Bifunctional perovskite-BiVO$_4$ tandem devices for uninterrupted solar and electrocatalytic water splitting cycles

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Abstract: Photoelectrochemical (PEC) fuel synthesis depends on the intermittent solar intensity of the diurnal cycle and ceases at night. Here, we describe an integrated device that does not only possess PEC water splitting functionality, but also operates as an electrolyzer in the nocturnal period to improve the overall capacity factor. The bifunctional system is based on an ‘artificial leaf’ tandem PEC architecture that contains an inverse-structure lead halide perovskite protected by a graphite epoxy/parylene-C coating (conferring 96 h stability of operation in water), and a porous BiVO$_4$ semiconductor. The light-absorbers are interfaced to a H$_2$ evolution catalyst (Pt) and a Co-based water oxidation catalyst, respectively, which can also be directly driven by electricity. Thus, the device can operate in PEC mode during irradiation and switch to an electricity-powered mode in the dark through bypassing of the semiconductor configuration. The bifunctional perovskite-BiVO$_4$ tandem provides a solar-to-hydrogen efficiency of 1.3% under simulated solar irradiation and an onset for water electrolysis at . The compact design and low cost of the proposed device may provide an advantage over other technologies for round-the-clock fuel production.
1. Introduction

Solar-driven water splitting to produce sustainable H\textsubscript{2} can be achieved through modular photovoltaic-electrochemical (PV-EC) and integrated photoelectrochemical (PEC) approaches\cite{1-4}. While PV-EC utilizes the external bias provided by solar cells to drive a separate electrolyzer module, PEC employs charges generated via photoexcitation of semiconducting materials to directly split water into its elements. There remains an open debate if PV-EC or PEC systems may be more efficient and economically viable in long-term development\cite{5, 6}. While PV-EC approaches benefit from the ability to utilize commercially available PV and electrolyzer units separately, these systems may still be limited by the cost and complexity of the individual components, wiring and reactors\cite{7, 8}. Despite their lower performance, integrated PEC designs provide the potential to produce fuel at lower costs, by operating under benign conditions and benefitting from improved reaction kinetics at elevated temperatures\cite{6, 8, 9}.

However, the arguments used in these analyzes commonly assume that the devices are only powered by sunlight. We propose that the economics and implementation of PV-EC and PEC systems can benefit from fuel production during diurnal and nocturnal cycles. Continuous operation can be achieved when the devices are light-driven when sunlight is available and can switch to water electrolysis, preferentially powered by renewable electricity, in the dark or at very low light intensities. While this approach can readily be envisioned for PV-EC, it does require adaptation of current PEC systems.

Here we present a bifunctional photoelectrochemical-electrochemical (PEC-EC) system based on a modified perovskite-BiVO\textsubscript{4} tandem device. The PEC-EC system can operate both in the presence and absence of sunlight and serves as a proof-of-concept prototype for uninterrupted fuel production (Figure 1). Under solar irradiation, a BiVO\textsubscript{4} photoanode and a
lead halide perovskite photocathode (abbreviated PVK) drive the catalysts for the overall water-splitting reaction.\textsuperscript{[10]} In the absence of sunlight, the device can also function as a water electrolyzer, where an external electrical bias can be applied directly to the water splitting catalysts. Thus, the PEC-EC system can uniquely operate as a compact PEC device during daytime, and switch to electrochemical (EC) water splitting via an external bias at night, addressing the limitations of both PV-EC (system complexity, loss of thermal energy from sunlight to enhance catalysis),\textsuperscript{[6-8]} and PEC (relies on the availability of daylight) approaches. Hence, the bifunctionality refers to the functions assumed by (photo)electrodes in its two modes of operation, namely PEC and EC mode. For this purpose, we developed two protocols to access the hydrogen and oxygen evolution catalysts (HEC and OEC, respectively) in EC mode, by wiring the protection layer of encapsulated perovskite photocathodes, and post-etching of BiVO\textsubscript{4} to deposit some OEC directly onto the fluorine doped tin oxide (FTO) substrate underneath the BiVO\textsubscript{4} (Figure 1a).

2. Results and Discussion
2.1. Perovskite (photo)cathodes
While the excellent light harvesting properties of lead halide perovskites have been extensively studied for photovoltaic applications,\textsuperscript{[11]} their moisture sensitivity has restricted their use for solar fuels production until recently.\textsuperscript{[12, 13]} In this work, we exploit the high photovoltage and photocurrent of perovskite devices by introducing improved strategies to significantly increase the moisture stability of perovskite-based photocathodes. A doped poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA)\textsuperscript{[14]} hole transport layer (HTL) was added to the perovskite device architecture to improve its intrinsic PV performance (Figure 1b).\textsuperscript{[15-18]} The open circuit voltage ($V_{oc}$) of the cesium formamidinium methylammonium (CsFAMA) triple cation perovskite PV increased from 1.00 ± 0.03 V to 1.07 ± 0.02 V upon addition of PTAA (Figure S1 and S2, Supporting Information).\textsuperscript{[10]} This improvement is due to a better alignment between
the work function of the intermediate PTAA HTL and the perovskite’s valence band, which allows for more efficient hole transfer from the perovskite light absorber to NiOx (Figure 1b).\cite{17-19} Energy-dispersive X-ray (EDX) spectra and elemental mapping of a perovskite PV cell with a PTAA layer confirmed the device architecture (Figure S3, Supporting Information).

The moisture sensitivity of metal halide perovskites requires their encapsulation for use in aqueous electrolyte solutions.\cite{12, 20} Previous strategies employed an eutectic alloy (In$_{51}$Bi$_{32.5}$Sn$_{16.5}$, Field’s metal, FM) encapsulation to reach stabilities up to 23 h for integrated perovskite photocathodes.\cite{10, 12, 21, 22} Metal alloys can be expensive and may suffer from degradation,\cite{22} whereas hydrophobic carbon-based materials such as graphite sheets show promise as alternative encapsulants for perovskite photoelectrodes.\cite{22-24} However, solid encapsulants do not ensure a homogeneous coverage and direct adhesion at the perovskite and catalyst interfaces, which may promote gradual moisture infiltration.\cite{21, 23, 25} Alternatively, commercial conductive polymers, inks or sealants commonly employ organic or aqueous solvents, which affect the perovskite device architecture. Here, we introduce graphite epoxy (GE) paste as a robust, metal-free perovskite encapsulant (abbreviated PVK|GE), which can be easily prepared by mixing graphite powder and epoxy in a 3:4 mass ratio and evenly spread onto perovskite devices,\cite{26} providing excellent adhesion for further catalyst or wire integration.

Hence, EC functionality for H$_2$ production can be readily achieved by attaching a Cu wire directly into the GE (Figure 1a), which enables applying an electrical bias. The (photo)cathode’s edges were covered with epoxy and a conformal parylene-C coating was deposited by chemical vapor deposition to ensure a complete seal of the PVK|GE device (see Supporting Information for details).\cite{27} A ∼5 nm Pt film was deposited by magnetron sputtering onto the exposed GE layer to function as a HEC (abbreviated PVK|GE|Pt).

The performance of the (photo)cathode was characterized in a potassium borate (KBi, 0.1 M, pH 8.5) solution with K$_2$SO$_4$ (0.1 M) under N$_2$ at room temperature in a three-electrode
setup (Ag/AgCl reference, Pt counter electrode), using AM 1.5G (100 mW cm\(^{-2}\), 1 Sun) irradiation (see Supporting Information for details). A cyclic voltammetry (CV) scan in PEC and EC mode showed a respective onset of approximately +1.0 V vs. RHE (highest among reported PVK photocathodes\(^{[10, 25, 28]}\)) and −0.25 V vs. RHE for H\(_2\) evolution (Figure 2a,b). To demonstrate the ability to switch between PEC and EC mode, we performed chronoamperometry (CA) at \(E_{\text{app}} = 0 \text{ V vs. RHE}\) under light irradiation and −0.7 V vs. RHE in dark, respectively. \(E_{\text{app}} = −0.7 \text{ V}\) was chosen for EC mode to emulate the applied bias provided by the perovskite element, i.e. to mimic the actual photocathode operating conditions. During the 2 h PEC-EC cycles (1 h light on / 1 h light off), currents of approximately −15 mA cm\(^{-2}\) and −7 mA cm\(^{-2}\) were achieved for PEC and EC, respectively. A total of 2.0 ± 0.3 mmol H\(_2\) were produced over five consecutive two-hour PEC-EC cycles, with cumulative H\(_2\) faradaic yield (FY) of 96 ± 6 % for PEC and EC mode (Figure 2c, Figure S4 and S5, Supporting Information).

We also compared the assembled PVK|GE|Pt (photo)cathode with previously reported FM-encapsulated electrodes.\(^{[10]}\) PEC and EC currents of PVK|FM|Pt degraded faster compared to PVK|GE|Pt (Figures S6-S8, Supporting Information). For example, the EC H\(_2\) evolution current decreased by 70% over 12 h for PVK|FM|Pt compared to only 20% for PVK|GE|Pt (Figure S8, Supporting Information). A conformal parylene-C coating (∼5 \(\mu\)m) further improved the encapsulation of PVK|GE|Pt by sealing all exposed pinholes,\(^{[29]}\) with a (photo)cathode operating for over 40 h of solar irradiation, (Figure S9 and S10, Supporting Information). A diurnal cycle was simulated by testing a device in 24 h PEC-EC cycles as shown in Figure 2d. The PVK|GE|Pt (photo)cathode showed good long-term stability for over 96 h under PEC-EC operation, which sets a benchmark for PVK-based photoelectrodes\(^{[10, 12, 23, 25, 28]}\). The choice of protection layers provides a major improvement in (photo)current stability over previously used encapsulants, as they are less prone to chemical corrosion. Hence,
this work provides an advance in terms of encapsulation strategies, which can be observed from a longer device operation compared to many state-of-the-art photocathodes\textsuperscript{[30-32]} (see Table S1, Supporting Information). This is particularly noteworthy, taking the moisture sensitivity of lead halide perovskites into account.

The perovskite light absorber displayed no visible moisture degradation during the long-term experiment (see Figure S11, Supporting Information). CVs performed after 0, 24 and 48 h revealed that the photocathodes maintained an early onset potential for H\textsubscript{2} evolution and low dark currents even after long-term operation (Figure S12, Supporting Information). This indicates that no interfacial degradation occurs within the layered perovskite architecture over the first 48 h, which is consistent with the stability reports of perovskite photovoltaic devices.\textsuperscript{[33]} Therefore, the decrease in photocurrent from Figure 2d is likely due to the slow decay of the platinum electrocatalyst (Figure S8, Supporting Information), combined with a later internal device degradation.\textsuperscript{[34]} This decay may be associated with nano-cracks forming on the GE|Pt surface, as revealed by SEM and EDX data in Figure S13 and S14, Supporting Information. All graphite epoxy encapsulated (photo)cathodes were stable for at least 10 h showing a similar behavior, which indicates a significant improvement in reliability over previous reports, where one third of all metal-encapsulated photocathodes degraded within 4 h (see examples and post-test CV characterization in Figure S4, and S15, Supporting Information).\textsuperscript{[10, 21, 35]} The improved long-term stability, reliability and performance of the (photo)cathode are due to the hydrophobic nature of the PTAA HTL,\textsuperscript{[14]} GE encapsulant and conformal parylene-C coating,\textsuperscript{[27]} which inhibit moisture infiltration.\textsuperscript{[23, 36, 37]} This increased (photo)cathode stability also emphasizes the benefits of introducing graphite epoxy as a robust, earth-abundant encapsulant, which favors scalable applications by decreasing material costs 37 times over FM encapsulated photocathodes (Table S1, Supporting Information).
2.2. BiVO\(_4\) (photo)anodes

Nanostructured BiVO\(_4\) photoanodes were chosen due to their known high photocurrent, early onset potential, long-term stability and compatibility for water oxidation under neutral pH conditions, which stand out among oxide-based photoanodes.\[^{38-40}\] Unlike PVK|GE|Pt, where the external bias can be applied to the catalysts through wiring directly to the conductive encapsulant, EC functionality was introduced in BiVO\(_4\) by partially exposing the underlying FTO-coated glass substrate through post-etching. This procedure allows the deposition of some OEC on the FTO for EC water oxidation under applied bias (Figure 1a).

BiVO\(_4\) was prepared via BiOI, which was electrodeposited onto FTO and subsequently annealed in the presence of a vanadium precursor.\[^{21, 38}\] SEM images and EDX analysis confirmed the expected composition and structure of the resulting ~1 \(\mu\)m thick nanoporous BiVO\(_4\) layer,\[^{38}\] which consists of irregular worm-like structures of ~100 nm in diameter (Figures S16-S23, Supporting Information). By submerging the FTO|BiVO\(_4\) electrodes in aqueous HCl (0.4 M) for 30-300 s, BiVO\(_4\) was gradually removed and the FTO surface was accordingly exposed (see SEM images in Figure S16 and S17, Supporting Information), whereas the FTO layer remained unaffected by the acidic solution (Figure S18, Supporting Information). After the etching step, 20 \(\mu\)L of a single source precursor solution of [Ti\(_4\)O(OEt)\(_{15}\)(CoCl)] in dry toluene (4.8 mg mL\(^{-1}\)) was spin coated onto the BiVO\(_4\) electrodes four times under air to produce an amorphous TiCoO\(_x\) (TiCo) OEC (abbreviated FTO|BiVO\(_4\)|TiCo) (see Supporting Information for details).\[^{41-44}\] EDX elemental maps of Ti and Co indicated a successful deposition of TiCo on both BiVO\(_4\) and exposed FTO for all samples with different etching times (Figures S19-S22, Supporting Information).

The etching time was optimized to achieve maximum \(O_2\) generation in PEC and EC modes. In PEC, chopped linear sweep voltammetry (LSV) scans showed a significant drop in photocurrent of samples etched for longer than 120 s throughout the scanning region (Figure 3a). In EC, an LSV of the etched FTO|BiVO\(_4\)|TiCo (photo)anodes showed an earlier onset for
O2 evolution than that of pristine FTO and the reference, 0 s etched FTO|BiVO4 (Figure 3b). When BiVO4 was exposed to the etching solution longer than 60 s, the onset approached the value of FTO|TiCo, 1.68 V vs. RHE, which indicates that water oxidation occurs at the FTO-TiCo interfaces introduced in the etched BiVO4 samples (Figure 3b, Figure S24 and S25, Supporting Information). From this point onwards, we used BiVO4 (photo)anodes etched for 60 s which gave the best performance in both PEC and EC operation for further characterization. A photocurrent of 1.5-2.0 mA cm\(^{-2}\) was achieved when operating CA at 1.23 V vs. RHE under 1 Sun irradiation (which is in line with reported PEC tests\(^{[10, 40]}\)), whereas the current of EC under a 1.9 V vs. RHE applied potential was approximately 1 mA cm\(^{-2}\) (Figure 3c). The BiVO4|TiCo (photo)anodes produced 82.2 ± 7.8 μmol O2 (cumulative 73.0 ± 5.4 % O2 FY) over five consecutive two hour PEC-EC cycles (Figure 3c, Figure S26, Supporting Information). Therefore, the partial etching of BiVO4 enabled the EC functionality, while retaining the PEC performance of the water oxidizing BiVO4 (photo)anode.

Post-catalysis CV characterization revealed again no shift in the onset potential or increasing dark currents for the BiVO4 photoanodes (Figure S27, Supporting Information). This was consistent with SEM analysis and EDX mapping, which indicated no changes in the sample morphology and catalyst distribution after the 10 h PEC-EC tests (Figure S23, Supporting Information). However, small spikes on the chopped scan CVs indicated an increased charge recombination,\(^{[45, 46]}\) which may account for the slight decrease in photocurrent from Figure 3c.

### 2.3. Perovskite-BiVO4 PEC-EC devices

Lastly, we demonstrate that the PVK|GE|Pt and FTO|BiVO4|TiCo electrodes can be combined in an integrated ‘artificial leaf’ configuration to obtain unassisted tandem PEC water splitting with integrated EC functionality for water electrolysis (Figure 1e-g, Figure S28, Supporting Information). CV scans in PEC mode showed an improved performance over reported
perovskite-BiVO₄ PEC tandems,¹⁰, ²⁸ with a very early onset of ~0.8 V for overall water splitting and approximately 1.5 mA cm⁻² initial photocurrent at zero applied bias (Figure 4a). In comparison, CV in EC mode showed an onset for overall water-splitting at 1.8 V (Figure 4b), which is comparable to electrolyzer systems in neutral-pH medium.⁴⁷, ⁴⁸

The current achieved for EC water electrolysis at 2.1 V applied bias was 0.3-0.6 mA cm⁻², whereas the PEC tandem photocurrent displayed the earlier described behaviors of the photoelectrodes (Figure S29 and S30, Supporting Information). A total of 85 ± 19 μmol cm⁻² H₂ (cumulative 60 ± 11% H₂ FY) and 29.4 ± 3.9 μmol cm⁻² O₂ (cumulative 53.9 ± 8.8% O₂ FY) accumulated after five consecutive two-hour PEC-EC cycles (Figure 4c and Figure S29, Supporting Information). The rates of O₂ and H₂ evolution decreased during the experiment in line with the (photo)current density. The deviations from a 2:1 H₂ to O₂ ratio may be explained by small gas leakages from the PEC reactor, which would lead to overestimations of the H₂ amount (quantified using an internal standard) and underestimations in the O₂ amount (quantified as absolute amount). The lower FYs observed were likely caused by bubble trapping, solubilized products, or O₂ reduction on the cathodic side, which is more likely to occur as O₂ accumulates in the one-compartment cell (Figure S29, Supporting Information).¹⁷

The improved PVK architecture and encapsulating technique resulted in an unassisted PEC solar-to-H₂ (STH) conversion efficiency of 1.26 ± 0.26% for daytime operation, which is the highest value reported among similar perovskite-BiVO₄ PEC devices (see comparison in Table S1).¹⁰, ²⁸ Alternatively, the energy efficiency in EC mode (i.e. as an electrolyzer during night time) amounted to 58.6% assuming an ideal FY of 100% for the dark process.

The proposed bifunctional perovskite-BiVO₄ tandem also compared favorably to more conventional PEC tandems in terms of performance and stability (Table S1), as many oxide- or dye-based tandems could only report efficiencies below 1% STH for a few hours.⁴⁹-⁵² While conventional electrolyzers can separately operate at currents 100 times higher, those employ
square-meter electrode surface areas, or complex flow setups with gas diffusion electrodes, even without taking into account the area required for the corresponding light-harvesting unit. Hence, corresponding wired perovskite PV-EC systems often only achieve STH efficiencies of 10-20%.\textsuperscript{[53]} However, those are more complex and employ corrosive (strongly acidic or basic) electrolytes, which makes them more costly to operate (Tables S2, and S3, Supporting Information). Nevertheless, further improvements in the PEC-EC performance are achievable through appropriate device design and catalyst optimization.\textsuperscript{[53-56]} Since the photocurrent of PEC devices is often limited to few mA cm\textsuperscript{-2} by oxide-based photoanodes, the efficiency of perovskite-based PEC-EC systems may also be increased beyond 5% in neutral pH solutions by optimizing state-of-the-art photoanodes for EC operation.\textsuperscript{[57, 58]} In this way, their efficiency may approach the ones of complex multijunction PV-EC,\textsuperscript{[55]} PV+PEC,\textsuperscript{[59]} or PEC\textsuperscript{[60-62]} devices (4-30% STH, see Table S1, ESI†), which are however more challenging to fabricate.\textsuperscript{[55, 60, 61]} The products, a gaseous mixture of hydrogen and oxygen, can be separated safely by introducing microporous gas separation membranes\textsuperscript{[63]} (e.g. molecular sieving microporous membranes with minimal energy losses\textsuperscript{[64]}). Alternatively, the tandems may operate in between two different compartments, as the back-to-back design already provides a physical separation between the oxidative and reductive sides.

From a material and cost perspective, the PEC-EC devices also have the potential to show advantages in comparison to more conventional PV-EC, or PEC + electrolyzer technologies for round-the-clock fuel synthesis (see cost analysis in Tables S2 and S3, Supporting Information). Since the (photo)electrodes consist of (nanostructured) thin films, only low amounts of photoactive material (< 0.4 mg) are used in each sample (Table S2, Supporting Information). In the present base-case estimate, the raw material cost for PEC-EC ($76 m\textsuperscript{-2}) can be considerably lower than the one of a commercialized PV-EC system ($161 m\textsuperscript{-2}).\textsuperscript{[7]} This can be accomplished in large-scale fabrication through bulk material purchase, or
roll-to-roll deposition techniques avoiding raw material losses.\textsuperscript{[56, 65]} The new device architecture plays a central role in achieving such low device costs, as a 27 times reduction in the PEC material cost is gained by replacing the FM encapsulant with graphite epoxy. Moreover, the balance of system (BoS) cost, which includes wiring, installation and operation costs, is also lower in case of PEC-EC. As a result, the total (raw materials + BoS) estimated cost of PEC-EC systems ($338 \text{ m}^{-2}$) is significantly decreased in comparison to their commercial PV-EC ($461 \text{ m}^{-2}$) and PEC + electrolyzer ($630 \text{ m}^{-2}$) counterparts.\textsuperscript{[7]}

Overall, these findings provide a conceptual proof-of-concept for continuous hydrogen generation with integrated PEC devices to overcome the intermittent nature of solar irradiation. As renewable electricity becomes more wide-spread, it is becoming increasingly important for PEC technology to work in synergy with wind or hydropower. By integrating PEC with EC technologies, a potential reduction in the overall system cost can be envisioned, as the number of components is reduced,\textsuperscript{[8]} whereas a similar performance can be sustained in both operation modes, maximizing the output and versatility of the bifunctional devices. The high additional driving force of the PEC tandems (0.8 V) may also act beneficially towards practical implementation, by powering autonomous control systems for optimal PEC-EC operation.

3. Conclusions
In conclusion, we have presented a bifunctional PEC-EC device prototype for uninterrupted solar fuels production. Such systems can efficiently use solar light during daytime and easily switch to EC activity during dark or when renewable electricity is more abundant. To demonstrate this concept, a perovskite-BiVO\textsubscript{4} tandem device was modified to introduce EC functionality for overall water splitting. On the cathodic side, this was achieved by directly wiring the conductive encapsulant to an external bias source in EC mode. The perovskite photocathode architecture was redesigned with a hydrophobic PTAA hole selective layer, a graphite epoxy encapsulant and a conformal parylene-C coating which provided additional
moisture protection, achieving a benchmark PEC onset potential of 1.0 V vs. RHE and overall stability beyond 96 h. On the other hand, EC functionality of the water oxidizing photoanode can be achieved via FTO|BiVO₄ post-etching, which provides an FTO-TiCo interface without compromising the photocurrents. In an ‘artificial leaf’ configuration, the bifunctional perovskite-BiVO₄ tandem showed a PEC onset bias of −0.8 V and a solar-to-hydrogen efficiency of 1.3% for daytime operation, with an onset for EC water-splitting at 1.8 V. These results extend the scope of traditional PEC devices and reveal how hybrid systems may bridge the gap between renewable fuel technologies, providing the complete functionality of PV-electrolyzer in a compact monolithic design.

**Experimental Section**

**Materials**

FTO-coated glass (∼7 Ω sq⁻¹, Sigma-Aldrich), H₂SO₄ (>95%, Fisher), H₂O₂ (>30% w/v, Fisher), Zn (dust, 98+%, ACROS), HCl (fuming, 36.5-38%, Honeywell), Ni(NO₃)₂·6 H₂O (≥98.5%, Sigma-Aldrich), ethylene glycol (99.8%, anhydrous, ACROS), ethylenediamine (absolute, ≥99.5%, Fluka), PbI₂ (99.99%, trace metals basis, TCI), PbBr₂ (for Perovskite precursor, TCI), formamidinium iodide (Dyesol), methylammonium bromide (Dyesol), N,N-dimethylformamide (anhydrous, 99.8%, Sigma-Aldrich), 1-methyl-2-pyrrolidone (99.5%, extra dry over molecular sieves, ACROS), dimethyl sulfoxide (ACS reagent, ≥99.9%), chloroform (99.9%, extra dry over molecular sieves, stabilized, ACROS), [60]PCBM (99%, Solenne BV), chlorobenzene (extra dry over molecular sieves ≥99.5%, ACROS) polyethylenimine (80% ethoxylated solution, 35-40 wt.% in H₂O, average MW 70,000, Sigma-
Aldrich), 2-propanol (≥99.5%, Honeywell), poly(triarylamine) (average MW 7,000-10,000, Sigma-Aldrich), PTAA (MW 17,700, EM INDEX), F4TCNQ (97%, Sigma-Aldrich), Field's metal (ingot, Bi:In:Sn = 32.5:51:16.5 wt.%, Alfa Aesar), graphite powder (20 μm, Sigma-Aldrich), Bi(NO₃)₃·5H₂O (98%, Sigma-Aldrich), Araldite 5-Minute Rapid two component epoxy, Araldite Standard two component epoxy, copper wire (0.25 mm diameter, 99.999%, Sigma-Aldrich), dichloro[2.2]-paracyclophane (Sigma-Aldrich), NaI (laboratory reagent grade, Fischer Scientific), p-benzoquinone (≥98%, Sigma-Aldrich), ethanol (absolute, VWR), vanadyl acetylacetonate (≥97.0%, Fluka), dimethyl sulfoxide (99+%, Alfa Aesar) and NaOH (analytical reagent grade, Fisher) were used without further purification unless otherwise stated.

**Preparation of perovskite PV cells**

The inverse-structure perovskite cells were prepared according to previously reported procedures with few modifications.[10] In brief, a NiOₓ hole transport layer (HTL) was first uniformly deposited onto the FTO substrate via spin-coating of 1.0 M Ni(NO₃)·6H₂O, 1.0 M ethylenediamine solution in ethylene glycol and annealing at 573 K. PTAA doped with F4TCNQ solution was spin coated onto the NiOₓ coated FTO substrate inside a N₂-filled glovebox as a second HTL. A cesium formamidinium methylammonium (CsFAMA) perovskite precursor solution was prepared by adding 48 μL of 1.5 M CsI in DMSO stock solution to 1000 μL of FAMA₀.₂₂Pb₁.₃₂I₁.₂Br₀.₆₆ solution in DMF (in 510μL), DMSO (340 µL), and NMP (150 μL). A smooth perovskite layer was then deposited by a two-step spin coating; first 10 s at 1000 rpm and then 35 s at 6000 rpm using chloroform as the antisolvent ~7 s before the end. The perovskite layer was then annealed at 373 K for 30 min. A thin PCBM layer was deposited as ETL by spin coating a 35 mg mL⁻¹ PCBM solution in chlorobenzene at 3000 rpm for 45 s. Next, 3.87 μL mL⁻¹ PEIE solution in isopropanol was spin coated under ambient conditions at 3000 rpm for 30s, before storing the samples under inert atmosphere.
Lastly, a 100 nm silver layer was evaporated through an aluminum mask to form the electrical contacts.

**Preparation of bifunctional (photo)cathodes**

Graphite powder was mixed with Araldite Standard two component epoxy in 3:4 mass ratio to create a graphite epoxy (GE) paste.\(^{[26]}\) The paste was evenly spread on top of the Ag contact layer of the PV device. The copper wire was then slightly pressed against the paste to form an electrical contact. The GE was allowed to settle for 24 hours. After sealing the edges with Araldite 5-Minute Rapid two component epoxy, the samples were coated with a 5.4 \(\mu\)m layer of Parylene-C via the Gorham process using the SCS Labcoter® 2 Parylene Deposition System (PSD 2010).\(^{[27, 37]}\) The active area of GE was masked with approximately 0.25 cm\(^2\) Blu tack prior to the deposition. Throughout the deposition process, a low pressure of \(~10^{-2}\) mbar was maintained and dichloro[2.2]-paracyclophane dimer was used as Parylene-C precursor. The dimer undergoes sublimation at \(~403\) K and pyrolysis at \(~923\) K, condensing and polymerizing at room temperature onto the underlying substrate. The deposited Parylene-C thickness was measured by the DektakXT Profilometer on a reference sample. Finally, a 5 nm Pt film was deposited by magnetron sputtering onto the GE layer. The final device is abbreviated as PVK|GE|Pt. For comparison, the FM encapsulated PVK (PVK|FM) was prepared according to the previously reported method and electroless deposition was used to form the PVK|FM|Pt assembly.\(^{[22]}\)

**Preparation of bifunctional (photo)anodes**

FTO|BiVO\(_4\)|TiCo photoanodes were prepared according to previously reported procedures.\(^{[10, 38, 41]}\) A first solution was prepared by dissolving Bi(NO\(_3\))\(_3\) (0.194 g, 0.4 mmol) and NaI (1.199 g, 8.0 mmol) in Milli-Q water (20 mL) using an ultrasonication probe (Fischer Scientific Model 120 Sonic Dismembrator) for 3 min. The pH was subsequently adjusted to 1.2 using
concentrated nitric acid. A second solution consisting of benzoquinone (0.292 g, 2.7 mmol, 0.3 M) in absolute ethanol (9 mL) was also sonicated for 3 min. The two solutions were mixed and stirred for 30 min at room temperature to obtain a dark brown BiOI precursor solution. 13 x 13 mm² FTO glass slides were selectively etched with Zn dust and 2 M HCl to provide a total FTO active area of approximately 0.45 cm² (0.5 x 0.9 cm²) before cleaning the glass slides in a Piranha solution. Then, an active area of ~0.25 cm² (0.5 x 0.5 cm²) was defined by tape prior to the electrodeposition leaving ~0.2 cm² (0.4 x 0.5 cm²) as FTO contact area. The orange BiOI layer was then electrodeposited onto the active area of the FTO slides, by maintaining a potential of −0.3 V against a Ag/AgCl reference electrode for 5 s, followed by −0.1 V for 180 s. A vanadyl acetyl acetonate (VO(acac)₂) solution was prepared by sonicating VO(acac)₂ (0.530 g, 2.0 mmol) in 5 mL DMSO for 5 min. 30 μL of the VO(acac)₂ solution was drop-casted onto the BiOI active areas, before heating the FTO slides at 723 K for 60 min with a ramp rate of 1 K min⁻¹. After the glass slides were left to cool down to room temperature, a NaOH (0.4 M) aqueous solution was used to wash the brownish V₂O₅ crust from the photoanode surface for 30-120 min, as necessary, resulting in a bright yellow BiVO₄ photoanode.

An etching technique was used to expose more FTO surface between the BiVO₄ nanostructures, which facilitates the deposition of the electrocatalyst (TiCo) not only on BiVO₄, but also FTO. For the etching, 0.25 cm² BiVO₄ photoelectrodes were submerged in a 0.4 M HCl aqueous solution for 30-150 s and then washed vigorously with Milli-Q water. A [Ti₄O(OEt)₁₅(CoCl)] oxygen evolution catalyst precursor was synthesized as previously reported.⁴² A [Ti₄O(OEt)₁₅(CoCl)] (TiCo, 0.024 g, 24.5 μ mol) solution in dry toluene (5 mL) was prepared under inert atmosphere. 20 μL of the TiCo solution was spin coated four times at 2000 RPM for 10 s under air, to obtain a transparent catalyst layer.

**Preparation of bifunctional PEC-EC tandems**
The photoanode and photocathode were adhered in a back-to-back configuration via a two-part epoxy and left to settle overnight (Figure S21e-g). Prior to further characterization, the active area was defined by a black tape surrounding the BiVO₄ active area of ~0.25 cm². This ensures that the light only reaches the PVK through the BiVO₄ photoanode as shown in Figure S21h-j.

**Photo/electrochemical characterization**

To investigate the performance of the photoelectrodes, a Newport Oriel 67005 setup was employed with an Air Mass 1.5 Global (AM 1.5G) solar filter. The light intensity was calibrated to 100 mW cm⁻² (corresponding to 1 sun) using a Newport 1916-R optical power meter. Electrochemical measurements such as cyclic voltammetry (CV), chronoamperometry (CA) were conducted on an Ivium CompactStat.e potentiostat in a three-electrode setup, where platinum and Ag/AgCl were used as counter and reference electrode, respectively. All the measurements were conducted in glass PEC H-cells with Selion (AGC Engineering) ion exchange membrane separation, which were employed for the characterization of 0.25 cm² photoelectrodes. Prior to the electrochemical measurement, the cell was sealed with rubber septa and purged through the solution with N₂ containing 2% CH₄ for 30 min. All purging needle holes were then sealed with Loctite superglue Universal adhesive. All devices were tested at a scan rate of 10 mV s⁻¹. The electrodes were measured in a 0.1 M potassium borate buffer (KBi) solution of pH 8.5, which contained 0.1 M K₂SO₄ as electrolyte. The potential versus the reversible hydrogen electrode (RHE) was determined using Equation 1 at a temperature of 298 K. Average values are based on triplicates unless otherwise noted, and the errors correspond to the standard deviation of data points from individual samples.

\[
E \ [V \ vs. \ RHE] = E \ [V \ vs. \ Ag/AgCl] + 0.059 \times pH + 0.197 \ (298 \ K) \quad (1)
\]
Similar conditions were employed for the PEC-EC tandem devices, where the scans were conducted in a two-electrode configuration in a one-compartment glass cell.

To characterize the EC performance of the photoelectrodes, the CV and CA measurements were conducted without illumination. For the PVK photocathode, the electrical contact of the working electrode was swapped manually when changing from PEC to EC measurement and vice versa. Due to mass transport limitations, the solution was stirred for the photoanodes and tandems, and left unstirred for PVK characterization.

The solar-to-hydrogen (STH) efficiency of this system was calculated using Equation 2, where $J_{0V}$ is the bias-free photocurrent density, FY is the faradaic yield taken after a 2 hour PEC-EC CA measurement, and $P_{\text{total}}$ is the total light intensity flux (100 mW cm$^{-2}$).[41]

$$\text{STH} = \frac{[J_{0V}] \times (1.23 V) \times \text{FY}}{P_{\text{total}}}$$

(2)

The energy efficiency in EC mode ($\eta_{\text{EC}}$) was calculated using Equation 3, where $U_{\text{cell}}$ is the applied bias, and FY is the faradaic yield.[66]

$$\eta_{\text{EC}} = \frac{(1.23 V) \times \text{FY}}{U_{\text{cell}}}$$

(3)

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

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References


Figure 1. Architecture of the bifunctional PEC-EC device for uninterrupted solar water splitting. a) Schematic representation of the device operating via three wires: wire (A) is connecting to the graphite paste, (B) to the CsFAMA triple cation perovskite (photo)cathode and (C) to the BiVO$_4$ photoanode, with a two-way electrical switch to select between PEC (daytime) and EC (dark) operation. b) Energy diagram of the perovskite architecture, based on reported values.[15-18] c) EDX mapping of a perovskite PV cell and d) BiVO$_4$ (photo)anode. e-g) Photographs of the PEC-EC bifunctional device in an ‘artificial leaf’ configuration: e) side view, f) Pt side, g) BiVO$_4$ side. The wire notation corresponds to frame a.
Figure 2. Data recorded for the 0.25 cm$^2$ PVK|GE|Pt (photo)cathodes. a) EC cyclic voltammetry indicates no degradation of the GE|Pt interface over repeated scans. b) PEC cyclic voltammetry scans under chopped, continuous, and no irradiation. c) PEC-EC chronoamperometric trace of the H$_2$ evolution current and cumulative H$_2$ amount. d) Long-term experiment of a PVK|GE|Pt. Chronoamperometry was recorded at $E_{app} = 0.0$ V and $-0.7$ V vs. RHE for PEC and EC, respectively. Experiments were performed in a 0.1 M KBi, 0.1 M K$_2$SO$_4$ buffer (pH 8.5), using simulated solar irradiation (AM 1.5G, 100 mW cm$^{-2}$, 1 sun). Light blue shades indicate PEC operation, while grey areas depict the EC mode.

Figure 3. Data recorded for 0.25 cm$^2$ FTO|BiVO$_4$|TiCo (photo)anodes with different post-etching times. a) Chopped-light PEC linear sweep voltammograms of 0-180 seconds etched FTO|BiVO$_4$|TiCo (photo)anode. b) EC LSV scans of 0-150 seconds etched FTO|BiVO$_4$|TiCo. c) PEC-EC chronoamperometric trace of the O$_2$ evolution current and recorded O$_2$ amount at $E_{app} = 1.23$ V and 1.9 V vs. RHE for PEC (light blue areas) and EC (grey shades), respectively (0.1 M KBi, 0.1 M K$_2$SO$_4$ electrolyte, pH 8.5; AM 1.5G, 100 mW cm$^{-2}$, 1 sun).
Figure 4. Data recorded for 0.25 cm² bifunctional PEC-EC tandem. a) PEC cyclic voltammetry scans under chopped, continuous and no irradiation. b) EC cyclic voltammetry scans. c) PEC-EC chronoamperometric trace of the water-splitting current and recorded H₂ and O₂ amount at $E_{\text{app}} = 0$ V and 2.1 V for PEC (light blue) and EC (grey), respectively (0.1 M KBi, 0.1 M K₂SO₄, pH 8.5; AM 1.5G, 100 mW cm⁻², 1 sun).
The table of contents entry

The mismatch in demand and supply of sustainable energy sources poses a growing challenge for renewable energy production. Photoelectrocatalysis offers a solution to turn solar energy directly into storable chemical fuels such as hydrogen, but its performance is dependent on light intensity, weather, and other external factors. Here, a hybrid device that can perform sunlight-powered water splitting during the day and switch to water electrolysis at night is presented.

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Bifunctional perovskite-BiVO₄ tandem devices for uninterrupted solar and electrocatalytic water splitting cycles

ToC figure