Chemically Stable Semitransparent Perovskite Solar Cells with High Hydrogen Generation Rates Based on Photovoltaic–Photoelectrochemical Tandem Cells

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Photovoltaic (PV)-assisted photoelectrochemical (PEC) tandem cells with elevated hydrogen (H₂) production rates are a practical approach for carbon-dioxide-free, green H₂ production. A semitransparent single-cell-based wide-bandgap perovskite solar cell (PSC) coupled with an Si photocathode provides sufficient potential for H₂ generation when combined with a sulfate oxidation reaction. While energetically favorable ZnO as an electron transport layer (ETL) increases the Vₜₒᴄ to 1.19 V for mixed-halide perovskite, phase decomposition is induced when Br ions contacted the ZnO ETL. The SnO₂ interlayer shows improved passivation, superior operational stability, and excellent performance among the various atomic layer deposited metal oxides tested. Furthermore, the resulting semitransparent PSC demonstrates reproducibility of its enhanced PV parameters (i.e., Vₜₒ_c 1.17 ± 0.01 V, FF 76.78 ± 1.39%, and PCE 11.95 ± 1.13%) due to better interface quality. The precise calculation of light absorption from both PV and Si for the overall tandem device leads to optimized light harvesting in the top and bottom electrodes, maximizing H₂ production. Overall, the PV-PEC device incorporated with a chemically stable semitransparent top PSC and bottom Si photocathode allows to accomplish stable H₂ production at 11.1 mA cm⁻² under unbiased conditions.

1. Introduction

Hydrogen (H₂) offers high energy density (141.9 MJ kg⁻¹) without emitting carbon dioxide (CO₂) and will play a significant role in the future of energy for society as an alternative to fossil fuels.[1] However, H₂ production has not yet come close to being CO₂-free (i.e., green H₂) because it continues to rely on carbon-containing fossil fuels due to their attractive low price ($1.0–1.80 kg⁻¹).[2,3] Solar-driven H₂ production, converting solar energy directly into H₂, is one promising candidate for clean and sustainable green H₂ production.[4] The major limitation to the commercialization of green H₂ is its high production cost ($2.50–6.80 kg⁻¹). Therefore, practical CO₂-free H₂ production should be cost-competitive and deliver high H₂ generation rates with long-term stability.[5]

Among various solar-driven H₂ production systems, including photocatalytic (PC), photoelectrochemical (PEC), and photovoltaic-electrochemical (PV-EC), PEC provides a practical approach with moderate efficiency, less device complexity, and cost-effectiveness compared to low-efficiency PC systems and high-efficiency but complex PV-EC systems.[1,5,6] A stacked dual-absorber PEC-PEC tandem cell containing two well-matched semiconductors is an efficient configuration that theoretically achieves a solar-to-hydrogen (STH) conversion efficiency of up to ≈30% due to its broad solar spectrum utilization.[7,8] The photoelectrodes should also retain the appropriate bandgap and band edge position for oxygen and hydrogen redox potentials to develop enough photovoltage for the water-splitting reaction.[9] However, limited photoelectrode availability and ineffective photogenerated carrier transfer efficiency lead to a low STH of ≈3% for PEC-PEC tandem water splitting.[4,10] In this regard, PV-assisted PEC tandem cells have emerged as a promising alternative, where PV provides additional photovoltage for redox potential, and a wide range of material candidates are available for PV and PEC.[11] Recently, semitransparent PV coupled with a Sb₂Se₃ photocathode reported a high STH of 10.2%.[11] In such a device, the transparency of the top PV needed to be tuned using anodized aluminum oxide (AAO) as a scaffold due to the low transparency of MAPbI₃ perovskite as a light absorber. Moreover, the use of two serially connected PV subcells provided the required potential for water splitting (≈1.7 V), inevitably halved the short-circuit current density (Jₛₐₑ) compared to a single-cell PV with an identical active area, and reduced the operating current of the PV-PEC tandem device. Therefore, to increase the solar-driven H₂ production rate from PV-PEC tandem devices, it is necessary to utilize an efficient...
single-cell-based semitransparent PV that provides sufficient photovoltage for H2 production.

To further alleviate the high required water splitting redox potential, the oxygen evolution reaction (OER) can be replaced by an alternative oxidation reaction.\[12\] The sulfide oxidation reaction (SOR) has been utilized as an alternative oxidation reaction to improve H2 production using Mo-doped BiVO4 and Pt as a photoanode and cathode.\[13\] As the required redox potential decreased, a negative shift in the onset potential of ≈0.5 V was observed using this method.\[10\] However, external bias was still needed for H2 production since BiVO4 cannot solely generate sufficient photovoltage. Therefore, using a bottom photocathode and metal anode for H2 generation and SOR, respectively, the additional photovoltage supplied by an efficient top semitransparent PV could present an excellent strategy to improve H2 production. In particular, achieving sufficient photovoltage using a single-cell-based semitransparent PV is necessary to reach elevated H2 generation rates from PV-PEC tandem cells.

Perovskite solar cells (PSCs) are promising semitransparent PV candidates for efficient PV-PEC tandem cells combined with SOR. For example, the PSC based on MAPbI3 develops a high open-circuit voltage (VOC) up to 1.14 V and can be further improved by simple compositional engineering.\[14\] Substituting iodide ions with bromide ions in lead-mixed-halide perovskite, i.e., APb(I1-xBrx)3 (A = methylammonium (MA), formamidinium (FA), and Cs), raises VOC due to the increased bandgap.\[15,16\] Furthermore, the wide-bandgap halide PSC without the AAO scaffold as a semitransparent top electrode in PV-PEC tandem cells can be advantageous for utilizing the solar spectrum while allowing adequate light to reach the bottom photocathode. However, VOC enhancement in the lead-mixed-halide perovskite likely reaches saturation when the bandgap exceeds 1.65 eV.\[16\] The VOC saturation is associated with improper band alignment between the charge transport layer and perovskite and interface recombination.\[17,18\] As a result, it is necessary to adopt a suitable electron transport layer (ETL) to create the proper band alignment and reduce interface recombination to improve VOC further. For example, ZnO is an excellent ETL for lead mixed-halide (I/Br) perovskite-based PSCs, which develop high built-in potential and reduce charge carrier recombination.\[19,20\] Nevertheless, lower device performance for ZnO ETL-based PSCs has been reported than TiO2 and SnO2 ETL-based PSCs because of poor interface compatibility between ZnO and perovskite.\[19,21,22\] In particular, the deprotonation reaction of perovskite organic cations by ZnO poses a significant instability issue and inferior performance.\[22–24\] Therefore, appropriate interfacial passivation is required for ZnO ETL-based PSCs to avoid chemical degradation and demonstrate high-performance through semitransparent PVs with significant VOC.

In this work, a PV-PEC tandem system comprised a top AAO-free semitransparent single-cell PSC and bottom Si photocathode to achieve elevated H2 production rates using a hydrogen evolution reaction (HER) and SOR was developed and studied. While ZnO ETL increased the VOC to 1.19 V for the SnO2 ETL-based PSC, the resulting PSC revealed poor device stability and low reproducibility. The influence of Br on the mixed-halide perovskite during decomposition, when contacted with ZnO, led us to test several atomic layers deposited (ALD) metal oxides as interfacial passivation candidates. The SnO2 interlayer inserted PSC device showed superior operational stability, better reproducibility, and excellent performance. Our well-designed PV-PEC tandem device with precisely distributed light absorption, high photovoltage, and chemical durability exhibited an H2 production density of 11.1 mA cm−2 without an external bias using SOR as an alternative oxidation reaction.

2. Results and Discussion

In PV-PEC tandem devices, the top PSC plays an essential role in providing sufficient potential for H2 production by harvesting photons in the short wavelength region. Cs/FA-based I/Br perovskite (i.e., Cs0.2FA0.8Pb(I1-xBrx)3) represents the most commonly used wide-bandgap compositions due to its excellent thermal stability and photo-stability.\[25\] It is well known that the bandgap of Cs0.2FA0.8Pb(I1-xBrx)3 is tunable by modulating the I/Br ratio so that its value increases with increasing Br.\[25–27\] Two perovskite compositions with different bandgaps were selected. For convenience, Cs0.2FA0.8Pb(I0.6Br0.4)3 perovskite is denoted as IBT(0.4) perovskite, while Cs0.2FA0.8PbI3 perovskite is denoted as I1 perovskite. A planar n-i-p structured PSC in an Au/hole transporting layer (HTL)/I1 perovskite/SnO2/ITO configuration was employed as a reference device. IBT(0.4) perovskite-based PSCs were prepared using two different HTLs with the optimum thickness as shown in Figure 1a. Lithium bis(trifluoromethane-sulfonyl)imide (LITFSI) doped 2,2’,7,7’-tetракис-(N,N-di-p-methoxyphenyl-amine)-9,9’-spirobiфluoreне (spiro-OMeTAD) was utilized as HTLs for all PSCs. The detailed fabrication methods are described in the Experimental Section.

Figure 1b presents the current density–voltage (J–V) curves for the three different champion PSCs, and their detailed PV parameters are listed in Table S1, Supporting Information. The SnO2/I1 perovskite/HTL device JSC value (17.65 mA cm−2) was slightly lower than the reported PSC with the identical perovskite composition (≈21.5 mA cm−2).\[27\] This is presumably because the thickness of the perovskite film was controlled to ≈220 nm to ensure light transmittance for the adequate provision of photons to the bottom photocathode. The SnO2/IBT(0.4) perovskite/HTL device had a lower JSC of 13.5 mA cm−2 than the SnO2/I1 perovskite/HTL, where the JSC drop can be attributed to the decreased absorption of photons. By contrast, a significant enhancement in VOC was observed from 0.99 to 1.15 V. It is well known that the VOC of PVs is proportional to the energy bandgap (Eg) of the absorber material.\[15,16\] VOC loss was calculated from the measured J–V curves using Equation (1), where q is the elementary charge

\[
\text{VOC loss} = \frac{E}{q} - \text{VOC}
\]  

(1)

The I1 and IBT(0.4) perovskite bandgaps were calculated from their absorbance spectra using Tauc plots (Figure S1, Supporting Information). As shown in the inset of Figure 1b, the VOC loss increased from 0.55 V to 0.63 V when wide-bandgap perovskite was used. The origin of VOC loss for mixed-halide perovskite was related to the heterojunction-induced nonradiative recombination between the perovskite and charge transport layers.\[15,17,28\] Therefore, controlling the energy band structure became a
practical approach to reduce interface charge carrier recombination, leading to minimized $V_{OC}$ loss. The band energy diagram for each component is depicted in Figure 1c. The energy levels of ETL and HTL were adopted from the published work,[26] while the band positions of the $I_3$ and $IBr_{0.4}$ perovskites and ETLs were obtained by ultraviolet photoelectron spectroscopy (UPS) and $E_g$ (Figure S2 and S3, Supporting Information). A favorable band alignment of the conduction band minimum (CBM) with a slight offset between ETL and perovskite was observed when ZnO was introduced, reducing $V_{OC}$ loss from 0.63 to 0.59 V.

Despite the favorable band alignment position, the hydroxyl groups on the ZnO surface reacted with the perovskite organic cations, causing phase decomposition.[23,24,29] Hence, many studies to improve the chemical stability between ZnO and perovskite by inserting passivation layers. For instance, Schutt et al. demonstrated that the stability of ZnO ETL-based PSCs with mixed-cation I/Br perovskite (Cs0.17FA0.83Pb(I0.83Br0.17)3) was enhanced by replacing MA cations with less acidic FA and Cs. However, it still lacked stability, resulting in a 50% reduction in power conversion efficiency (PCE) over 2 h.[30] Therefore, it is essential to further understand the decomposition mechanism of Cs0.2FA0.8Pb(I1–xBrx)3 perovskite, especially in terms of its halide composition, to apply additional strategies that enhance device stability. The $I_3$ and $IBr_{0.4}$ perovskites deposited on ZnO-coated ITO glass substrate were prepared to examine the chemical reactivity between perovskite and ZnO. It should be noted that the solution-processed ZnO on ITO glass was heat-treated at 250 °C for 30 min to reduce the hydroxyl group on ZnO before perovskite deposition.[30] Figure 2a,b show the X-ray diffraction (XRD) patterns for the $I_3$ and $IBr_{0.4}$ perovskites on ZnO, followed by annealing at 100 °C for durations of 0 – 60 min. Interestingly, a PbI2 peak was not observed until the 60 min annealing for $I_3$ perovskite and appeared within 10 min for $IBr_{0.4}$ perovskite (Figure 2b). By contrast, $I_3$ perovskite coated on bare ITO glass without ZnO exhibited weaker structural stability than $IBr_{0.4}$ perovskite as the PbI2 peak was observed after a 3 h annealing (Figure S4, Supporting Information). The stoichiometry of perovskite alters the overall symmetry of the perovskite lattice that can determine the intrinsic phase stability of perovskite.[31] An I/Br perovskite system (e.g., MAPb(I1–xBrx)3, FAPb(I1–xBrx)3, and CsPb(I1–xBrx)3) can undergo a tetragonal-to-cubic phase transition because the lattice constant decreases as Br is increased due to octahedral tilting yielding higher symmetry perovskite that is more stable than its lower symmetry counterpart.[32,33] In this regard, it can be speculated that the specific contact between Br-substituted perovskite and ZnO accelerates perovskite decomposition despite the better intrinsic stability of $IBr_{0.4}$ perovskite.

To clarify the role of Br for perovskite decomposition, we fabricated $IBr_{0.2}$ perovskite on ZnO/ITO substrate containing less Br than $IBr_{0.4}$ perovskite. While the decomposition occurred within 10 min for $IBr_{0.4}$ perovskite, the PbI2 peak started to appear after 20 min of annealing for $IBr_{0.2}$ perovskite (Figure S5, Supporting Information). The relative peak intensity
The ratio of perovskite to PbI₂ represents the degree of decomposition. Figure 2c reveals that the perovskite decomposition was a function of its I/Br ratio, where high Br accelerated the reaction between ZnO and perovskite. It is worth noting that the Cs/FA cations bind with Br and I anions in mixed-halide perovskites, whereas in iodide-based perovskite they only bind with I. Br has a stronger Pauling electronegativity than I, promoting stronger electrostatic interactions with the FA cations. Therefore, we speculated that the organic FA cations bound to Br have relatively weaker interactions with I in the mixed-halide perovskite (i.e., IBr(0.2) and IBr(0.4) perovskite) than with I in the iodide-based perovskite (i.e., I$_3$ perovskite). The weaker interactions triggered the migration of FA cations, inducing the chemical reaction between FA cations and hydroxyl group of ZnO. This hypothetical decomposition mechanism is schematically depicted in Figure S6, Supporting Information.

When IBr(0.4) perovskite comes in contact with ZnO, its chemical instability indicates the necessity for a suitable protective layer to avoid performance loss. Optoelectronic properties such as conductivity, energy-level alignment, and transmittance can be improved by inserting an appropriate interlayer to suppress charge recombination.$^{[34-39]}$ For instance, a PCBM interlayer effectively suppressed the thermal decomposition of the perovskite layer, enhancing its PCE from 17.5% to 19.07% due to the reduced interfacial barrier.$^{[17]}$ However, PCBM/ZnO showed instability due to PCBM aggregation during the annealing process, revealing the limitations of using thermally unstable organic materials as interlayers.$^{[36]}$ Metal oxides can be suitable candidates for interface engineering because of their excellent thermal stability and high electrical conductivity. Various metal oxides, such as SnO$_2$,$^{[38,39]}$ TiO$_x$,$^{[35]}$ and Al-doped ZnO$^{[34]}$ have been used to improve chemical stability and electrical performance. Among these, the TiO$_x$ and SnO$_2$ interlayers effectively suppressed charge recombination during the transfer process of photogenerated charge carriers,$^{[35,38,39]}$ while Ga$_2$O$_3$ played as dense permeation barrier in PSCs by potentially inhibiting the diffusion of FA cations.$^{[40]}$ In this regard, we fabricated ALD-derived TiO$_2$, SnO$_2$, or Ga$_2$O$_3$ interlayers to test their effect on interface engineering.

Before evaluating the protection offered by the metal oxide interlayers, their thicknesses were optimized by their PV performance (Figure S7, Supporting Information). The optimum thicknesses of interlayers were determined to be 1 nm for Ga$_2$O$_3$, 5 nm for TiO$_2$, and 10 nm for SnO$_2$. Ga$_2$O$_3$ has a wide-bandgap and is believed to have a much thinner optimized thickness because the photogenerated charge carriers need to tunnel through a subnanometer layer.$^{[40]}$ The PV device parameters of PSCs using a metal oxide interlayer are summarized in Table S2, Supporting Information. It should be noted that LiPF$_6$ dopant was added instead of LITFSI to spiro-OMeTAD for further $V_{OC}$ enhancement. Figure 2d-f shows the XRD patterns for IBr(0.4) perovskite deposited on Ga$_2$O$_3$/ZnO, TiO$_2$/ZnO, and SnO$_2$/ZnO substrates. A PbI$_2$ peak was observable after a 10 min-annealing for IBr(0.4) perovskite on Ga$_2$O$_3$/ZnO and 60 min-annealing for IBr(0.4) perovskite on TiO$_2$/ZnO. By contrast, there was no PbI$_2$ peak even after a 60 min-annealing for IBr(0.4) perovskite on SnO$_2$/ZnO, indicating that it offered better protection.

The performance of ZnO ETL-based PSCs with ALD SnO$_2$ interlayers (denoted as PSZ-ALD) was systematically...
investigated, and the statistics of the device parameters obtained from 15 cells are presented in Figure 3a and Table 1. The ZnO ETL-based PSC without a SnO 2 interlayer (denoted as PZ) exhibited a champion PCE of 12.26%, \( J_{SC} \) of 14.12 mA cm \(^{-2}\), \( V_{OC} \) of 1.21 V, and FF of 71.63%, whereas the PSZ-ALD device revealed a champion PCE of 12.84%, \( J_{SC} \) of 13.85 mA cm \(^{-2}\), \( V_{OC} \) of 1.19 V, and FF of 78.19%. The PZ device suffered from poor reproducibility with a broad distribution of PV parameters (i.e., \( V_{OC} \approx 0.92 \pm 0.44 \) V, \( FF = 57.27 \pm 14.61\% \), and \( PCE = 8.01 \pm 3.91\% \)) despite a slightly better photocurrent density. By contrast, the PSZ-ALD device showed better reproducibility than the PZ device, as reflected by the narrow parameter distribution (i.e., \( V_{OC} = 1.17 \pm 0.01 \) V, \( FF = 76.78 \pm 1.39\% \), and \( PCE = 11.95 \pm 1.13\% \)). It should be noted that the PSZ-ALD device benefits from the improved FF because the PV provides a maximized photocurrent for a high \( H_2 \) production rate in the PV-PEC tandem system.\(^{[4,7]}\) Despite the improved performance, Cs containing perovskite reveals the limitation of lower \( J_{SC} \) compared to other wide bandgap perovskites due to the small grain size.\(^{[41]}\) Therefore, it is expected that increasing the grain size with additional additives such as Pb(SCN)\(_2\) likely improves \( J_{SC} \) and consequently the \( H_2 \) production rate in the PV-PEC tandem systems.\(^{[41,42]}\)

Atomic force microscopy (AFM) analysis was conducted to examine the surface morphologies of ZnO ETL and the interlayer. Figure S8, Supporting Information, shows that the root-mean-square (RMS) roughness for ZnO/ITO was 3.77 nm, and SnO\(_2\)/ZnO/ITO was 3.79 nm. The surface characteristics indicate that the surface roughness was not the contributing factor to better reproducible PV performance in the PSZ-ALD device. The \( J-V \) hysteresis behavior indirectly correlates with the interface quality between the perovskite and ETL because hysteresis originated from the capacitive effect induced by charge accumulation at the interface.\(^{[28,43]}\) Figure 3b shows the measured \( J-V \) curves in reverse and forward scans, exhibiting less hysteresis associated with the PSZ-ALD device than the PZ device. Therefore, the lower hysteresis suggests reduced charge accumulation and improved interfacial quality. Since the perovskite films deposited on both ETLs were nearly identical as demonstrated by SEM and XRD patterns (Figure S9, Supporting Information), steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) are powerful tools to directly investigate the contact properties. A weak light of 0.1 \( \mu \)W was irradiated on both samples in the perovskite/ETL/ITO configuration to analyze the extraction dynamics of the photo-excited carriers. Figure 3c shows reduced PL intensity in the SnO\(_2\)/ZnO

| Device | \( V_{OC} \) [V] | \( J_{SC} \) [mA cm\(^{-2}\)] | FF [%] | PCE [%] |
|--------|-----------------|-----------------|--------|--------|
| PZ Champion | 1.21 | 14.12 | 71.63 | 12.26 |
| Average | 0.92 ± 0.44 | 12.92 ± 0.99 | 57.27 ± 14.61 | 8.01 ± 3.91 |
| PSZ-ALD Champion | 1.19 | 13.85 | 78.19 | 12.84 |
| Average | 1.17 ± 0.01 | 13.30 ± 1.24 | 76.78 ± 1.39 | 11.95 ± 1.13 |

Table 1. Device performance parameters of the PZ and PSZ-ALD devices.
ETL sample, indicating that a faster quenching occurs at the perovskite/SnO₂/ZnO interface, enhancing electron extraction compared to the perovskite/ZnO interface. The TRPL spectra of both samples were obtained to investigate the charge carrier dynamics further. As shown in Figure 3d and Table S3, Supporting Information, the TRPL curves were fitted with a bi-exponential decay function consisting of a fast decay (τ₁) component and a slow decay component (τ₂). The fast decay component is on a short time scale of a few tens of nanoseconds and represents carrier transport from the perovskite to the ETL, whereas the slow decay component is on a scale of a few hundreds of nanoseconds and represents the radiative decay in the perovskite layer.[44] The τ₁ for perovskite/SnO₂/ZnO decreased from 6 to 5.3 ns compared to perovskite/ZnO, while its weight fraction (A₁) value increased from 40.33 to 50.56%. The reduced τ₁ value implies that the charge extraction from the perovskite to SnO₂/ZnO was enhanced, consistent with the steady-state PL spectra. Likewise, considering the A₁ of τ₁, the perovskite deposited on SnO₂/ZnO presented a higher A₁ value than its ZnO counterpart, suggesting that charge extraction was the dominant decay mechanism.[44] This observation implies that introducing a SnO₂ interlayer suppressed the charge carrier recombination and extracted the charge carriers, resulting in less charge accumulation. Both of these observations lead to enhanced device performance and reproducibility.

Maximum power point tracking (MPPT) is a reliable way to assess PSC performance stability.[45] In particular, the top PV device in the tandem system needs to continuously operate under AM 1.5G illumination and ambient conditions to provide sufficient photovoltage for H₂ generation. SnO₂ nanoparticles (NP) were deposited on ZnO as an interlayer for comparison with the PSZ-ALD device. Table S4, Supporting Information, shows the optimized SnO₂ NP/ZnO ETL-based PSC (denoted as PSZ-NP device), which had similar PV performance to the PSZ-ALD device. Figure 4a shows the normalized steady-state output performance for the three devices: PSZ, PSZ-NP, and PSZ-ALD. After tracking for 100 min, the performance of the PSZ device plunged to less than ≈3%, while the PSZ-NP device showed slightly improved stability, and the PCE remained at 36.3% of its initial value. By contrast, the PCE of the PSZ-ALD device maintained 77.9% of its initial value, representing a remarkable improvement in performance stability. Based on the XRD results (Figure S10, Supporting Information), the low device stability of PSZ-NP device likely resulted from chemical degradation of the perovskite, as in the PSZ device. An additional MPPT test was performed on the PSZ device at constant temperature (25 °C). Interestingly, the PSZ device maintained 93.7% of the initial PCE for 200 min during MPPT (Figure S11, Supporting Information). This result indicates that heat energy, originating from continuous illumination that typically raises the temperature to ≈50 °C,[46] aggravated the perovskite stability where the thermally driven chemical reaction between ZnO and perovskite became the dominant degradation mechanism.

The surface structure and chemical states of ZnO covered with NP- or ALD-derived SnO₂ were comparatively analyzed by X-ray photoelectron spectroscopy (XPS) analysis. The XPS spectra were calibrated to 284.8 eV according to the C 1s binding energy for adventitious (aliphatic) carbon. Figure S12a, Supporting Information, shows two prominent peaks in the Zn 2p level spectra at 1021 and 1044 eV, ascribed to ZnO 2p²/³ and Zn 2p¹/², respectively.[47] The Sn 3d level spectra were deconvoluted to 487 eV and 496 eV, attributed to the binding energy of Sn⁴⁺ ions in the SnO₂ lattice (Figure S12b, Supporting Information).[48] The only strong Sn peak was observed for ZnO covered with ALD-derived SnO₂, whereas the Zn and Sn peaks appeared for NP-derived SnO₂ coated ZnO. The O 1s spectra were deconvoluted into three different oxygen peaks at 530, 531, and 532 eV, ascribed to oxygen bonded to metal atoms, non-lattice oxygen species (i.e., oxygen vacancies), and surface hydroxyl groups, respectively.[10] Figure 4b,c and Figure S13, Supporting Information, show that the hydroxyl group was observed in the ZnO sole layer and NP-derived SnO₂-coated ZnO, whereas there was no hydroxyl group in ALD-derived SnO₂ deposited on ZnO. This observation indicates that ALD-derived SnO₂ conformally covered the entire surface of ZnO, while SnO₂ NP deposition led to partial coverage. The cross-sections of SnO₂ coated ZnO were visualized via transmission electron microscopy (TEM) and electron dispersive X-ray spectroscopy (EDS) elemental mapping analysis (Figure 4d,e). The ALD-derived SnO₂/ZnO revealed a discernable bilayer of ZnO and SnO₂ (Figure 4d). However, for NP-derived SnO₂/ZnO, there was no boundary between ZnO and SnO₂, indicating a mixture of these materials (Figure 4e). It was speculated that the deposition of the basic SnO₂ colloidal dispersion (at pH 10.0–12.0) onto the ZnO layer inevitably caused the partial dissolution of ZnO into zinc ion complexes (e.g., Zn(NH₃)₄²⁺), which were then recrystallized into a particle mixture.[49] Therefore, solution-derived SnO₂ NPs inevitably damaged ZnO-ETL, suggesting that ALD-derived SnO₂ is a more suitable protective layer for ZnO ETL-based PSCs.

The HER and SOR occur at the bottom photocathode and serially connected metal anode, respectively, in the PV-PEC tandem device. The bottom photocathode generates H₂ by efficiently harvesting transmitted long-wavelength photons through the top PV cell. Si harvests solar photons with wavelengths up to 1100 nm due to its low Fₘ (1.12 eV). We developed the interface-engineered Si-based photocathode via polyethyleneimine ethoxylated (PEIE) as a bottom electrode as shown in Figure S14a, Supporting Information. Figure S14b, Supporting Information, shows that the Si photocathode demonstrated a high incident photon to current efficiency (IPCE) of 78.3% at 900 nm in an electrolyte containing Na₂SO₄ when HER was coupled with SOR. To develop an efficient tandem device, we needed the optimized PV as a top electrode with the appropriate transmittance to allocate similar photocurrent values to the top and bottom electrodes. As the transmittance and performance of semitransparent PSCs were correlated to each other, these factors need to be precisely controlled to maximize the hydrogen generation rate. Figure S15, Supporting Information, shows the calculated solar photon harvesting capability of the top semitransparent PSC and the bottom Si photocathode relative to the transmittance of the top PV. The absorbance of IBr₀.₆₄ perovskite/ITO was experimentally measured in accordance with the perovskite thickness to determine the light absorption by the top PV (Figure S16, Supporting Information). The following assumptions were made to determine the operating current of the PV-PEC tandem device: all the light absorbed by the top PV contributed to the photocurrent, and all the photons transmitted...
through the top PV reached the bottom Si, followed by complete conversion into the photocurrent according to the IPCE values in Figure S14b, Supporting Information. The overall current value of the serially connected tandem device was determined by the lower current cell between the top and bottom electrodes. Although there were some deviations from the actual device, we believed this was an appropriate way to estimate the maximum current density of our system and predict the optimal thickness of $\text{IBr}_{(0.4)}$ perovskite in terms of its transmittance. Figure S15a, Supporting Information, shows that when the perovskite layer was too thin ($\approx 80$ nm), the number of photons harvested by the bottom Si photocathode (blue line) became significantly larger than that harvested by the top PV (red line). In this case, the overall current was limited by the top PV cell, and the operating current was approximately $9 \text{ mA cm}^{-2}$. On the other hand, when the perovskite layer was sufficiently thick ($\approx 420$ nm, Figure S15b, Supporting Information), most of the incident photons below 700 nm were harvested by the top PV without sufficient transmission. In such a case, the efficiency was limited by the low photocurrent of the bottom Si photocathode. With an optimum thickness of $\approx 220$ nm, similar high photocurrent values were produced by the top and bottom electrodes,
revealing a theoretical maximum photocurrent of \( \approx 18 \text{ mA cm}^{-2} \) (Figure S15c, Supporting Information). By varying the thickness of the \( \text{IBr}_{0.4} \) perovskite (from \( \approx 80 \) to \( \approx 420 \text{ nm} \)), the operating current density for the PV-PEC device was adjustable (Figure S15d, Supporting Information).

SOR is thermodynamically an ideal alternative reaction for OER because the required potential for generating \( \text{H}_2 \) is reduced when SOR is coupled with HER.\(^{[50]} \) SOR involves the oxidation reaction of \( \text{Na}_2\text{SO}_3 \), which is a byproduct of flue gas treatment. Flue gas is typically treated with aqueous sodium hydroxide (NaOH) solution to absorb highly toxic \( \text{SO}_2 \) gas, leaving behind \( \text{Na}_2\text{SO}_3 \) (i.e., \( 2\text{NaOH} + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \)).\(^{[51]} \) Since most fossil-fuel-based power plants and oil refineries are regulated to emit ultralow levels of \( \text{SO}_2 \) gas, massive amounts of \( \text{Na}_2\text{SO}_3 \) are readily available, indicating the promising viability of SOR for solar-driven hydrogen generation.\(^{[50]} \) Additionally, SOR leaves behind \( \text{Na}_2\text{SO}_4 \) as a byproduct. \( \text{Na}_2\text{SO}_4 \) is a chemically inert and nontoxic compound and can be also used in the paper industry, glass production, and various other applications.\(^{[52]} \) Hence, SOR is not just used as a sacrificial oxidation reaction, but increases the \( \text{H}_2 \) production rate and effectively converts the toxic \( \text{SO}_2 \) gas into a value-added product for the industry. Moreover, there is no need for a gas separation when OER is replaced by non-gas evolving SOR. A commercially available dimensionally stable anode (DSA, i.e., Ir-, Ru-, and Pt-coated Ti plate) was utilized for the anode to examine SOR. Figure S17, Supporting Information, exhibits the advantage of SOR, where a negative shift in the onset potential was observed when SOR replaced OER.

The \( J-V \) response of the \( \text{I}_3 \) and \( \text{IBr}_{0.4} \) perovskite-based PSCs were plotted with the \( J-V \) curves of the PEC cells (i.e., the DSA and Si photoelectrodes were utilized as the anode and the photocathode, respectively, denoted as the DSA \( || \) Si photocathode) to predict the operating points for each tandem device before the stand-alone PV-PEC tandem device was tested. The semitransparent PSC was in front of the electrolyte, and the performance of the DSA \( || \) Si photocathode was measured with a two-electrode configuration where the photocathode received transmitted light through the front semitransparent PV cell, as shown in the inset of Figure 5a,b. The current values at the intersection of the PV and PEC curves represent the operating point of the PV-PEC tandem device. A low operating current density of \( 5.0 \text{ mA cm}^{-2} \) was observed when the \( \text{I}_3 \) perovskite-based PSC was combined with the Si photocathode (Figure 5a). Additionally, the operation current density reached \( \approx 11.4 \text{ mA cm}^{-2} \) for the \( \text{IBr}_{0.4} \) perovskite-based PSC-Si tandem device (Figure 5b). An insufficient photovoltage of \( \approx 0.9 \text{ V} \) for the \( \text{I}_3 \) perovskite-based PSC was responsible for the low operating current in the PV-PEC tandem.

**Figure 5.** \( J-V \) curves of top semitransparent perovskite PVs plotted with the \( J-V \) curves of the DSA \( || \) Si photocathode located behind: a) \( \text{I}_3 \) perovskite and b) \( \text{IBr}_{0.4} \) perovskite PVs in the two-electrode configuration. The Si photocathode was immersed in an electrolyte containing \( \text{Na}_2\text{SO}_3 \) (pH of 13), and AM 1.5G illumination was applied. c) Photographs of the \( \text{I}_3 \) (left) and \( \text{IBr}_{0.4} \) (right) perovskite film on ITO glass. d) EQE and IPCE for the \( \text{IBr}_{0.4} \) perovskite-based PV and Si photocathode located behind the top PV.
device. Moreover, inefficient absorbed photon distribution induced by less transparency of perovskite film is another disadvantage for I$_3$ perovskite-based PSC (Figure 5c and Figure S18, Supporting Information). In addition, external quantum efficiency (EQE) and IPCE measurements allowed us to understand the photon-harvesting mechanism of the PV-PEC tandem device (Figure 5d). The EQE and IPCE plots measured from the top PV and bottom photocathode resembled the distribution shapes predicted by the theoretical analysis in Figure S13, Supporting Information. The results indicate that our estimate of the optimal thickness for IBr$_{0.4}$ perovskite to utilize the photons in a broad wavelength efficiently was in agreement with the experimental device measurement.

The stand-alone PV-PEC tandem device, shown in Figure 6a, was fabricated with the bottom Si photocathode and DSA anode connected in a series to the top semitransparent PCS where the electrons were transferred from the PSC to the photocathode, and the holes were moved to the DSA. It should be noted that the size of the DSA ($\approx$10 cm$^2$) was much larger than the active area of the tandem device ($\approx$0.12 cm$^2$), meaning that the active area of the DSA did not constrain the HER and SOR. Moreover, as shown in Figure S19, Supporting Information, although there was a slight decline of current density as the size of DSA decreased, 93.5% of current density at 1 V is maintained when 20% small-sized DSA was used. This indicates that the overall performance does not vary significantly depending on the size of the DSA. In addition, DSA showed a slightly higher current density at a faster scan speed (50 mV s$^{-1}$) than slower (10 mV s$^{-1}$), especially at the lower-potential region, indicating that there was a capacitive current (Figure S20, Supporting Information). For this reason, a scan speed of 10 mV s$^{-1}$ was used to test the tandem device. The $J$–$V$ curve measurements for the PV-PEC tandem assembled in a two-electrode configuration were performed to confirm the device’s performance. Figure 6b shows the $J$–$V$ curve for the H$_2$ generating device. A photocurrent value of 0 V represented the unbiased reaction rate in the two-electrode mode. The measured unbiased solar H$_2$ production current density for the device was 11.1 mA cm$^{-2}$, which agreed with the estimated value in Figure 5b. Moreover, the Faradaic efficiency of the Si photocathode was close to 100% at a current similar to the tandem device (Figure S21, Supporting Information), corresponding to high STH efficiency (13.7%) from a device based on HER and OER. Our results marked the second highest H$_2$ production current density among PV-PEC tandem, while Karuturi et al. demonstrated the record-high STH efficiency by generating 14.3 mA cm$^{-2}$ under unbiased condition.[53] Figure 6c reveals the $I$–$t$ curve under 1-sun illumination without an additional electrical bias. Our tandem system demonstrated operational stability during H$_2$ generation for 1 h. After 4 h of continuous operation,
≈66.7% of the initial photocurrent was maintained (Figure S22, Supporting Information). The time-dependent PL spectra of $IBr_{0.4}$ perovskite was conducted for the $IBr_{0.4}$ perovskite after light soaking under 1 sun condition for different durations of 10, 30, 60, 90 min prior to the PL spectrum measurement. Although the PL peak position of the $IBr_{0.4}$ perovskite did not shift until 60 min, phase segregation appeared after the 90 min light soaking (Figure S23, Supporting Information). It is well known that perovskite with a Br ratio higher than 20% exhibits photoinduced phase segregation, which likely explains for the decreased performance of PV as shown in Figure 4a. The degraded current density presumably originated from the degradation of the top PV cell, as shown in Figure 4a. To the best of our knowledge, there are only a few notable reports on PEC-driven H2 generation coupled with SOR.[54–57] Moreover, none of the reported devices generated H2 under unbiased conditions, and the photocurrent density lagged far behind our benchmark performance (Table S5, Supporting Information). In this regard, the current findings suggest that the high hydrogen generation rate produced by the PV-PEC tandem device was achieved by developing an optimal semitransparent single-cell PSC for the sulfite oxidation assisted H2 generation system.

3. Conclusions

We presented a PV-PEC tandem device comprising semitransparent top PV and bottom Si photocathodes, enabling high-rate H2 generation when combined with SOR at the anode. Replacing the anodic OER with SOR reduced the required potential for H2 generation. While a sufficient $V_{OC}$ of 1.19 V to produce H2 was achieved for the ZnO ETB-based $IBr_{0.4}$ perovskite PSC, severe interfacial incompatibility including phase decomposition was demonstrated when the I/Br perovskite was in contact with ZnO. The presence of more electronegative Br ions than I ions in the mixed-halide perovskite induced the migration of FA to ZnO. The presence of more electronegative Br ions than I ions demonstrated when the I/Br perovskite was in contact with TiO2 (0.4) perovskite with a Br ratio higher than 20% exhibits photoinduced phase segregation. As the I/Br ratio increased, the PL peak position of the $IBr_{0.4}$ perovskite did not shift until 60 min, phase segregation appeared after the 90 min light soaking (Figure S23, Supporting Information). It is well known that perovskite with a Br ratio higher than 20% exhibits photoinduced phase segregation, which likely explains for the decreased performance of PV as shown in Figure 4a. The degraded current density presumably originated from the degradation of the top PV cell, as shown in Figure 4a. To the best of our knowledge, there are only a few notable reports on PEC-driven H2 generation coupled with SOR.[54–57] Moreover, none of the reported devices generated H2 under unbiased conditions, and the photocurrent density lagged far behind our benchmark performance (Table S5, Supporting Information). In this regard, the current findings suggest that the high hydrogen generation rate produced by the PV-PEC tandem device was achieved by developing an optimal semitransparent single-cell PSC for the sulfite oxidation assisted H2 generation system.

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4. Experimental Section

Materials: FAI was purchased from Greatcell Solar (Queanbeyan, Australia). SnO2 nanoparticle colloidal dispersion (tin (IV) oxide, 15% size, 99.9%), cesium iodide (CsI, trace-metal basis, 99.999%), lead bromide (PbBr2, 99.999% metal basis), dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%), chlorobenzene (anhydrous, 98.9%), bis(trifluoromethane)sulfonamide lithium trifluoromethane sulfonate (LiTFSI, 99.95%), lead bromide (PbF2, 99.999%), 4-tert-butylypyridin (TBP, 96%), and 2,2',7,7'-tetrakis(N,N-dimethylphenylamino-9,9'-spirobi fluorine (spiro-OMeTAD) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Diethyli ether (99%) and ammonia water (25–30%) were purchased from Duksan (Seoul, Korea). All chemicals were used as received without any modification. Fabrication of Semitransparent Perovskite Solar Cells: The ITO glass was patterned using laser etching equipment (Korthem Science Co. Ltd, Incheon, Korea). The patterned ITO was cleaned via sequential sonication with deionized (DI) water, isopropanol, and acetone for 15 min each. After partially tapping the bottom electrode contact, O2 plasma treatment was conducted for 15 min. Zinc oxide powder (10 mg mL$^{-1}$) was dissolved in a 50% ammonia hydroxide and 50% water solution by stirring for 3 h. The solution was filtered with a 0.22 μm PTFE syringe filter and sonicated for 15 min before use. The zinc oxide solution was spin-coated at 4000 rpm for 30 s and annealed at 120 °C for 30 min. The Ga2O3, TiO2, and SnO2 layers were deposited using ALD (Lucida D100, NCD Inc., Daejeon, Korea). Deposition of the TiO2 layer was performed at 120 °C with tetrakis(dimethylamido)tinanium (TDMAT) and H2O as the Ti and O precursors. Each cycle comprised a TDMAT pulse of 0.3 s followed by 15 s of N2 purging and a 0.2 s H2O pulse followed by 15 s of N2 purging. The SnO2 layer was prepared at 110 °C with tetrakis(dimethylamino)tin (TDMASn), and H2O was used as the Sn and O precursors, respectively. Each cycle comprised a TDMASn pulse of 0.3 s followed by 15 s of N2 purging and a 0.3 s H2O pulse followed by 15 s of N2 purging. Ga2O3 layer was prepared at 180 °C with Bis(μ-dimethylamino)tetrakis(dimethylamino)digallium and H2O used as the Ga and O precursors, respectively. Each cycle was composed of a Bis(μ-dimethylamino)tetrakis(dimethylamino)digallium pulse of 2 s followed by 10 s of N2 purging and a 0.5 s H2O pulse followed by 10 s of N2 purging. The TiO2, SnO2, and Ga2O3 approximate growth rates were 0.55, 1, and 1 Å per cycle, respectively, estimated with an ellipsometer (alpha SE, J.A. Woollam Co. Ltd, Lincoln, USA). A SnO2 colloid suspension was diluted with DI water to make a 2.67 wt% dispersion and spin-coated at 3000 rpm for 30 s under ambient conditions followed by annealing at 150 °C for 30 min for the NP derived SnO2 interlayer. To fabricate the semitransparent perovskite absorber layer, a 0.65 M Cs0.8FA0.2PbI3Br1 precursor solution was prepared by dissolving FAI, CsI, Pbi2, and PbBr2 in 1 mL of a mixed solvent of DMF and DMSO with a volume ratio of 3:1, followed by stirring for 3 h. Perovskite precursor was deposited on the preheated substrate and then spin-coated at 500 rpm 2 s and 4000 rpm for 60 s with 750 μL diethyl ether drying. After 25 s of the second deposition step, the perovskite film was annealed at 100 °C for 10 min in a dry-air-filled glove box. An HTM layer was spin-coated at 3000 rpm for 30 s using a mixture of a spiro-OMeTAD solution. The spiro-OMeTAD solution consisted of 72 mg of spiro-OMeTAD with 28.8 μL of TBP in 1 mL of a mixed solvent of DMF and DMSO with a volume ratio of 3:1. The spiro-OMeTAD solution was spin-coated at 3000 rpm for 30 s using a mixture of a spiro-OMeTAD solution. The spiro-OMeTAD solution consisted of 72 mg of spiro-OMeTAD with 28.8 μL of TBP in 1 mL of acetonitrile. Either 17.5 μL of a LiTFSI solution (520 mg of LiTFSI in 1 mL of acetonitrile) or 31.86 μL of a LiPF6 solution (151.9 mg of LiPF6 in 1 mL of acetonitrile) was used to dope the spiro-OMeTAD solution. After the HTM coating, an 80 nm thick Au top electrode for the opaque electrode was deposited via thermal evaporation. The 250 nm thick ITO electrode was sputtered, and a 10 nm MoOx buffer layer was thermally evaporated onto the ITO electrode to fabricate the whole semitransparent solar cell for the top PV cell. Finally, a 137.5 nm thick MgF2 antireflection coating was thermally evaporated onto the bottom side of ITO. Fabrication of Si Photocathode: The Si photocathodes were fabricated as follows: p-Si wafer (Boron doping, 10–30 Ω cm, single-side polished) was ultrasonicated in acetone, DI water, ethanol each and immersed in 2% HF solution to etch the native oxide. After the rinsing with water, samples were then bathed in 0.025 wt% diluted polyethyleneimine 80% ethoxylated aqueous solution. Following the PEIE deposition, ~50 nm TiO2 layer was deposited by the ALD method with a growth rate of ~0.4 Å per cycle. Pt co-catalyst was deposited on top of the TiO2 protection layer via 108 Auto sputter coater (Ted Pella, Redding, CA, USA). A copper wire was connected by Ag paste on the bottom electrode and the unnecessary parts of the electrode were then passivated with an insulating resin (HYSOL 9642, Henkel).
Characterizations: The cross-section profiles of the samples were analyzed by field emission scanning electron microscopy (FESEM, IT-500HR, JEOL Ltd, Tokyo, Japan). The optical absorbance of the perovskite film was measured using a UV-Vis spectrophotometer (V-670, JASCO, Tokyo, Japan). The UPS measurements (AXIS NOVA, Kratos, Manchester, UK) were recorded using the He I (21.22 eV) radiation line with an energy resolution of 0.1 eV at a pressure of 5 × 10⁻¹⁰ Torr. The phase evolution of the perovskite film was determined using an XRD instrument (Rigaku Miniflex 600, Woodlands, Rigaku Co. Ltd., USA). The surface profile of ETL was measured by AFM (SPA 400, Seiko Instruments Inc., Chiba, Japan). The steady-state PL spectra were collected at 780 nm for the perovskite films after excitation at 470 nm (MAPLE-II, Dongwoo Optron, Gwangju, Korea). The TRPL study was performed using an inverted-type scanning fluorescence lifetime microscope (MicroTime-200, Picoquant, Berlin, Germany) with a 4× objective. The lifetime measurements were performed at the Korea Basic Science Institute (KBSI, Daegu Center, Korea). A single-mode pulsed diode laser (470 nm with a pulse width of ≈30 ps and an average power of ≈0.1 mW in 0.5 MHz repetition rate) was used as an excitation source, and the laser was irradiated from the backside of the ITO glass. A dichroic mirror (490 nm/540 nm, HAAO, Aichem, USA) under AM 1.5G (100 mW cm⁻² sun intensity) was used to collect emission from the samples. A time-correlated single-photon counting system (PicoHarp300, PicoQuant GmbH, Berlin, Germany) was used to count emission photons. Exponential fittings for the PL decays were obtained using Sympotime-64 software (Ver. 2.2). The XPS measurements (AXIS NOVA, Kratos, Manchester, UK) were recorded using Al Kα radiation (hv = 1486.6 eV). The PSC device performances were evaluated using a solar simulator (SoLiSt Class AAA, Oriel Instruments, Stratford, USA) under AM 1.5G (100 mW cm⁻²) conditions with a Keithley 2400 source measurement unit. A standard Si reference cell certified by the Newport Corporation (Irvine, USA) was used to calibrate to 1 sun intensity. The selected area (0.06 cm²) of the PSCs covered by the aperture metal mask was exposed to the light. Scanning was conducted under ambient conditions without additional encapsulation. Prior to the MPPT tracking, the J–V curve was measured for each sample to define the maximum power point (VMP, JMP). The MPPT tracking was conducted by monitoring changes according to the previous report.[43] The VMP of each sample was applied, respectively, and the corresponding current density values were measured as a function of time using the potentiosl (1260, Solartron, Leicester, UK). PV cell was in contact with a temperature-controlled stage (LT5024E-P84, Linkam, USA) during the MPPT tracking test when the temperature of the PV was maintained at 25°C. PV-PEC Tandem Device Assembly and Characterizations: The active area of the semitransparent top perovskite cell was defined by a 0.12 cm² metal mask. The mask was sufficiently thick to block all the photons. The DSA was positioned at the back, ≈2 cm from the photocathode. The PEC quartz reactor was filled with an aqueous electrolyte, and an Ar flow was bubbled through the cell. An aqueous solution containing NaOH (0.5 M) and Na₂SO₃ (0.25 M) was prepared, and a 1 M NaOH solution was also prepared for comparison. The ITO bottom contact of the top PV cell (i.e., electron collector) was connected to the photocathode by a Cu wire, while the ITO top contact of the PV cell (i.e., hole collector) was connected (through a potentiostat in the two-electrode configuration) to the DSA. A Si diode (Newport Corporation) was used for calibrating the light intensity so that the PV was located at the position corresponding to 1 sun intensity. The scan rate for the J–V curves was 10 mV s⁻¹. The perovskite cell was in front of the Si photocathode in tandem configuration during the IPCE measurement (Zennium, Zahner, Kronach, Germany), and a potential of 0 VREF was applied to the photocathode. Gas chromatography (6500GC system, YL Instruments, Seoul, Korea) was conducted for gas-product analysis.

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.

Data Availability Statement
Research data are not shared.

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