−, and PbI2− ions at the perovskite surface before integration of the Spiro-OMeTAD HTL. These defects have been proved to be carrier traps, which can be effectively passivated by using Lewis acid or base.[48] However, a small excess of PbI2 at the perovskite grain boundaries that we observed was proved to passivate defect traps at the grain boundaries. Combined, the uncoordinated ions at the Spiro-OMeTAD/HOIP interface should be the dominated traps, causing recombination within our HOIP/n+Si PEC device during operation that competes with the HER as a function of time. This conclusion was proved by the work by Wang et al. who recently reported that charge recombination observed in a similar HOIP/Si tandem PV+E device comprised of two series-wired junctions coupled to NiMo-HER and NiFe-OER catalyst could be reduced by using a cationic detergent to passivate the Spiro-OMeTAD/HOIP interface to reduce charge recombination.[49]

2.9. PEC Durability

To measure interfacial durability under HER operation, chronocamperometry (CA) was performed for the PV+E configurations using the identical interfaces as described in Figure 4k (HOIP/n+Si as the PV assembly and a vacuum-annealed Pt/TiO2/TiN/unpolished/n+Si cathode). The CA data show that irreversible degradation starts after 1 min when a maximum photocurrent density is achieved within the HOIP/n+Si photoabsorber and continues to degrade by ≈41% at 130 min. To examine the source of the degradation, this PV+E configuration was analyzed by LSV before and after the CA analysis as described in Figure S24 (Supporting Information). There was no degradation in HER activity observed using the Pt cathode. By contrast, the photocurrent loss was mainly confined to the HOIP/n+Si interfaces. Prior photoluminescence (PL) studies of HOIPs have shown that an applied bias can induce ion migration followed by accumulation of mainly I− anions, and the accumulated negative ions cause non-radiative recombination of light-induced charge carriers.[49] This can explain the initial large decreasing rate of photocurrent density when the decay happened at ≈5 min and its further slowing down with time during the CA durability test. Also, irreversible loss of photocurrent occurs under large, applied bias, which is due to the decomposition to the PbI2 phase.[49,50] This is the likely source of decomposition of the HOIP photoabsorber under bias (0 V vs RHE) in our experiments. A large excess formation of relatively insulating PbI2 due to HOIP decomposition is expected to cause an increase in the series resistance within the PV+E system, which is reflected by the significantly reduced FF factor of the PV+E configuration after the CA durability test (see the shape change of the J–V curves before and after the CA measurement in Figure S24, Supporting Information).

3. Conclusion

We succeeded in connecting an efficient, room-temperature-stable HOIP thin film photoabsorber, with n+Si, and a Pt catalyst using a TiN connection layer/diffusion barrier and a TiO2 layer (used as an ETL and protection layer) in alkaline electrolytes. The use of TiN allowed for high temperature treatments to obtain stable crystalline TiO2 and catalyst layers without formation of SiOx insulators on Si. Vacuum annealing is necessary for extending the EC lifetime of the Pt/TiO2/TiN/n+Si interfaces. A relatively high FF (72.5%) and high current density at 0 V versus RHE (~15.9 mA cm−2) were achieved for the resulting HOIP/n+Si solar cell and integrated PEC device, respectively. A significant light-induced charge recombination was observed at the HOIP/HTL(Spiro-OMeTAD) interface, slowing the photocurrent response of the PEC device under a fixed bias, while irreversible degradation was observed for the HOIP single junction photoabsorber under bias at 0 V versus RHE for the HER. In future, a more hole selective HTL can be used to further improve the FF factor; a cationic detergent can be used to passivate the HTL/HOIP interface to reduce charge recombination; and a n-i-p Si bottom junction can be used to assist unbiased water splitting reactions, avoiding the irreversible bias-induced degradation of the HOIP top junction. Applying our strategy with potentially useful modifications inspired by this work and the literature, a STH efficiency of >20% is achievable for a future integrated HOIP/Si tandem PEC device to perform stable, unassisted hydrogen production in alkaline electrolytes under 1-sun illumination. To further lower the cost, expensive Pt can be replaced with low-cost thin-film catalysts with comparable activity.[33,51]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
H.G. performed conceptualization, methodology, formal analysis, validation, investigation, data curation, and writing original draft, review and editing. F.Z. and K.Z. performed methodology, formal analysis, validation, investigation, data curation, and writing review and editing. S.H. and A.B.L. performed conceptualization, methodology, formal analysis, investigation, data curation, and writing original draft, review and editing. E.G. and G.C.D. performed conceptualization, methodology, formal analysis, writing review and editing, supervision, project administration, and funding acquisition. The other authors performed formal analysis, investigation, data curation, and writing review and editing.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
fill factor, hybrid organic–inorganic perovskites, hydrogen production, photocathodes, photoelectrochemical water splitting, silicon, titanium nitride diffusion barriers

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