1. Introduction

As society’s energy demands increase, the production and storage of sustainable energy becomes a critical issue.[1–4] While photovoltaic (PV) modules may cover this demand on their own, large scale applications still require alternatives to batteries and supercapacitors for a more effective energy storage and transport.[1,2,5–9] From this perspective, solar fuels represent a promising option, due to their high specific energy density, which makes them favorable for transport or conversion to more conventional liquid fuels. To harness sunlight into chemical energy, several routes have been developed spanning from connecting photovoltaic modules to separate electrolyzers,[10] to developing solution immersed photovoltaic (PEC) systems.[11–13] Since the energy conversion efficiency of a single photoabsorber is theoretically limited[14] (below 13% for water splitting to produce H2,[15]), tandem systems of two complementary absorbers are preferably employed for PV, PEC, and hybrid PV–PEC applications.[12,15–18] Such photoelectrode tandem systems are particularly interesting for the field of solar fuels, where one of the main aims is driving electrochemical processes (e.g., water splitting or CO2 reduction) without applying an additional electrochemical bias.[19] The end goal for those PEC systems is the broad implementation of lightweight monolithic (i.e., wireless) devices, which are also known as artificial leaves.[20]

Although several examples of using tandem photoabsorbers for water splitting have been previously reported, most of them were hybrid systems combining a photoanode with a wired/buried silicon,[21–24] or dye-sensitized[25–35] PV cell. In this case, the use of double- or multifunctional photoelectrics was occasionally required to obtain an appropriate driving force for water splitting.[21,22,36–40] In contrast, only a few photoelectrocatalytic tandems employing oxide,[41–46] or silicon[47–50] based photocathodes could operate under bias-free conditions. For example, 0.6 V were required to reach a 0.11% applied bias solar-to-hydrogen (AB-STH) efficiency in Cu2O[NiO2xWO3] tandem (with only a small photocurrent at zero bias)[42] whereas a more optimized fluoride doped tin oxide (FTO)[AuCu2O(x)ZnO[TiO2]RuO2–BiVO4|Co–Pi system could later reach a bias-free photocurrent density of 0.32 mA cm–2 and a stability of 1.4 h.[43] Similarly, the combination of a silicon-based photocathode with a BiVO4|TiCo photoanode could achieve a maximal AB-STH efficiency of 0.59% at 0.6 V bias.[47]
which was later improved to a bias-free value of 0.57% using a p-Si nanoarray/Pt–Mo:BiVO₄/Co–Pt tandem.[48]

Due to the rapid growth in the efficiency of lead halide perovskite photovoltaics, rising from the initial 3.8% reported by Miyasaka and co-workers[51] to beyond 22% nowadays,[52] these photoabsorbers have also attracted attention from the solar fuel community. The initial prototypes involved wired systems, where several solar cells were connected in series to separate electrocatalysts, resulting in successful proton,[53–57] CO₂,[58] or H₂S reduction.[59] Since the use of wired systems provides several disadvantages by requiring gas separating membranes, wiring, external connections and additional device packaging,[13,60] several recent reports proposed more compact designs for PEC-PV tandem devices.[61,62] Nevertheless, to prevent degradation of the perovskite layer, the photovoltaic component was again physically separated from the solution, with a conductive wire ensuring the connection to the electrocatalyst. Such devices mainly combined a perovskite cell with a wide band gap oxide layer (i.e., BiVO₄,[61,63–66] WO₃,[67] TiO₂,[68] or hematite[62,69,70]) to drive water splitting,[63] or CO₂ reduction.[71] In those cases, bias-free devices could be achieved due to the high open circuit voltage (VOC) of the perovskite component, which enabled a good overlap between the cathodic and anodic photocurrents.

While previous attempts to directly interface the regular structure perovskite surface to an electrolyte solution through a thin nickel layer have produced a moderate stability of 10–30 min with photocurrents varying between 2 and 17 mA cm⁻² for the oxygen evolution reaction,[72–74] a significant improvement was recently demonstrated in our group by employing the low melting point Field’s metal (FM) instead.[75] This InBiSn alloy could simultaneously provide encapsulation and electrical contact to a platinum nanoparticle (Pt-NP) catalyst, sustaining an encouraging hydrogen generation photocurrent of -6.9 ± 1.8 mA cm⁻² at 0 V against the reversible hydrogen electrode (RHE) beyond one hour.[75] In this case, an inverse structure perovskite cell was necessary to collect electrons for the proton reduction at the outer device surface (see schematic depictions in Figure 1).

With an onset potential of 0.95 ± 0.03 V versus RHE, this initial system represented a promising example of a perovskite-based photocathode, on the basis of which wireless tandems for solar fuel production could be developed.

While most of these initial results employed the moisture, air, and temperature sensitive methylammonium lead triiodide (MAPbI₃) perovskite,[51,76] more recent photovoltaic reports have shown that improvements in both efficiency and stability can be obtained when using complex precursor solutions. In particular, mixtures including the formamidinium (FA) and methylammonium cations (MA), together with iodide and bromide anions, achieved efficiencies beyond 20%,[77,78] whereas the addition of further (earth) alkali cations (e.g., cesium, magnesium, or potassium) have increased both efficiency (above 21%) and stability (beyond a few weeks).[79–85] Still, the limited scalability of perovskite cells remained an issue until very recently, when large scale deposition procedures such as spray coating, doctor blading or vacuum techniques[86] started to be optimized alongside spin coating[82,87] for larger photovoltaic modules, leading to efficiencies between 10% and 16% for areas above 36 cm².[16,82,88,89]

Accordingly, although organic–inorganic lead halide perovskite photovoltaics have experienced a rapid development in performance within the last decade, the field has mostly continued to suffer from the same challenges of device up-scaling as photoelectrocatalysis. To address some of those issues, in this work we investigate the scalability of tandem PEC devices for water splitting, combining a cesium formamidinium...
methylammonium (CsFAMA) triple cation perovskite-driven photocathode with a bismuth vanadate photoanode. To gain a complete understanding of the limiting factors, the performance and scalability are investigated separately for the photovoltaic cells and for the derived photocathodes. In order to evaluate devices of various sizes, we also propose a straightforward design for a modular 3D-printed PEC cell, which can be easily assembled or adapted for large scale studies.

2. Results and Discussion

2.1. Perovskite Photovoltaic Cells

A NiO$_x$ hole transport layer$^{[90]}$ was deposited on top of the FTO coated glass substrate by spin-coating a Ni(NO$_3$)$_2$·6H$_2$O precursor solution followed by annealing. A state-of-the-art CsFAMA triple cation perovskite photosorber was deposited by spin-coating using the established anti-solvent method.$^{[78,79,85,90]}$ Polyethyleneimine (PEIE)$^{[91]}$ was spin-coated on top of the thin [6,6]-phenyl C$_{61}$ butyric acid methyl ester (PCBM) electron selective layer, to prevent interfacial degradation$^{[92]}$ from the reaction of silver with the halide ions. The additional physical separation provided by the PEIE layer is noticeable when comparing Figure 1a of a complete device with Figure S7a (Supporting Information) of the bare PCBM on a perovskite substrate. This design provided a performance improvement over our previously reported devices.$^{[75]}$ where a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole transport layer (HTL) and a MAPb$_x$ photoabsorber were used.

To draw an accurate comparison between the performance of a photocathode and the underlying photovoltaic component, all devices have been first investigated as solar cells. In this way, thorough batch statistics of the photocathodes could be made, by taking already faulty PV devices into account.

The average photovoltaic parameters are depicted as a function of the device area in Figure 2, with the exact values given in Table 1. The corresponding histograms for the 0.045, 0.25, and 1 cm$^2$ devices can be found in Figures S2–S6 of the Supporting Information. Examples of typical I–V curves are also presented in Figure 3a.

In general, the small 8-pixel devices (area 0.045 cm$^2$) present the best performance, with the champion device reaching an efficiency of 16.4% in backward scan direction, with an open circuit voltage ($V_{OC}$) of 0.99 V, a short circuit current density ($J_{SC}$) of 19.7 mA cm$^{-2}$ and a fill factor (FF) of 83.1%. The improved $V_{OC}$ of 1.00 ± 0.02 V is also consistent with previous reports, which indicate a better alignment between the work function of NiO$_x$ and the perovskite’s valence band edge level than in the case of PEDOT:PSS, which typically only delivers $V_{OC}$ values between 0.5 and 0.9 V.$^{[91–97]}$

As observed from Figure 2d, a roughly logarithmic decrease in the photovoltaic cell efficiency (PCE) with the active area occurs above a surface of 0.25 cm$^2$, due to resistive losses.$^{[98,99]}$ These losses manifest mainly through a decrease in the

![Figure 2](image.png)

Figure 2. Dependence of the photovoltaic parameters of the perovskite devices on their photoactive area: a) open circuit voltage ($V_{OC}$), b) short circuit current density ($J_{SC}$), c) fill factor (FF), and d) photovoltaic cell efficiency (PCE). The average data of backward and forward scans is indicated by blue dots and red circles, respectively.
fill factor (see Figures 2c and 3a), which induces a similar behavior in the \( J_{SC} \) (Figure 2b). This leads to a limitation of the maximum short circuit current below 100 mA, as observed for the 4 and 10 cm\(^2\) devices. The less pronounced decrease in the \( V_{OC} \) (Figure 2a) may be due to an increasing shunt resistance originating from more defects and pin-holes in the layer structure of the larger devices. Nevertheless, our study on the scalability of single pixel perovskite PV cells (as opposed to serially connected modules) reveals that efficiencies above 1% can be obtained even for 10 cm\(^2\) devices, whereas the Field’s metal is also first demonstrated as a valid encapsulant for photovoltaic applications. These observations indicate that metal fingers at distances between 0.5 and 1 cm from each other are required for maintaining a high performance in large scale perovskite applications, similar to the ones available for silicon panels.

Another interesting aspect of our findings is that the NiO\(_x\) layer can also effectively cover the rougher surface of bare FTO (Figure 4a,b). In this case, a very thin coating of NiO\(_x\) nanoclusters is formed, which does not present additional peaks in the X-ray powder diffraction (XRD) spectra (Figure S8, Supporting Information). This smoothing of the underlying surface appears to result in more homogeneous and better packed perovskite grains (Figure 4c,d). While the higher surface roughness of FTO has made indium tin oxide (ITO) glass the preferred choice for planar inverse-structure perovskite cells,[100,101] these results show that the former can be also successfully employed. Since FTO is chemically more robust to aggressive cleaning methods (e.g., Piranha solution) and has a typically lower sheet resistance, its use has a potential advantage for large scale, industrial applications.

### Table 1

Numerical data of the photovoltaic parameters illustrated in Figure 2. The open circuit voltage, short circuit current density, fill factor and photovoltaic cell efficiency are given as a function of the photoactive area for both forward (f) and backward (b) scans, whereas the number of working devices from the total amount produced is also shown.

| Area [cm\(^2\)] | \( V_{OC,b} \) [V] | \( J_{SC,b} \) [mA cm\(^{-2}\)] | FF\(_b\) [%] | PCE\(_b\) [%] | \( V_{OC,f} \) [V] | \( J_{SC,f} \) [mA cm\(^{-2}\)] | FF\(_f\) [%] | PCE\(_f\) [%] | Devices working (total) |
|----------------|-------------------|-------------------|------|------|----------------|-------------------|------|------|---------------------|
| 0.045          | 1.00 ± 0.02       | 17.3 ± 1.5        | 80.0 ± 3.6 | 13.8 ± 1.3 | 0.99 ± 0.02 | 17.0 ± 1.3 | 69.2 ± 2.3 | 11.9 ± 1.2 | 47(48)               |
| 0.25           | 0.95 ± 0.05       | 18.8 ± 1.4        | 72.9 ± 3.2 | 13.0 ± 1.2 | 0.94 ± 0.05 | 19.3 ± 1.2 | 59.8 ± 5.4 | 10.9 ± 1.3 | 22(24)               |
| 1              | 0.86 ± 0.01       | 20.7 ± 1.3        | 46.9 ± 4.7 | 8.3 ± 1.2  | 0.86 ± 0.01 | 20.6 ± 1.2 | 45.3 ± 4.7 | 8.0 ± 1.2  | 10(12)               |
| 4              | 0.89 ± 0.03       | 16.5 ± 1.7        | 28.4 ± 1.5 | 4.2 ± 0.6  | 0.89 ± 0.03 | 16.1 ± 2.1 | 27.8 ± 1.2 | 4.0 ± 0.6  | 6(6)                 |
| 10             | 0.87 ± 0.04       | 6.1 ± 2.4         | 25.6 ± 0.9 | 1.36 ± 0.58| 0.88 ± 0.03 | 5.8 ± 2.2  | 26.2 ± 0.8 | 1.35 ± 0.54| 6(6)                 |

Figure 3. Typical photocurrents observed for the photovoltaic and photoelectrochemical devices of areas between 0.045 and 10 cm\(^2\) (100 mW cm\(^{-2}\), AM 1.5G): a) PV cells, b) perovskite-based photocathodes, c) BiVO\(_4\)|TiCo photoanodes, d) perovskite-BiVO\(_4\)|TiCo PEC tandems (scan rates 100 mV s\(^{-1}\) for the PV cells and 10 mV s\(^{-1}\) for the PEC devices, gray arrows indicate starting points and direction).
of the resulting PVK layer through exfoliation of the Ag layer. Following contact was ensured, while preventing a degradation of the device stability for only 20–40 s, a good adhesion to the underlying silver layers was obtained via a Peltier thermoelectric element and sealing the edges with epoxy resin. By maintaining the Field’s metal in a liquid state for H₂ evolution. Typical examples of the results are depicted in Figure 5a, red curves, and Figure S16 of the Supporting Information. For those devices, the average faradaic yield (FY) amounted to 78.8 ± 3.5 % after 4 h. Losses are possibly caused by the entrapment of small H₂ bubbles along the measuring cell’s glass walls or by leakage due to overpressure in the cathodic compartment.

2.2. Perovskite-Based Photocathodes

After the photovoltaic characterization, the 0.25 cm² perovskite PV devices (abbreviated PVK) were encapsulated by briefly melting a thin Field’s metal (FM) sheet on top of the silver contact via a Peltier thermoelectric element and sealing the edges with epoxy resin. By maintaining the Field’s metal in a liquid state for only 20–40 s, a good adhesion to the underlying silver contact was ensured, while preventing a degradation of the perovskite layer through exfoliation of the Ag layer. Following the electrosynthetic Pt nanoparticle deposition, the performance of the resulting PVK|FM|Pt photocathodes was investigated for H₂ evolution. Typical examples of the results are depicted in Figure 5a,b, where the sign of the photocathode traces is reversed for convenience. Further data from all devices can be found in Figures S16–S18 of the Supporting Information.

In order to determine the reliability of the device fabrication procedures, performance statistics have been performed on an initial batch of eight 0.25 cm² PV devices (V_OC, b 0.867 ± 0.002 V, J_SC, b 21.1 ± 1.3 mA cm⁻², FF, b 50.2 ± 4.7%, PCE, b 9.2 ± 1.2%, no shorted cells). In this case, a comparable average photocurrent of −9.3 ± 1.1 mA cm⁻² at 0 V versus RHE was determined for all four corresponding photocathodes, and the more noisy voltammetric signal was likely caused by the vigorous hydrogen evolution (see Figure S17 and Video S1 of the Supporting Information). Two devices lasted beyond 2 h (FY 74.7 ± 3.0%, see Figure S17 of the Supporting Information), with the slight loss in stability due to a higher probability of water leakage with increasing area, combined with additional mechanical stress during the transport of the encapsulated devices for PV characterization.

2.3. BiVO₄|TiCo Photoanodes

The BiVO₄|TiCo photoanodes of corresponding sizes were prepared similarly to reported procedures. BiOΙ was electrodissolved onto FTO glass and annealed in the presence of a vanadium precursor. The TiCo catalyst was spin-coated from a single source precursor solution.

A photoelectrochemical batch analysis has also been conducted for the BiVO₄|TiCo photoanodes; results for all the devices are presented in Figures S19–S21 of the Supporting Information and typical linear sweep voltammetry (LSV) scans are depicted in Figure 5a (blue curves). For a batch of six 0.25 cm² devices, the average photocurrent density amounted to 1.61 ± 0.28 mA cm⁻² at an applied potential of 1.23 V versus RHE (see Figure S19 of the Supporting Information), whereas it reached 1.31 ± 0.10 mA cm⁻² at 1.23 V versus RHE for three 1 cm² devices (Figure S20, Supporting Information).

Since the comparatively high stability of BiVO₄ under use is well known, the chronoamperometric measurements at 1.23 V versus RHE have only been conducted for 4 h, to match the stability of the perovskite-based photocathodes. An example is given in Figure S12 (Supporting Information), which also reveals the corresponding amount of oxygen detected by the fluorescence sensor after subtraction of the initial background.
leakage (see Figures S19 and S20 of the Supporting Information for the linear fitting of the raw fluorescence lifetime $\tau$ signals, and Scheme S2 of the Supporting Information for a clarification on the extracted information). The resulting faradaic yield only amounted to $38.4 \pm 10.7\%$ for the 0.25 cm$^2$ devices, due to the particular affinity of the O$_2$ bubbles to the glass walls of the measuring cells. The oxygen-glass affinity also explains why a slow equilibrium is reached after the end of the chronoamperometry, since the oxygen needs to first dissolve from the bubbles into the solution, then diffuse to the upper gas space (Figure S12, Supporting Information). A similar value of $31.2 \pm 9.2\%$ was obtained for the 1 cm$^2$ devices.

### 2.4. Perovskite-BiVO$_4$TiCo PEC Tandem Devices

For the tandem systems, a back-to-back configuration has been preferred over a wired PEC design due to several reasons. The back-to-back monolithic design is closer to the idealized artificial leaf and also provides sufficient spatial separation between the H$_2$ and O$_2$ evolution sites. Thus diffusion of the produced oxygen to the cathodic compartment and its subsequent reduction is less likely even in the absence of an ion exchange membrane. High performing BiVO$_4$ photoanodes are designed to maximize scattering.$^{[103,107–110]}$ Therefore, the small gap between the BiVO$_4$TiCo front side and the perovskite back side ensures that most of the scattered light actually reaches the perovskite photoactive area. The use of 3D printed sample holders of custom size also ensures that no additional scattered light reaches the perovskite component (i.e., by circumventing the BiVO$_4$ active area).

Examples of typical cyclic voltammetry scans and long term stability tests of the 0.25 cm$^2$ photoelectrochemical tandems are found in Figure 5c,d, respectively. The data for all tandems can be found in Figures S22–S25 of the Supporting Information.

As seen from Figure 5c, using the BiVO$_4$TiCo photoanode enables the construction of a bias-free water splitting PEC tandem with an inverse-structure perovskite-based photocathode. Four of the five 0.25 cm$^2$ devices investigated present an average photocurrent density of $0.39 \pm 0.15$ mA cm$^{-2}$ at zero applied potential bias (see Figure S22 of the Supporting Information). This corresponds to a bias-free photon-to-current efficiency of $0.49 \pm 0.18\%$, which lies close to the maximum achieved at around 0.2 V (see the calculated applied bias photon-to-current conversion efficiency (ABPE) curve from Figure S13 in the Supporting Information). The onset potential for water splitting lies around $-0.6$ V, the most negative reported for photoelectrochemical devices, which means that

![Figure 5.](image-url)
the tandems can provide enough driving force for simultaneous solar fuel and electricity production. The tandem devices possess an excellent stability of up to 20 h (see a 1 cm² device in Figure S23a of the Supporting Information), with an average faradaic yield toward hydrogen production of 71.4 ± 13.0% after 12 h. The slower increase in the FY value may be caused by the larger volume of the 3D-printed PEC cell and the textured nature of its polylactic acid (PLA) walls, which favors gas leakage and the entrapment of bubbles for the smaller samples even more. Accordingly, the solar-to-hydrogen conversion efficiency of the devices amounts to 0.35 ± 0.14%.

The BiVO₄ light filtering and scattering is responsible for a lower perovskite photocathode response of −1.73 mA cm⁻² at 0 V versus RHE, as exemplified in Figure 5a (green curves). This shifts the intersect between the perovskite and BiVO₄/TiCo photosignals (i.e., the ideal bias-free photocurrent) from 1.13 to 0.85 mA cm⁻². Assuming ideal conditions (100% FY, no ohmic or optical losses), the bias-free 0.85 mA cm⁻² would correspond to a STH efficiency of 1.05%.

The 1 cm² devices (Figure S23, Supporting Information) reached a similar bias-free photocurrent density of 0.43 ± 0.08 mA cm⁻², corresponding to a photon-to-current efficiency of 0.53 ± 0.10% and an STH efficiency of 0.37 ± 0.08%. Three out of the four investigated devices delivered an average hydrogen faradaic yield of 69.9 ± 5.2% within 12 h.

The excellent stability of the tandem devices also gives a hint toward the degradation pathways. Since the back side of the electrodes is completely sealed by epoxy resin in the back-to-back configuration, this suggests that water is infiltrating the encapsulated devices from the glass/epoxy interface. Another explanation for the improved stability may be found in the lower photocurrent density, which allows the gases to diffuse away from the electrode surface without vigorous bubbling. The gas bubble formation may also affect the stability of the Field’s metal/epoxy interface, as observed from a decreased stability when purging the measuring cell with the perovskite photocathodes immersed in solution.

2.5. Scalability Studies

In order to test the scalability of the PEC tandems and corresponding photoelectrodes beyond the commonly reported sizes of up to 1 cm²,[21,48,65,107] larger devices of 4 and 10 cm² were also prepared using the same deposition techniques (see the Supporting Information for particular fabrication details). All larger devices were characterized within the 3D-printed PEC cell, in either a 2- or 3-electrode configuration. A comparison of typical photocurrents is found in Figure 3 for the PV and PEC devices of various sizes. The raw data recorded for the perovskite-based photocathodes, BiVO₄/TiCo photoanodes, and PEC tandems can be found in Figures S16–S18, S19–S21, and S22–S25 (Supporting Information), respectively.

The photocurrent response of the perovskite photocathodes follows a decreasing trend similar to the one observed for the PV components in respect to their size (Figure 3a,b). As with the efficiency of the photovoltaic cells (Figure 2), the absolute value of the photocathode current density at 0 V versus RHE decreases exponentially with the photoactive area (Figure S11a, Supporting Information), reaching only −2.68 ± 0.80 mA cm⁻² for the 10 cm² devices (22% of the 0.25 cm² photocathodes’ signal). The photocathodes also show a lower fill factor than the PV cells, due to a combination of the series resistance with the solution resistance and the electrochemical overpotential for H₂ evolution.

While the photocurrent density of the BiVO₄/TiCo electrodes is lower than that of their perovskite counterparts in the 3-electrode configuration, the former appear to scale up better, with values stabilizing around 1.2–1.4 mA cm⁻² at 1.23 V versus RHE for the backside irradiated photoanodes (see Figure 3c and Figure S11b, Supporting Information). The finding is consistent to previous reports,[107,111] which indicate that higher photocurrent densities are obtained when irradiating a small area. This observation may be explained by a higher overall homogeneity for larger devices (see higher error bar for the 0.25 cm² photoanodes; Figure S11b, Supporting Information), as well as by lower kinetic limitations through ionic diffusion to the electrode surface.[112] The influence of the mass transport limitations on the shape of the cyclic voltammograms and absolute photocurrents are clearly visible from Figure S14 of the Supporting Information, which compares the voltammetric traces recorded in a stagnant solution to the ones under stirring. Accordingly, we report all PEC characterization of the individual BiVO₄/TiCo photoanodes under stirring.

The perovskite-BiVO₄/TiCo PEC tandems also demonstrated a remarkable scalability, as shown by the roughly similar bias-free photocurrents of 0.2–0.5 mA cm⁻² plotted in Figure 3d. However, a combination of greater series resistance and mass transport limitations have an increasing impact especially for the 10 cm² devices, which present a lower bias-free photocurrent of 0.23 ± 0.10 mA cm⁻² (Figure 3d and Figure S11c, Supporting Information) and a current peak around 0.6 V (Figure 3d and Figure S25, Supporting Information). While the BiVO₄ performance commonly depends on the irradiated side, the back-to-back tandems with front-side irradiated BiVO₄/TiCo still present similar photocurrents to the ones of the characterized photoanodes (~0.8 mA cm⁻² at 0.9 V applied bias, a close estimate of 1.23 V versus RHE). Nevertheless, the low transparency of Perspex acrylic glass at wavelengths below roughly 380 nm (see Figure S10 in the Supporting Information) may also explain the lower photocurrents.

Due to a higher probability of defects and pin-holes in the perovskite deposition, Field’s metal film, or epoxy encapsulation, the larger area devices presented a lower stability in use, which only reached up to 6 and 14 h for the 4 and 10 cm² tandems, respectively (see Figures S24 and S25 in the Supporting Information). Nevertheless, the results obtained for our handmade devices remain very promising, showing potential for further stability improvements in an automated fabrication process.

2.6. External Quantum Efficiency (EQE) Spectra

To gain a deeper insight on the processes influencing the light conversion to fuel, EQE spectra are also recorded for both photovoltaic and photoelectrocatalytic components
with the averaged results given in Figure 6. The spectra are recorded at applied biases of 0 V for the perovskite PV cells, 0 V versus RHE for the perovskite photocathodes, 1.23 V versus RHE for the BiVO₄/TiCo photoanodes and 0 V for the perovskite-BiVO₄/TiCo PEC tandems. As expected, the average EQE spectrum of the six 0.25 cm² BiVO₄/TiCo electrodes plateaus around 30% at wavelengths below 500 nm, whereas the perovskite PV cells harvest light with an efficiency around 80% over the entire visible range (the upward drift in the lower wavelength region is due to instrumental limitations). The integrated photocurrents obtained from the EQE spectra amount to 1.66 ± 0.44 mA cm⁻² at 1.23 V versus RHE and ~18.8 ± 1.3 mA cm⁻² at short circuit conditions, respectively, which are consistent to the IV data obtained under 1 sun irradiation.

Surprisingly, the EQE spectrum of the perovskite-based photocathodes was similar to that of the underlying solar cells. Its integration results in an ideal $J_{SC}$ of ~19.3 ± 1.9 mA cm⁻² at 0 V versus RHE, which differs significantly from the ~12.1 ± 0.3 mA cm⁻² recorded by cyclic voltammetry. This indicates that the maximal performance of the photocathodes is limited by kinetic effects, namely the fast depletion of protons and the vigorous formation of bubbles in the vicinity of the electrode surface, which decreases the active electrochemical area and inhibits a fast diffusion of protons from within the solution. The finding is consistent to reports of similar limitations in BiVO₄ photoanodes and water splitting systems. The mass transport limitation is also observable when recording the cyclic voltammograms in a 0.1 M potassium borate buffer solution (KBi, pH 8.50) without the 0.1 M K₂SO₄ electrolyte salt, as shown in Figure S15 of the Supporting Information. This observation also contributes toward explaining why the performance of various wired perovskite-based systems is similar regardless of their photovoltaic efficiency, since the concentration and nature of the electrolyte solution actually plays the major limiting role.

### 2.7. Comparison with State-of-the-Art and Outlook

Overall, these findings reveal the scalability of the perovskite-BiVO₄/TiCo photoelectrochemical tandem devices. While the STH efficiency of around 0.3% is lower than the 2–6% reported for PV and PEC multijunction systems (i.e., overall >3 photoabsorbers[21,22,57,113]) its value compares favorably to state-of-the-art devices containing oxide-,[45,115] or single-junction silicon-photocathodes.[47,48,50,116] Moreover, the stability reaching 20 h and scalability of up to 10 cm² presented in this work counts among the highest reported values, even surpassing most PV-PEC and wired systems (see Table 2 for a detailed literature comparison), which emphasizes the relevance of our findings as an early step toward commercial implementation.

From this point of view, a lower bias-free photocurrent can even prove beneficial for commercial systems by preventing bubble formation.[117] In this case, the dissolved gas could be removed from the PEC cell and separated in a recirculating system, which can be powered by the additional driving force of up to 0.6 V of the tandems. To mitigate the effect of device degradation and resistive losses on the overall performance of such assemblies, a tiled design consisting of smaller wireless tandems could be constructed, where any faulty device could be simply replaced. For larger tandem devices, the lateral resistive losses caused by the FTO sheets may be again avoided by introducing metal fingers.[120] In those cases, the total footprint area of the module would also need to be taken into account.[37,86] Alternatively, a low temperature HTL[121–123] and BiVO₄[124,125] deposition on flexible, thin-film substrates[126–128] would provide further commercial advantages, by obtaining lighter devices which may be mass-produced by scalable roll-to-roll techniques.[86,89] Concerning the device encasing, modular designs similar to the one presented here could be easily scaled-up.

Beyond the practical side, the facile 3D-printed design could also enable widespread research on solar fuels in developing countries, since the raw materials (PLA, Blu Tack, acrylic glass) cost only a fraction of the price of highly specialized commercial PEC cells. Accordingly, a few national 3D-printing workshops could provide small- and medium-scale reactors for local laboratories, bringing this fundamental science closer to the communities most in need.

### 3. Conclusions

In conclusion, we have investigated the potential of using perovskite-BiVO₄ photoelectrochemical tandems for bias-free solar water splitting. By employing the CsFAMA triple cation mixed halide perovskite as the photoabsorber and NiOₓ as the hole selective layer, substantial improvements have been achieved in the performance (~12.1 ± 0.3 mA cm⁻² at 0 V versus RHE) and stability (up to 7 h) of 0.25 cm² photocathodes, with the corresponding PV devices reaching an efficiency of 13.0 ± 1.2%. The 1 cm² back-to-back PEC tandems presented a remarkable stability of up to 20 h for the bias-free water splitting, with a corresponding solar-to-hydrogen conversion efficiency of 0.37 ± 0.08%. Their very negative onset bias of around ~0.6 V enables simultaneous solar fuel and electricity production, providing also flexibility for either operation mode.
Table 2. Comparison between our results and several state-of-the-art PEC, PV–PEC, and PV-electrolyzer water splitting devices. Data is reported under 1 sun simulated irradiation (100 mW cm$^{-2}$, AM 1.5G), for bias-free systems only.

| Tandems | $J_{SC}$ [mA cm$^{-2}$] | FY [%] | STH [%] | Stability [h] | Area [cm$^2$] | Electrolyte solution | Reference |
|---------|------------------------|--------|---------|----------------|-------------|----------------------|-----------|
| PEC     |                        |        |         |                |             |                      |           |
| PVK/FM/[Pt–BiVO$_4$/TiCo] | 0.39 ± 0.15 | 71.4 ± 13.0$^{a}$ | 0.35 ± 0.14 | 18 | 0.25 | 0.1 M KBI, K$_2$SO$_4$ (pH 8.50) | This work |
| PVK/FM/[Pt–BiVO$_4$/TiCo] | 0.43 ± 0.08 | 69.9 ± 5.2$^{b}$ | 0.37 ± 0.08 | 20 | 1 | 0.1 M KBI, K$_2$SO$_4$ (pH 8.50) | This work |
| PVK/FM/[Pt–BiVO$_4$/TiCo] | 0.43 ± 0.04 | 46.2 ± 4.5$^{c}$ | 0.25 ± 0.03 | 6 | 4 | 0.1 M KBI, K$_2$SO$_4$ (pH 8.50) | This work |
| PVK/FM/[Pt–BiVO$_4$/TiCo] | 0.23 ± 0.10 | 52.2 ± 5.3$^{d}$ | 0.15 ± 0.06 | 14 | 10 | 0.1 M KBI, K$_2$SO$_4$ (pH 8.50) | This work |
| Au(CuO)[Al–ZnO]/TiO$_2$/RuO$_{2–x}$ | 0.318 | – | <0.5 | 1.4 | 0.283 | 0.5 M Na$_2$SO$_4$, 0.09 M KH$_2$PO$_4$ | [45] |
| BiVO$_4$/Co-P | 0.01 ± K$_3$HPO$_4$ (pH 6) | | | | | | |
| pSi[TiNi–BiVO$_4$/TiCo] | 0.045 ± 0.018 | 91 ± 5.3 | 0.05 | 24 | 0.5–4 | 0.1 M KBI, K$_2$SO$_4$ (pH 9.2) | [47] |
| p-Si(TiO$_2$)[Fe$_2$O$_3$, csh-NW] | =0.15 | 100$^{f}$ | =0.18 | – | – | NaPi, 0.25 M Na$_2$SO$_4$ (pH 7.1) | [50] |
| TiO$_2$/TiO$_2$ cs-NT | | | | | | | |
| p-Si nanoarray[Pt–Mo:BiVO$_4$/Co-Pi] | 0.46 | 100$^{f}$ | 0.57 | 3.5 | 0.28 | 0.1 M KPi (pH 5.5) | [48] |
| PV–PEC | | | | | | | |
| DSC–WO$_3$ | 2.52 | =100 | 3.10 | =9 | 0.2 | 1 M HClO$_4$ (pH 0) | [28] |
| DSSC–WO$_3$/W:BiVO$_4$/FeOOH/ NIOOH | 4.7 | =100 | 5.7 | 12 | =0.3 | 0.1 M NaPi (pH 6.9) | [32] |
| (1-jn a-Si)–W:BiVO$_4$/Co-Pi | 3 | 100$^{f}$ | 3.6 | 1 | 1 | 0.1 M KPi (pH =7.3) | [21] |
| PVK–Mo:BiVO$_4$/Co-Ci (wireless) | =3.5 (–) | =100 | 4.3 (3) | 12 | 0.42 (1.3) | 0.1 M KHCO$_3$ (pH =7) | [61] |
| PVK–Mo:BiVO$_4$/Fe(Ni)OOH | 5.01 | =92 | 6.2 | 10 | 0.25 | 0.5 M KH$_2$PO$_4$ (pH =7) | [65] |
| Multi-jn PV–PEC | | | | | | | |
| (2-jn a-Si)–W:BiVO$_4$/Co-Pi | 4 | 100$^{f}$ | 4.9 | 1 | 0.38 | 0.1 M KPi (pH =7.3) | [21] |
| (a-Si:H/nc-Si:H)–W:BiVO$_4$/Co-Pi | 4.22 | 100$^{f}$ | 5.2 | 1 | 1 | 0.1 M KPi (pH =7) | [22] |
| Multi-jn PV–electrolyzer | | | | | | | |
| a-Si:H/a-Si:H/ZnO/Al[Pt–RuO$_2$] | 3 | 100$^{f}$ | 6.8 | 50 | 0.5 | 0.1 M H$_2$SO$_4$ | [39] |
| (2-seral PVK)–NiFe LDH | 10 | 100 | 12.3 | 4 | 0.318 | 1 M NaOH | [53] |
| (2-seral PVK)–CoP, NiFe LDH | 10.35 | 100 | 12.7 | 16 | 0.32 | 0.5 M H$_2$SO$_4$ | 1 M KOH | [55] |
| Co3jn–a-Si/ NiMoZn wireless | – | =100 | 2.5$^{d}$ | 32 | 2 | 1 M KBI (pH 9.2) | [113] |
| (3-seral PVK)–CP[N–CNT: NiO/C$_2$O$_4$] | =5 | 100 | 6.2 | 0.5 | 0.12 | 0.1 M KOH (pH 13) | [57] |

$^{a}$FY after 12 h; $^{b}$FY after 1 h; $^{c}$assumed value; $^{d}$electrolyte: 0.5 M KBI, 1.5 M KNO$_3$.

Due to significant progress in production techniques, an excellent reproducibility and reliability have been obtained for both single pixel solar cells and photoelectrodes. These advantages enabled a further comprehensive study on the device up-scaling from 0.25 to 10 cm$^2$, which revealed valuable insights into the resistive and kinetic limitations affecting both photovoltaics and photoelectrocatalysis. The excellent scalability of our perovskite and BiVO$_4$ electrodes allowed us to obtain a comparable activity for 10 cm$^2$ PEC tandems, which are to the best of our knowledge the largest reported devices of their kind. To characterize the performance of the larger bias-free PEC tandems, an affordable 3D-printed measuring cell was also designed, which may be easily adjusted for laboratory research or consumer-based applications.

Our results reveal that encapsulated perovskite photocathodes and the corresponding photoelectrochemical tandems can compete in terms of stability and scalability with more established PV–PEC or PV-electrolyzer wired systems. More generally, this study indicates that both perovskite-based photovoltaic and photoelectrocatalytic systems have potential for large scale applications, as long as low-cost designs and the series resistance of the substrates are taken into account.

4. Experimental Section

Preparation of Perovskite Solution: A 1.0 M solution of the FAMA$_{22}$Pb$_{11.2}$Br$_{66}$ perovskite precursor was made by dissolving methylammonium bromide (MABr, 24.3 mg), lead bromide (PbBr$_2$, 80.0 mg), formamidinium iodide (FAI, 172.0 mg), and lead iodide (PbI$_2$, 507.1 mg) in a 1000 µL mixture consisting of N,N-dimethylformamide (DMF, 510 µL), dimethyl sulfoxide (DMSO, 340 µL), and 1-methyl-2-pyrrolidone (NMP, 150 µL). A 1.5 M stock solution of cesium salt was prepared by dissolving CsI (194.9 mg) in 500 µL DMSO. 48 µL of this cesium solution was added to the 1000 µL FAMA$_{22}$Pb$_{11.2}$Br$_{66}$ solution, to give the final precursor solution.

Inverse-Structure Perovskite Cells: The inverse-structure perovskite cells were prepared using a modified procedure based on previous reports.$^{[75,78,83,90]}$ The FTO layer was selectively etched away with the device up-scaling from 0.25 to 10 cm$^2$, which revealed advantages enabled a further comprehensive study on their kind. To characterize the performance of the larger bias-free PEC tandems, an affordable 3D-printed measuring cell was also designed, which may be easily adjusted for laboratory research or consumer-based applications.
334 µL ethylenediamine (1.0 M in the final solution).[90] The solution was filtered twice through a 0.20 µm polytetrafluoroethylene (PTFE) Millipore Millex-GF filter and spin-coated on the FTO glass slides at 5000 RPM for 45 s. The samples were annealed in two steps, at 373 K for 30 min, and at 573 K for 60 min, to give the NiOx HTL. Full details of the NiOx preparation can be found in ref. [90] by Hoye et al.

The hot samples were next transferred inside the glovebox for the perovskite and electron transport layer (ETL) deposition. A two-step spin-coating program was employed for the perovskite layer, with an initial spreading at 1000 RPM for 10 s, followed by spinning at 6000 RPM for 35 s. For the 8- and 0.25 cm² devices, a smooth perovskite film was achieved by dropping 75 µL chloroform onto the spinning sample 7 s before the end of the program, followed by tempering at 373 K for 30–70 min.[78,79,85,90] A PCBM (99%, Solenne BV) solution in chlorobenzene (CB, 35 mg mL⁻¹) was stirred at 343 K for 30 min and filtered through a 0.2 µm PTFE filter before use. The PCBM solution was spin-coated at 3000 RPM for 45 s to form the ETL. 35 µL of a PEIE (5.8 µL solution in isopropanol (IPA, 1.5 mL) was next spin-coated under ambient conditions (3000 RPM, 30 s), before returning the samples under inert atmosphere for storage. Lastly, a 100 nm silver layer was evaporated to form the electrical contacts of the solar cells. The deposited layers are visible from the magnified cross-section of a 0.25 cm² inverse-architecture device in Figure 1a and from its schematic depiction in Figure 1b. Specific details regarding the preparation of larger devices are given in the Supporting Information.

Field’s Metal-Epoxy Encapsulation: To prevent degradation of the perovskite layer by the aqueous electrolyte, a Field’s metal-epoxy encapsulation was employed.[71,72] In this case, 0.5–1 mm thick protective foils were obtained by melting the bulk alloy onto a clean hotplate at 363 K and spreading the liquid using common glass slides. After cooling below 323 K, the large area foils could be peeled off the hotplate, and cut into the desired dimensions. A small piece of the metal foil was first melted on top of the silver contact, by applying a 2.4 A current for 30 s to a Peltier thermoelectric module, and then solidified by applying −2.4 A for 30 s (2-step chronopotentiometric sequence on a IviumStat instrument). After sealing the edges with Araldite 5-Minute Rapid two component epoxy, the photoelectrodes were stirred in a K₂PtCl₆ (21.4 mg, 51.6 mmol) aqueous solution (5.16 µL polytetrafluoroethylene (PTFE) Millipore Millex-FG filter and spin-coated on the FTO glass slides at 5000 RPM for 45 s. The samples were annealed in two steps, at 373 K for 30 min, and at 573 K for 60 min, to give the NiOx HTL. Full details of the NiOx preparation can be found in ref. [90] by Hoye et al.

The hot samples were next transferred inside the glovebox for the perovskite and electron transport layer (ETL) deposition. A two-step spin-coating program was employed for the perovskite layer, with an initial spreading at 1000 RPM for 10 s, followed by spinning at 6000 RPM for 35 s. For the 8- and 0.25 cm² devices, a smooth perovskite film was achieved by dropping 75 µL chloroform onto the spinning sample 7 s before the end of the program, followed by tempering at 373 K for 30–70 min.[78,79,85,90] A PCBM (99%, Solenne BV) solution in chlorobenzene (CB, 35 mg mL⁻¹) was stirred at 343 K for 30 min and filtered through a 0.2 µm PTFE filter before use. The PCBM solution was spin-coated at 3000 RPM for 45 s to form the ETL. 35 µL of a PEIE (5.8 µL solution in isopropanol (IPA, 1.5 mL) was next spin-coated under ambient conditions (3000 RPM, 30 s), before returning the samples under inert atmosphere for storage. Lastly, a 100 nm silver layer was evaporated to form the electrical contacts of the solar cells. The deposited layers are visible from the magnified cross-section of a 0.25 cm² inverse-architecture device in Figure 1a and from its schematic depiction in Figure 1b. Specific details regarding the preparation of larger devices are given in the Supporting Information.

The simulated solar irradiation was achieved using a Sun 2000 Solar Simulator (Abet Technologies), which was calibrated to 100 mW cm⁻² (1 sun) using a silicon reference solar cell RS-OD4, and by taking a mismatch factor of 1/1.12 into account. The 8-pixel and 0.25 cm² devices were investigated under inert atmosphere using gas-tight sample holders, whereas the I–V curves of the larger devices were recorded in their encapsulated form, using the Field’s metal as an electrical contact. All devices were characterized without additional masking. The applied potential was varied by a Keithley 2635 source meter, which also recorded the generated current. Reverse and forward I–V curves were determined separately between −0.1 and 1.2 V, with a scan rate of 100 mV s⁻¹. The EQE of the working devices was determined using a Newport Oriel 66881 setup, an Oriel 74000 Cornerstone monochromator, the Keithley 2635 source meter, a Keithley 2000 multimeter for the Thorlabs SM05PD1A reference photodiodes, a LIA-MV-200-H lock-in-amplifier and a Thorlabs PDA200C photodiode amplifier. The spectra were recorded between 375 and 900 nm, with a 5 nm step size, a 50 ms delay and at 0 V bias.

Characterization: Photoelectrochemical Devices: To investigate the operation of the 0.25–4 cm² photoelectrodes, a Newport Oriel 67005 solar light simulator was employed with an Air Mass 1.5 Global (AM 1.5G) solar filter. A LOT-QD LS0816-H large area solar simulator was instead used for the 10 cm² devices. The light intensity was calibrated to 100 mW cm⁻² (1 sun) using a Newport 1916-R optical power meter. Electrochemical measurements (e.g., cyclic voltammetry, chronoamperometry) were conducted on Ivium CompactStat.e potentiostats, with a sample as the working electrode, a Ag/AgCl/KCl(1 M) (Bas) reference electrode and a platinum mesh counter electrode. The electrodes were submerged in a 0.1 M K₂SO₄ solution of pH 8.50, which contained 0.1 µM K₃[47][48]VO₃ as supporting electrolyte. In the 3-electrode configuration, the anodic and cathodic compartments were separated by Selenium (AGC Engineering) or Nafion ion exchange membranes for the 0.25 and 1 cm² photoelectrodes, respectively. Due to mass transport limitations, the solution was only stirred in case of the photoanodes, and left unstirred otherwise. The cyclic voltammetry measurements were conducted between −0.2 and 1.2 V versus RHE for the photocathodes, and between 0.1 and 1.4 V versus RHE for the photoanodes, at a scan rate of 10 mV s⁻¹. The potential versus RHE was determined using Equation (1) at a temperature of 298 K[71]

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \log \frac{I}{0.197}
\]

Similar conditions were also employed for the tandem devices, where the scans were conducted in a two electrode configuration, between −0.6 and 1.4 V. To allow ionic movement, a narrow opening was made below the sample instead of using a gasket, which prevented the current from leaking through the sample (see Figure 7b). The front BiVO₄ active area of the PEC tandem was additionally surrounded by opaque adhesive tape, to prevent any unfiltered light from reaching the perovskite photocathode (see Figure 7b,c).

The EQE was determined using a LOT MSH-300 monochromator, a Thorlabs PM100D power meter with a Thorlabs S302C thermal power sensor, and an IviumStat potentiostat. The wavelength \(\lambda\) (full width at half maximum of 15 nm) was typically varied between 300 and 800 nm in 25 nm steps every 30 s. The resulting EQE was determined using Equation (2), where \(h\) is the Planck constant, \(c\) is the speed of light, \(J\) is the photocurrent density, \(e\) is the electron charge, and \(P\) is the wavelength-dependent light intensity flux (or irradiance)[129]

\[
\text{EQE} = \frac{h \nu}{e P}\left(\frac{\lambda}{\lambda_0}\right)^2
\]

A Shimadzu GC-2010 Plus gas chromatograph (GC) was employed for \(\text{H}_2\) evolution measurements. The gas-tight electrochemical cells were purged with nitrogen containing 2% methane as an internal standard. The amount of \(\text{H}_2\) was determined by manually injecting 100 µL from the PEC cells’ headspace using gas-tight sample syringes. A NeoFox-GT fluorometer and Fospor-R fluorescence oxygen sensor probes from Ocean Optics.
Figure 7. Various representations of the modular 3D-printed PEC cell. a) 3D rendering of the cell’s components, revealing the removable sample holder (depicted in green), which can slot in along the exchangeable side rails (yellow). b) Back side view of the PEC cell under use for tandem characterization, with the Field’s metal–Pt nanoparticle interface exposed to the electrolyte solution. c) Front side view of the anodic compartment, showing the BiVO4|TiCo photoanode of a 4 cm² tandem under 1 sun irradiation.

were used to determine the amount of produced O₂. The Faradaic yield (FY) of the photoelectrodes was determined by comparing the amount of evolved gas (nmax) to the total charge passed (Q), as shown in Equation (3). The equivalent charge used per gas molecule amounts to z = 2 for the H₂ generation, and to z = 4 for the O₂ evolution, while F is the Faraday constant.

\[ FY = \frac{n_{\text{max}}F}{Q} \]  

(3)

The total charge was obtained by integration of the recorded current (I) over the duration (t) of chronoamperometry. This is illustrated in Equation (4), where \( t_0 \) and \( t_f \) represent the beginning and end-points of the measurement.

\[ Q = \int_{t_0}^{t_f} I(t)\,dt \]  

(4)

Henry’s law was employed to compensate for the small effect of dissolved gases,[130] although it is worth noting that the concentration in solution of an evolving gas is probably higher than its equilibrium level.

In order to characterize the performance of tandem devices, the ABPE was additionally calculated using Equation (5), where \( U_{\text{bias}} \) is the applied bias, and \( P_{\text{total}} \) is the total recorded light intensity flux (100 mW cm⁻²) [47].

\[ \text{ABPE} = \frac{(1.23V - U_{\text{bias}})}{P_{\text{total}}} \]  

(5)

Similarly, the AB-STH efficiency can be also calculated as the product of ABPE and FY at a given applied bias (in our case, \( U_{\text{bias}} = 0 \) V).

**Characterization:** Statistics: The reported values were averaged from the data of at least three PV or PEC devices unless otherwise noted. The given errors correspond to the calculated standard deviation. Examples of typical data are taken from stable devices which follow the general trend, having around or above average performance.

**Characterization:** Materials: An FEI SFE XL30 scanning electron microscope (SEM) was employed to investigate the surface and cross-plane topology of the devices. Energy-dispersive X-ray (EDX) spectra were recorded using an Oxford Instruments X-Max silicon drift detector to confirm the elemental composition of various samples. The formation of the polycrystalline perovskite phase was confirmed by XRD measurements, which were conducted on a Panalytical Empyrean X-ray diffractometer. The spectra were recorded using Cu Kα radiation, in a θ–2θ configuration. The angle of the incident beam was varied between 10° and 90° with a step size of 0.008. The thin film samples were rotated at a speed of 30 RPM.

**3D-Printed PEC Cell:** Common glass PEC H-cells with membrane separation were employed for the characterization of 0.25 and 1 cm² photoelectrodes (see ref. [75] and Video S1 in the Supporting Information). A 3D-printed cell was developed for the larger electrodes and all back-to-back tandems, to maintain a constant sample position and ensure a certain separation between the cathodic and anodic compartments. In comparison to other recent models which have employed 3D-printing for electrodes,[131–133] electrochemical flow reactors,[134–137] or biased photoelectrodes,[138] this represents the first reported 3D-printed PEC cell design for bias-free tandems.

While existing (mainly glass) PEC cell models are often made to accommodate samples of fixed dimensions, our modular design provides a facile way to measure samples of different sizes in various configurations (i.e., 3-electrode, monolithic, wired, or even colloidal systems). For this purpose, replaceable sample holders are employed which can slide along the side rails. The holders cover the nonactive area of the devices, to prevent additional unfiltered light from reaching the back-side of the tandems. The working principle is illustrated by the 3D model in Figure 7a, where the thin slides supporting the sample are highlighted in green and the lateral rails are depicted in yellow. Photographs of the 3D-printed PEC cell during use can also be found in Figure 7b,c, revealing the back- and front-side of a 4 cm² tandem, respectively.

In order to obtain a lightweight, inexpensive, and easily adjustable PEC cell, the 3D components were designed in SolidWorks, and created from PLA using an Ultimaker 2 Extended+ 3D printer. Sketches of the main components and their assembly are given in Figure S1 of the Supporting Information. The PEC cell’s windows consisted of 3 mm thick Perspex acrylic glass, whereas Blu Tack reusable adhesive was used as a sealant.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author. The raw data that support the findings of this study are available from the University of Cambridge data repository, https://doi.org/10.17863/CAM.24084.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

BiVO₄ photoanodes, PEC tandems, perovskite photocathodes, scalability, water splitting

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