

Scalable All-Inorganic Halide Perovskite Photoanodes with >100 h Operational Stability Containing Earth-Abundant Materials

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The application of halide perovskites in the photoelectrochemical generation of solar fuels and feedstocks is hindered by the instability of perovskites in aqueous electrolytes and the use of expensive electrode and catalyst materials, particularly in photoanodes driving kinetically slow water oxidation. Here, solely earth-abundant materials are incorporated to fabricate a CsPbBr_3 -based photoanode that reaches a low onset potential of $+0.4 V_{\text{RHE}}$ and 8 mA cm^{-2} photocurrent density at $+1.23 V_{\text{RHE}}$ for water oxidation, close to the radiative efficiency limit of CsPbBr_3 . This photoanode retains 100% of its stabilized photocurrent density for more than 100 h of operation by replacing once the inexpensive graphite sheet upon signs of deterioration. The improved performance is due to an efficiently electrodeposited NiFeOOH catalyst on a protective self-adhesive graphite sheet, and enhanced charge transfer achieved by phase engineering of CsPbBr_3 . Devices with $>1 \text{ cm}^2$ area, and low-temperature processing demonstrate the potential for low capital cost, stable, and scalable perovskite photoanodes.

direct conversion of solar energy into solar fuels and feedstocks to achieve net zero CO_2 emission.^[9–11] Applying perovskite photoactive layers in photoelectrodes opens a way of delivering high photocurrent densities (j_{ph}) close to the radiative efficiency limit.^[12,13] However, the application of such photoelectrodes is currently limited by the instability of halide perovskites in an aqueous environment, especially in the oxidative conditions found at the photoanode side of PEC cells.^[14]

Advances in the stability of halide perovskite photoelectrodes have been achieved by applying electrically conductive protecting layers such as Field's metal (high-cost eutectic InBiSn alloy), Ti foil, Pt coating, and graphite-containing epoxy, but most efforts have focused on photocathodes utilized for two-electron-transfer processes such as H_2 or CO evolution.^[15–20]

1. Introduction

Solution-processed halide perovskites have been applied in solar cells reaching remarkable power conversion efficiencies (up to 25.8%)^[1–4] due to their exceptional optoelectronic properties such as high absorption coefficient, long charge-carrier diffusion lengths, and electronic defect tolerance.^[5–8] Halide perovskites are also ideal absorber layers for photoelectrodes of photoelectrochemical (PEC) cells, which offer a promising way for the

Few reports have covered the fabrication of the more challenging photoanodes dealing with four-electron reactions such as O_2 evolution: we previously applied a mesoporous carbon layer and a self-adhesive graphite sheet in a CsPbBr_3 photoanode for photoinduced hole extraction and protection from water-induced degradation, but the mesoporous carbon layer required 400°C annealing and a high-cost Ir-based electrocatalyst was needed to reach an onset potential (E_{on}) of $+0.55 V_{\text{RHE}}$, both of which would limit its wide-scale application.^[21] Other attempts applied the same graphite sheet coated with Ni or carbon layer with Ni foil, but in both cases, expensive Spiro-OMeTAD hole transport layers (HTLs)^[22] and Au contacts were needed, while the E_{on} was still above $+0.56 V_{\text{RHE}}$.^[23,24] Importantly, these photoelectrodes showed continuous decay of j_{ph} (50–60% loss of the initial performance), plausibly due to the instability of hybrid organic–inorganic halide perovskites under reverse bias.^[24] Inexpensive, scalable, and highly performing halide perovskite photoanodes with low E_{on} and long-term stability remain a challenge.

In this work, we present an all-inorganic CsPbBr_3 halide perovskite photoanode that incorporates solely earth-abundant materials and does not contain an expensive selective HTL or any noble metal. We apply CsPbBr_3 as a photoactive layer (optical bandgap of 2.3 eV), low-temperature (70°C) printed carbon as the top electrode, and commercially available self-adhesive protective graphite sheets of different porosities. The

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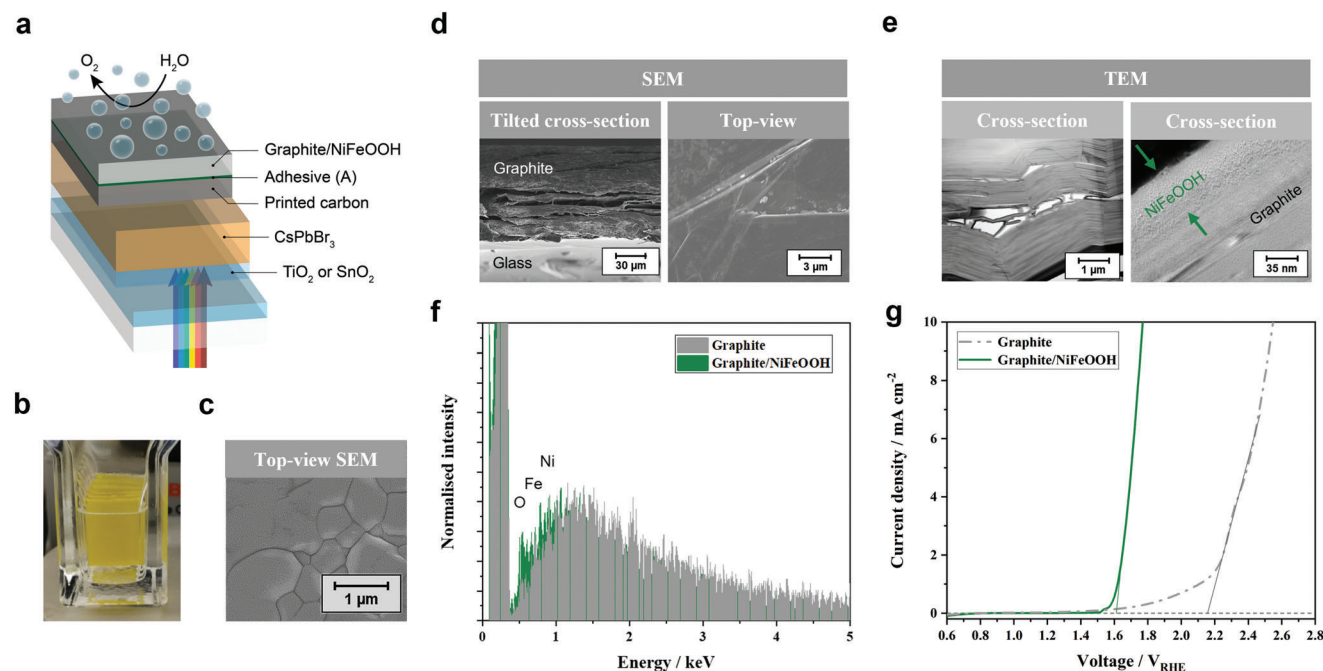


Figure 1. Solution-processed CsPbBr₃ photoanode with NiFeOOH functionalized graphite sheet. a) Schematic representation of the n-i-p structure perovskite photoanode with printed carbon electrode and self-adhesive graphite-sheet conductive protection layer (not to scale). b) Photograph of CsPbBr₃ layers deposition in a chemical bath. c) Top-view SEM image of 3D CsPbBr₃ perovskite film. d) Cross-section and top-view SEM images of the 70 μm-thick graphite sheet on glass. e) Slightly tilted cross-section HRTEM images of the bulk and surface of NiFeOOH functionalized graphite sheet. The green arrows indicate the amorphous catalyst on top of the highly ordered graphite sheet. f) EDS spectra recorded over an area of 20 × 20 μm² comparing graphite sheets with and without electrodeposited NiFeOOH. g) OER polarization scans (50 mV s⁻¹ scan rate) of graphite-sheet electrodes on glass with and without NiFeOOH at pH 14 (1 M NaOH aqueous electrolyte).

uniqueness of the photoanode lies partly in reaching high catalytic activity on the surface of the porous graphite sheet upon straightforward electrodeposition of nickel-iron oxyhydroxide (NiFeOOH) oxygen evolution reaction (OER) catalyst, and partly in the improved bulk and interfacial charge transfer achieved by phase engineering of the all-inorganic perovskite layer. These crucial developments enable nearly doubling of j_{ph} compared to previous CsPbBr₃ photoanode reports up to 8 mA cm⁻² at +1.23 V_{RHE}, which is close to the radiative efficiency limit of CsPbBr₃ under 1 sun illumination and corresponds to >95% incident photon-to-current efficiency (IPCE). Moreover, the developed photoanode shows an E_{on} as low as +0.4 V_{RHE} and record stability of 110 h, retaining 100% of its stabilized j_{ph} throughout the continuous operation. This operational stability can be further extended to weeks by replacing the inexpensive graphite/NiFeOOH sheet upon signs of deterioration. The developed CsPbBr₃ photoanodes show high potential for upscaling due to the combination of low-temperature solution-processed transport and photoactive layers, the chemical bath step of CsPbBr₃ formation, and the ease of deposition and replacement of the graphite sheet functionalized by electrodeposited NiFeOOH. We demonstrate scalability by achieving an all low-temperature solution-processable device, and photoanodes with >1 cm² area reaching ≈90% j_{ph} compared to their smaller area counterparts.

2. Results and Discussion

2.1. Perovskite Photoanode Fabrication Applying Earth-Abundant Materials

The n-i-p structure perovskite photoanode (Figure 1a) consists of fluorine-doped tin oxide (FTO)-coated glass substrate, titanium dioxide (TiO₂) electron transport layer (ETL), CsPbBr₃ absorber layer, printed carbon electrode layer, self-adhesive graphite sheet, and electrodeposited NiFeOOH co-catalyst (experimental details in the Supporting Information). The first step in the synthesis of CsPbBr₃ was the spin-coating of a PbBr₂ layer on FTO/TiO₂, followed by annealing at a low temperature (60 °C) for 30 min. For the second step, we have developed a novel chemical bath method of applying CsBr: The PbBr₂ layer was immersed for 5 min into a chemical bath of CsBr in methanol, followed by washing with 2-propanol and 5 min annealing at 250 °C (Figure 1b). The chemical bath and annealing steps were repeated 1–3 times to obtain different samples (denoted as 1–3× CB). Scanning electron microscopy (SEM) reveals relatively small grains (0.5–1 μm) for the 1× CB CsPbBr₃ film (Figure S1, Supporting Information), while UV-vis spectroscopy shows limited absorbance (Figure S4, Supporting Information). The optimized 2× CB CsPbBr₃ layer was more uniform with significantly reduced roughness, large 1–3 μm grains, and enhanced absorbance (Figure 1c and Figure S4, Supporting Information). The 3× CB

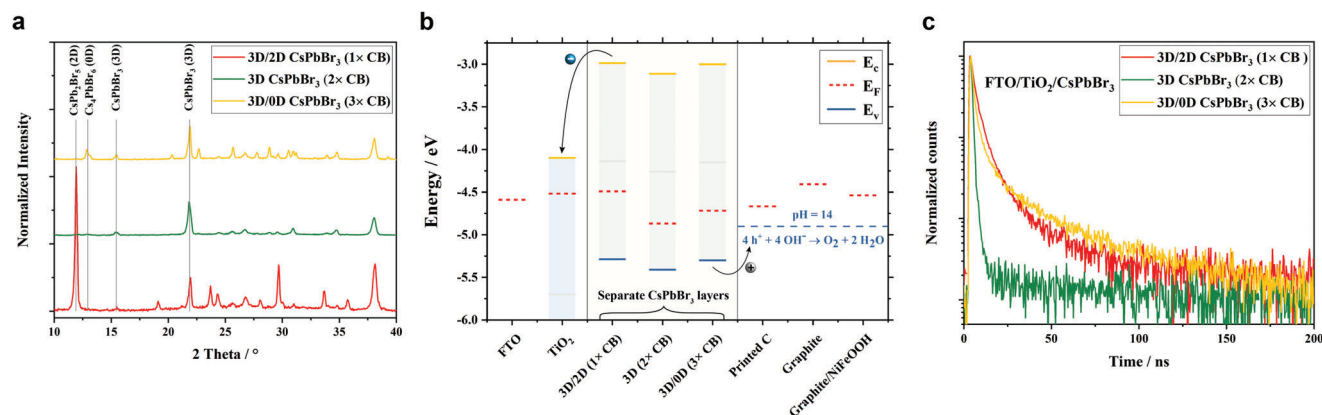


Figure 2. Phase engineering of perovskite photoactive layer. a) X-ray diffractograms (normalized to the (110) CsPbBr_3 peak) of perovskite layers prepared by varying numbers of chemical bath deposition and annealing steps. b) Energy band diagrams of the constituent layers of the photoanode. The electrochemical potential of OER at pH 14 is indicated with a blue dashed line, while the preferred direction of photogenerated electron and hole transfer is illustrated by curved arrows. c) Normalized transient PL decay curves (excitation at 405 nm) of the CsPbBr_3 layers with different phases deposited on FTO/TiO_2 .

CsPbBr_3 film showed additional smaller grains (Figure S1, Supporting Information), which increased the roughness leading to substantial reflectance of the sample and consequently reduced absorption of light (Figure S4, Supporting Information). Annealing these rough layers at a higher temperature (380°C) resulted in a significantly reduced reflectance (observed as a large shift of baseline in the UV-vis spectra, Figure S5, Supporting Information), in agreement with the decomposition of the small grains (later identified as 0D Cs_4PbBr_6).

A low-annealing-temperature (70°C) carbon electrode layer was blade-coated directly on the perovskite layer without using any selective HTL. This carbon layer was covered by a $70\text{ }\mu\text{m}$ -thick pyrolytic graphite sheet with the help of a pre-deposited adhesive (A) layer. The graphite sheet consists of highly oriented layers with a lattice spacing of $3.3\text{ }\text{\AA}$ (Figure S2, Supporting Information) and occasional gaps between the layers (SEM and HRTEM images in Figure 1d,e). These gaps and the larger pores ($10\text{--}50\text{ }\mu\text{m}$) between the graphite domains (optical microscopy images in Figure S3, Supporting Information) result in a density of 1.2 g cm^{-3} , equivalent to 50% porosity. As the OER catalytic activity of the graphite sheet is low, we have developed a quick and easy-to-perform electrodeposition method of NiFeOOH , an OER catalyst containing solely earth-abundant metals.^[25,26] Applying electrodeposition is advantageous not only for its scalability but also as it allows uniform deposition of the electrocatalyst on the large surface area of the graphite sheet.^[27] The successful deposition of the amorphous NiFeOOH on graphite is confirmed by a cross-sectional HRTEM image (Figure 1e) showing clearly a thin ($20\text{--}30\text{ nm}$) amorphous layer on the surface of the pyrolytic graphite. Energy-dispersive X-ray spectroscopy (EDS) analysis confirms the NiFeOOH deposition, based on increased intensity at the characteristic energies of oxygen, nickel, and iron compared to a reference graphite sheet (Figure 1f). Importantly, the NiFeOOH -functionalized graphite sheet decreased the OER E_{on} by 150 mV at pH 7 (Figure S6, Supporting Information), and by 540 mV at alkaline solution (pH 14), where NiFeOOH is known to work most efficiently,^[28] achieving an OER E_{on} of $+1.61\text{ V}_{\text{RHE}}$ (Figure 1g).

2.2. Phase Engineering of CsPbBr_3 Photoactive Layer

X-ray diffraction (XRD) patterns of the perovskite layers deposited on FTO/TiO_2 show the presence of 3D CsPbBr_3 phase for all fabrication methods (Figure 2a). The 3D phase is identifiable by the characteristic (100), (110), and (111) diffraction peaks at 15.4° , 21.8° , and 26.7° 2θ , respectively.^[29,30] Other phases and dimensionalities appear depending on the method followed, but importantly, we found that their formation can be controlled by the number of CsBr chemical bath steps. A 3D/2D perovskite layer is formed after the $1\times$ CB step, evidenced by an intense (002) diffraction peak at 11.9° assigned to the CsBr -deficient 2D CsPb_2Br_5 .^[31,32] This 2D perovskite peak is decreased but still present for layers prepared by a combination of spin coating and chemical bath steps (Figure S8, Supporting Information), or by repeated spin coating steps (Figure S9, Supporting Information). Temperature-dependent XRD measurements reveal that the 2D CsPb_2Br_5 phase can be decomposed into CsPbBr_3 and PbBr_2 at higher ($>345^\circ\text{C}$) annealing temperatures (Figure S10, Supporting Information), however, such a treatment adds substantial extra cost and typically increases the density of pinholes due to the sublimation of PbBr_2 .^[33] Repeating twice the chemical bath and annealing steps provides a novel, lower temperature (250°C), robust, and scalable way of directly producing pure 3D CsPbBr_3 phase, with no low-dimensional perovskite peaks observable on the X-ray diffractogram (Figure 2a). On the other hand, $3\times$ CB steps result in the formation of a rough 3D/0D perovskite layer, evidenced by (120) and (110) diffraction peaks of 0D Cs_4PbBr_6 at 12.8° and 13.1° , which grow even further upon $4\times$ CB steps (Figure S11, Supporting Information).^[34,35] Both the high relative intensity of the XRD peaks of the 2D and 0D phases under the used 2θ geometry and the layer and grain restructuring observed by SEM, as well as the methodology followed without the use of any 2D additives,^[36,37] indicate that the 2D and 0D phases are present both in the bulk and surfaces of the perovskite layer.

To understand the effect of different perovskite phases on the band alignment of the formed layers, the energy band diagrams of all constituent layers were constructed and are displayed in

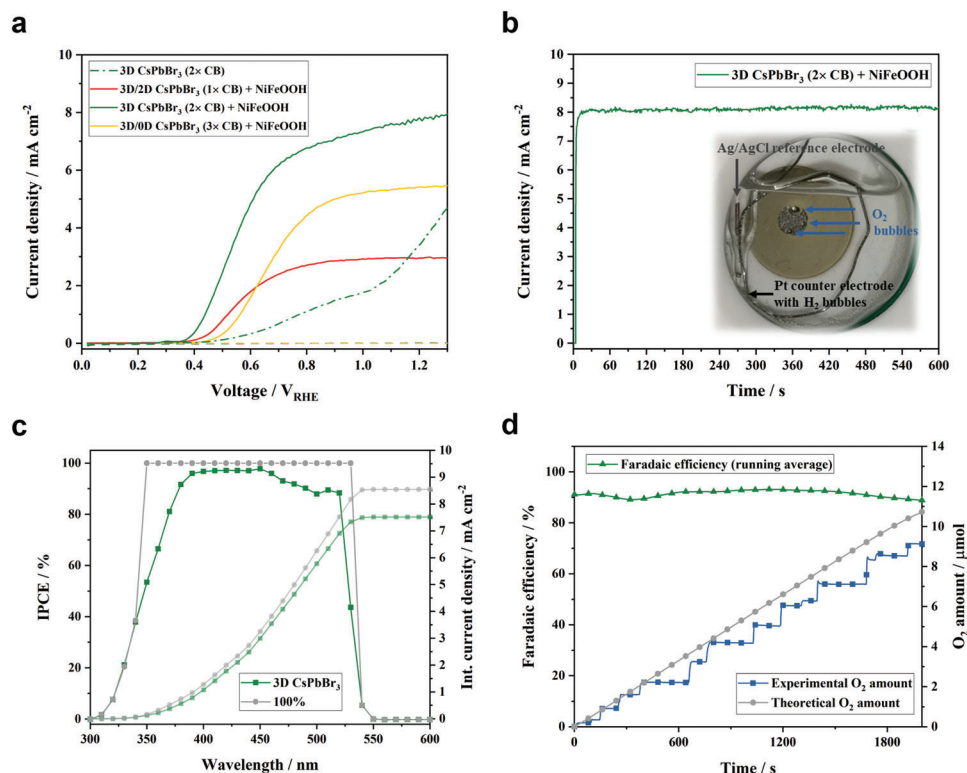


Figure 3. Photoelectrochemical performance of CsPbBr₃ photoanodes. a) OER polarization scans (50 mV s⁻¹ scan rate) in the dark (dashed lines) and under 1 sun illumination for photoanodes with (solid lines) and without (dash-dotted lines) NiFeOOH catalyst, applying CsPbBr₃ fabricated by varying number of chemical bath deposition and annealing steps (1–3× CB). b) 600 s operational photocurrent stability at +1.23 V_{RHE} of the highest performing 3D CsPbBr₃ photoanode. Inset: Photograph of the graphite-sheet-protected perovskite photoanode under operation in a three-electrode setup. c) IPCE spectra and integrated photocurrent density at +1.23 V_{RHE} of the 3D perovskite photoanode and a theoretical 100% IPCE device. d) Faradaic efficiency of the 3D CsPbBr₃ photoanode calculated from the experimental O₂ amount and the theoretical O₂ amount based on the measured photocurrent. All measurements were performed in an aqueous 1 M NaOH electrolyte.

Figure 2b (measurements in Figures S12 and S13, Supporting Information). The valence band edge (E_v) and Fermi level (E_F) values of the halide perovskite layers were measured by ambient photoemission spectroscopy and Kelvin probe, respectively. The conduction band edge (E_c) values of the halide perovskites were calculated from the E_v values and the 2.3 eV optical bandgap extracted from IPCE spectra (Figure 3c). The E_c of the perovskite layers are well positioned for electron transfer to the E_c of TiO₂ ETL; however, due to the lack of selective HTL, electron transport toward the carbon electrode could also happen, which would lead to non-radiative interfacial electron–hole recombination loss. For the 3D/2D CsPbBr₃ layer, such recombination loss is likely significant, as the Fermi level of the TiO₂ and the perovskite layers are close to each other, meaning that there is no interfacial band bending (i.e., electric field) driving photogenerated electrons toward the TiO₂.^[38,39] In contrast, the Fermi level of the 3D CsPbBr₃ is significantly deeper (–380 meV) leading to large band bending at the TiO₂/CsPbBr₃ interface and consequently enhanced photogenerated charge-carrier separation and transport. The Fermi level of the 3D CsPbBr₃ is also deeper (–150 meV) than that of 3D/0D CsPbBr₃. Regarding the E_v , the pure 3D CsPbBr₃ shows the deepest value at –5.4 eV, around 110 mV deeper compared to the E_v of other layers containing low-dimensional perovskites.

A deeper E_v with respect to the electrochemical potential of OER contributes to an increased driving force for water oxidation.^[40]

In order to gain a deeper understanding of the charge-carrier dynamics, steady-state and time-resolved photoluminescence (PL) measurements were performed. The normalized transient decay curves (Figure 2c) recorded for the perovskite layers deposited on top of FTO/TiO₂ show a much shorter PL lifetime (τ) for the 3D CsPbBr₃ (monoexponential decay, $\tau = 0.95$ ns) in comparison with the 3D/2D CsPbBr₃ (biexponential decay, $\tau_1 = 1.96$ ns, $\tau_2 = 7.84$ ns) and the 3D/0D CsPbBr₃ (biexponential decay, $\tau_1 = 1.61$ ns, $\tau_2 = 14.6$ ns). The exponential fitting parameters are summarized in Table S1, Supporting Information. In the presence of a good charge-transport layer (such as TiO₂ here), the first fast PL decay phase is typically assigned to charge transfer, while the second slower decay phase to bimolecular recombination.^[41] The much faster lifetime and lack of a second decay phase provide experimental evidence for the expected improved charge-carrier transfer from the 3D CsPbBr₃ to the TiO₂ ETL,^[42,43] in agreement with its deeper Fermi level and larger interfacial band bending. Such reduced PL lifetime and enhanced charge transfer have been shown to correlate with reduced non-radiative recombination and enhanced photovoltage.^[41,44] The steady-state PL results (Figure S14, Supporting Information)

confirm the same trend: negligible PL intensity of the 3D CsPbBr₃ layer, small intensity of the 3D/2D layer, and an order of magnitude higher PL intensity of the 3D/0D layer. In addition to the change in interfacial band bending at the TiO₂/perovskite interface, the presence of 2D and 0D perovskite phases in the bulk of the perovskite film is also expected to hinder charge transport.^[45,46] Note that this is different from the application of a very thin 2D perovskite top layer on top of a 3D one, used as a surface treatment in perovskite solar cells.^[36,47]

2.3. Photoelectrochemical Performance of Perovskite Photoanodes

The n-i-p structure photoanodes with different compositions were tested in a three-electrode setup in the dark and under 1 sun (AM1.5, 100 mW cm⁻²) illumination to identify the effect of electrodeposited NiFeOOH and CsPbBr₃ phases on the OER performance (Figure 3). Photoanodes with pure 3D CsPbBr₃ photoactive layer show a photocurrent E_{on} of +0.96 V_{RHE} (E_{on} was conservatively determined by linear fitting of the photocurrent rise above 1 mA cm⁻²). The same devices, but with NiFeOOH OER catalyst electrodeposited on the protective graphite sheet have a 560 mV lower E_{on} (+0.40 V_{RHE}). A similar shift of photocurrent E_{on} upon electrodeposition of NiFeOOH was also observed for 3D/2D CsPbBr₃ photoanodes (Figure S15, Supporting Information). Such significant improvement in performance confirms that the high OER catalytic activity of electrodeposited NiFeOOH on graphite sheet was successfully integrated into the perovskite-based photoanode.

Next, we focus on the effect of the perovskite phase on photoelectrode performance, while applying the same electrodeposited NiFeOOH-functionalized graphite sheet in each case (Figure 3a). The 3D/2D perovskite-based photoanode shows an E_{on} at +0.42 V_{RHE} and a relatively low j_{ph} (3 mA cm⁻² at +1.23 V_{RHE}), which are in accordance with its limited interfacial charge transfer observed by transient PL (Figure 2c) and its low absorption (Figure S4, Supporting Information). The pure-phase 3D CsPbBr₃ photoactive layer shows excellent performance, E_{on} of +0.40 V_{RHE} and j_{ph} of 7.9 mA cm⁻² at +1.23 V_{RHE}, superior to both the 3D/2D and 3D/0D perovskite-based photoanodes (Figure 3a). The 3D-CsPbBr₃-based device also shows a stabilized j_{ph} reaching 8.1 mA cm⁻² at +1.23 V_{RHE} (Figure 3b). The high performance of this 3D perovskite is in good agreement with its improved bulk and interfacial charge-carrier dynamics (Figure 2), its uniform perovskite layer with micrometer-sized large grains (Figure 1c), and its high absorption (Figure S4, Supporting Information). 3D CsPbBr₃ devices prepared in 6 different batches confirmed the low E_{on} at +0.40 ± 0.04 V_{RHE} and high j_{ph} at 7.9 ± 0.2 mA cm⁻² (Figure S16, Supporting Information). The enhanced charge transfer by the interfacial electric field reducing non-radiative recombination could also explain why the addition of Spiro-OMeTAD HTL did not improve further the performance of the 3D CsPbBr₃ photoanodes compared to the device without HTL (Figure S17, Supporting Information). Some hysteresis, which is typical for CsPbBr₃ solar cells, was observed for the photoanodes (Figure S18, Supporting Information).^[29,33] Although the 3D/0D perovskite layers also show high absorption, their devices reach a lower j_{ph} (5.4 mA cm⁻² at +1.23 V_{RHE}) and higher

E_{on} (+0.50 V_{RHE}), which can be explained by the poorer charge transfer due to their shallower energy levels (Figure 2) and unfavorable morphology (Figure S1, Supporting Information) leading to increased recombination losses. The E_{on} and j_{ph} values, as well as the observed trends, are in close correlation with the current-voltage curves of the photoelectrodes measured as solar cells, with the 3D CsPbBr₃ sample reaching the highest short-circuit current density of 8.1 mA cm⁻² (Figure S19, Supporting Information).

The high j_{ph} of the 3D CsPbBr₃ photoanode was confirmed by measuring IPCE at +1.23 V_{RHE}, which reached >95% in the wavelength range of 390–410 nm (Figure 3c). This demonstrates that the 2.3 eV optical bandgap perovskite photoanode is close to its theoretical, radiative j_{ph} limit (8.96 mA cm⁻²).^[48,49] with j_{ph} values nearly twice as high (up to 8.1 mA cm⁻²) as previously reported for CsPbBr₃ photoanodes.^[21] The onset of IPCE spectra at 540 nm allows the calculation of the effective optical bandgap of the 3D CsPbBr₃ layer at 2.3 eV, which is also confirmed by the absorption spectra (Figure S4, Supporting Information). The average Faradaic efficiency for O₂ evolution of the perovskite photoanode is 93% as displayed in Figure 3d. The measured amount of photoelectrochemically generated O₂ increases in steps, which is due to the formation of relatively large bubbles on the surface of the photoelectrode and their stepwise detachment (Figure 3b and Video S1, Supporting Information).

2.4. Operational Stability of CsPbBr₃ Photoanodes

The stability of OER j_{ph} under 1 sun illumination was tested for the 3D CsPbBr₃ photoanode at +1.23 V_{RHE}, and the porosity of the graphite sheet, as well as the thickness of the NiFeOOH catalyst layer, was investigated (Figure S20, Supporting Information). We discovered that the best stability could be achieved by applying a less porous (1.9 g cm⁻³ dense, 25 μm-thick) graphite sheet under the porous (1.2 g cm⁻³ dense, 70 μm-thick) graphite sheet, the latter functionalized by a ten times increased amount of NiFeOOH OER catalyst (Figures S3 and S7, Supporting Information). The stack of these two graphite sheets of different porosity allows both effective protection and high surface area for efficient OER reaction on NiFeOOH, leading to a record 70 h long operational stability at a stabilized photocurrent density of 6 mA cm⁻² (and 83% of initial j_{ph}). Moreover, these graphite sheets can be easily replaced upon signs of deterioration, extending the device lifetime to 110 h with one single replacement (Figure 4a). Strikingly, at the end of the stability measurement, 100% of the stabilized photocurrent density (j_{st}) was maintained while using only earth-abundant materials and both low-cost carbon-based electrodes and protection layers. This is in contrast with previously reported perovskite photoanodes (Figure 4b and Table S2, Supporting Information) that typically show a continuous decrease of the photoanode performance due to insufficient protection or instability of the hybrid organic-inorganic perovskite under reverse bias, and apply high-cost protection (e.g., Field's metal containing In) or expensive metal electrode layer (Ag or Au) and Spiro-OMeTAD HTL.^[16,23,24] Furthermore, the ability to repeatedly replace the inexpensive protective graphite sheet upon signs of degradation allows demonstration of even longer than

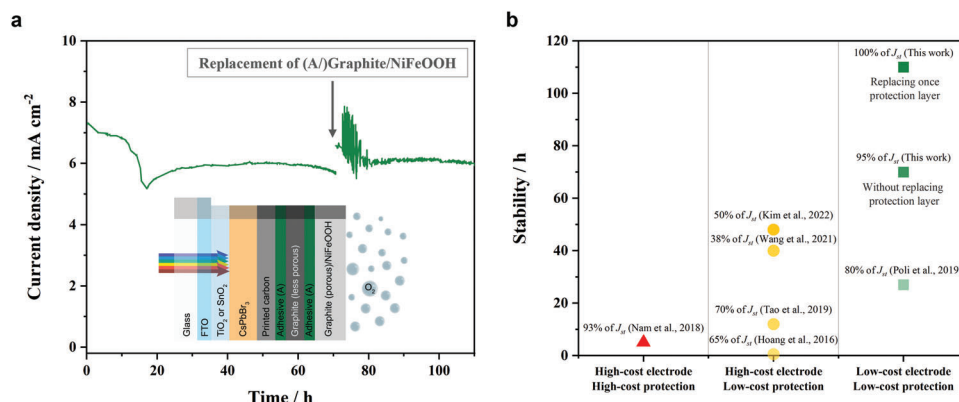


Figure 4. Operational OER stability of the perovskite photoanode. a) Continuous OER photocurrent stability under 1 sun illumination at +1.23 V_{RHE} of the optimized 3D CsPbBr₃ protected by a denser (25 μm-thick) graphite sheet and a NiFeOOH-functionalized graphite sheet (70 μm). The top graphite sheet was replaced after 70 h of operation with a freshly functionalized one. Inset: Schematic structure of the most stable perovskite photoanodes (not to scale). b) Comparison of OER photocurrent stabilities of reported perovskite photoanodes containing high- and low-cost electrodes and protection layers. The percentage of stabilized photocurrent density (j_{st}) maintained at the end of the stability measurement is indicated above the data points.

100 h operation, for example, >200 h (>1 week) stability (Figure S21 and S22, Supporting Information).

The replacement of the graphite sheet with freshly deposited NiFeOOH results in the recovery of initial j_{ph} , which is important in terms of upscaling, and confirms that the perovskite and transport layers remain intact in the first phases of device degradation. An initial decay (and sometimes fluctuation of j_{ph}) is observed each time the graphite sheet is replaced, which we assign to morphological changes of the graphite sheet due to bubbles forming between its buried layers resulting in increased porosity and loss of some of the catalyst, and partially to bubble formation reducing the electrochemically active surface area (even under stirring). If the NiFeOOH is not replaced, the graphite sheet will start degrading next (which can be delayed by increasing the amount of electrodeposited electrocatalyst) and become more permeable to water (SEM images in Figure S23, Supporting Information), which will reach and degrade the photoactive layer as a third step, leading to non-recoverable losses (Figure S22, Supporting Information). The presented >100 h photoanode stability

was achieved considering all these degradation mechanisms: the loss of NiFeOOH was successfully addressed by replacing the top, catalyst-functionalized graphite sheet or by depositing a thicker layer of NiFeOOH. The increasing porosity of the top graphite sheet was circumvented by applying a thicker graphite sheet or a second denser graphite sheet underneath (Figures S20 and S21, Supporting Information).

2.5. Scalable and Low-Temperature-Processed Perovskite Photoanodes

To demonstrate the scale-up potential of the stable 3D CsPbBr₃ photoanodes, devices with the increased photoactive area were fabricated (Figure 5a,b and Figure S24, Supporting Information). The smallest area (0.03 cm²) devices reach an average j_{ph} of 8 mA cm⁻² at +1.23 V_{RHE}, of which 100% and ~90% is maintained when increasing the area nine times (0.28 cm²) and over 35 times (up to 1.13 cm²), respectively. Finally, cost-effective

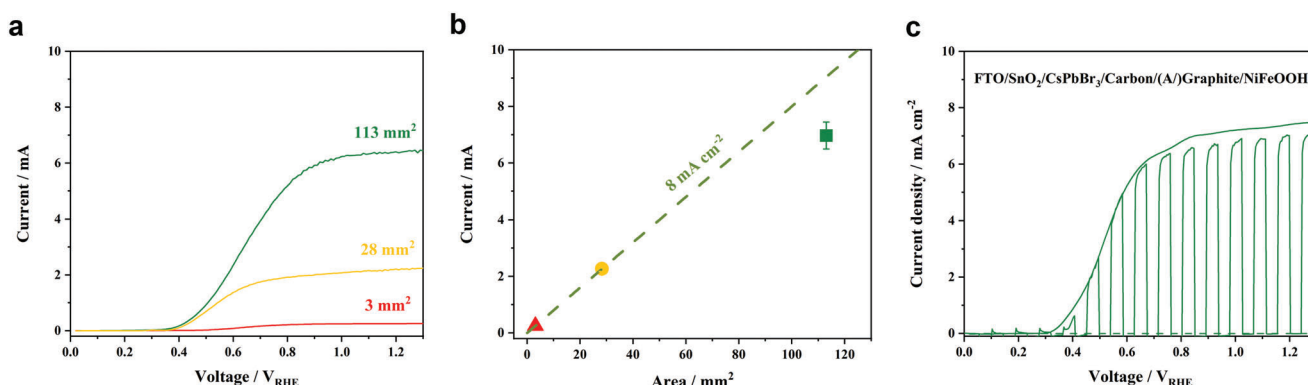


Figure 5. Scalable and low-temperature processed, earth-abundant materials containing perovskite photoanodes. a,b) OER polarization scans (50 mV s⁻¹ scan rate) under 1 sun illumination of 3D CsPbBr₃ photoanodes with different active areas, and comparison of the photocurrents generated at +1.23 V_{RHE}. The error bars represent one standard deviation in all cases (if not visible, it is because they are smaller than the symbol size). c) OER polarization scans (50 mV s⁻¹ scan rate) under continuous and chopped 1 sun illumination (solid line) and in dark (dashed line) of low-temperature processed perovskite photoanodes.

processability was further demonstrated by changing the TiO₂ ETL that needs annealing at 500 °C to a tin oxide (SnO₂) layer fabricated by low-temperature (90 °C) CB deposition. The SnO₂ ETL together with low-annealing-temperature carbon paste (70 °C) and relatively low-temperature (70 and 250 °C) processed 3D CsPbBr₃ photoanodes allowed reaching j_{ph} of 7.5 mA cm⁻² at +1.23 V_{RHE} (Figure 5c). These developments are expected to significantly reduce (more than 50%) the cost of such photoelectrodes, especially considering the application of solely earth-abundant materials.^[50]

3. Conclusion

A low-cost, solution-processed CsPbBr₃ photoanode containing only earth-abundant materials was presented, applying no selective HTL, low-annealing-temperature carbon paste, self-adhesive protective graphite sheets of different porosity, and electrodeposited NiFeOOH electrocatalyst. The electrodeposition of the catalyst provided a straightforward, quick (1–2 min), and inexpensive way of increasing the OER catalytic activity over the large surface area of the graphite sheet, leading to 560 mV cathodic shift in the OER onset potential value of photoelectrodes, reaching as low as +0.40 V_{RHE}. Controlling the perovskite phase via a simple, low-temperature (70 °C) and quick (2× 5 min) chemical bath deposition step allowed to achieve a 3D CsPbBr₃ layer with micrometer-size grains and increased electric field at the ETL/perovskite interface helping separation and transfer of photogenerated charge-carriers. These enhancements allowed the fabrication of 3D CsPbBr₃ photoelectrodes reaching above 95% IPCE and 8.1 mA cm⁻² j_{ph} at +1.23 V_{RHE} with record perovskite photoanode stability: 83% of the initial and 100% of the stabilized photocurrent being maintained after 110 h of continuous operation. The high potential of the photoanodes in real-world applications was evidenced by large area (>1 cm²) devices reaching ≈90% j_{ph} of their small area counterparts, as well as applying chemical bath deposited SnO₂ ETL to achieve low-temperature solution-processed, low-cost perovskite photoanodes.

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

The data that support the findings of this study are openly available in the Imperial College London Research Data Repository at <https://doi.org/10.14469/hpc/13248>.

Keywords

earth-abundant materials, halide perovskites, photoanodes, photoelectrochemical, weeks-long stability

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