Electrochemical Deposition of CsPbBr₃ Perovskite for Photovoltaic Devices with Robust Ambient Stability

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ABSTRACT: Alkali halide perovskites have emerged as representative candidates for novel opto-electronic devices owing to their balanced efficiency and stability. However, their fabrication method still remains a challenging topic with conflicts among their effectiveness, complexity, and cost. Herein, a complete two-step electrochemical method has been applied in the fabrication of inorganic perovskites for the first time. The dimension and microstructure of CsPbBr₃ can be easily controlled by variation of simple physical parameters during the fabrication. By optimizing the parameters, high-quality CsPbBr₃ films are obtained, and the champion device has achieved an efficiency of 7.86% with a high open-circuit voltage of 1.43 V. More importantly, the as-fabricated materials have shown an extraordinary robust stability against environmental conditions even after 150 days of exposure to air without encapsulation. This has evidently proved the electrochemical methods as an effective route for perovskite synthesis in its future development.



KEYWORDS: inorganic perovskite, electrochemical fabrication, controllability, long-term stability, photovoltaics

1. INTRODUCTION

In the past decade, novel hybrid halide perovskites have attracted widespread attention because of their low cost, easy fabrication,^{1,2} and excellent photovoltaic characteristics (tunable band gap,³⁻⁵ high absorption coefficient,⁶ and long carrier diffusion length⁷⁻¹⁰). Until now, the efficiency of perovskite solar cells (PSCs) has exceeded 25%, already comparable to that of high-level commercial silicon cells.¹¹⁻¹³ However, despite their rapid development, the related research works toward practical applications have been haunted by the stability problem caused by the reactivity between unstable contents such as methylammonium (MA⁺) and formamidinium (FA⁺) ions versus alien ions and influence from other environmental factors (heat, light, etc.).¹⁴⁻¹⁶ As one alternation, inorganic halide perovskites have shown much better stability against those factors by substituting the organic groups with alkali metals, especially Cs.¹⁷⁻²² Furthermore, the stability of inorganic perovskites has so far shown the highest enhancement using Br as the halide component.²³⁻²⁷ This has made cesium-lead bromide perovskite (e.g., CsPbBr₃) a suitable candidate for a short-wave absorber in novel highefficiency tandem solar cells as well as in other opto-electronic devices.²⁸⁻³⁰

Generally, most fabrication methods for CsPbBr₃ can be categorized into two routes: solution-based chemical reactions and vacuum-based gaseous evaporation, since the first synthesis of CsPbBr₃ PSCs by Kulbak et al. in 2015 (with $\eta \sim 5.95\%$).³¹ The mainstream solution-based methods are

one-¹² or two-step^{24,32,33} spin-coatings, with alternations such as multistep spin-coating by the Tang group (achieved up to 10.18% efficiency with modifications),^{34,35} or further modifications such as layer and interfacial engineering by Liu et al. (up to 8.79% efficiency by solution-dipping, multistep spincoating, and layer passivation).²⁷ The solution-based methods normally require less instrument support; however, they normally contain many steps that can bring more complexity and thus deteriorate the reproducibility. Comparatively, the vacuum-based evaporation methods can easily deposit higher quality films and in the meantime have adequate production rate. For instance, Liu et al. have achieved efficiencies of $CsPbBr_3$ PSCs up to 8.65% and 6.95% by single- and dual-source evaporation, respectively. 36,37 A higher 8.86% record has been achieved by Cheng et al. using a multistep sequential dual-source method.³⁸ Finally, with the coexistence of CsPb₂Br₅ and Cs₄PbBr₆ phases, a record efficiency of 10.91% has been achieved by the Qi group, so far the best by the evaporation method.³⁹ Nevertheless, evaporation methods have much more requirement on the fabrication criteria, for example, good vacuum as the preliminary condition to ensure

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Figure 1. Overview of the EC fabrication of $CsPbBr_3$: (a) schematic illustration of the EC method for the preparation of $CsPbBr_3$ films and the corresponding top-view SEM images of Pb and $CsPbBr_3$; (b) XRD patterns of Pb and $CsPbBr_3$ films; (c) UV-vis absorption spectrum and steady-state PL spectrum of $CsPbBr_3$ films; (d) structure of the integrated PSCs; and (e) energy-level diagram for the charge-transfer process.

high quality of products. There are still other alternate methods such as spray-assisted deposition, quantum dotbased dissolution and recrystallization, pulsed laser deposition, and so forth but can be more or less concluded to the above two routes.^{40–42} In general, a more feasible method is expected that combines the advantages of both routes while avoiding their disadvantages, which calls up electrochemical (EC) methods that have been proved as a route with good balance in all the above manners with controllable motion of the reactive species (normally ions) and their reactions and low instrumental criteria.^{43–46}

In this work, we have applied the unconventional EC deposition strategy on the direct fabrication of inorganic alkali halide perovskites for the first time. This method can be totally carried out in air at room temperature, with highly controllable grain size and thickness of the products and fast fabrication within a few minutes. The grain size and thickness of CsPbBr₃ films can be easily controlled by adjusting the Pb deposition current and time; meanwhile, the crystallinity of the perovskite layer can be controlled by regulating the CsPbBr₃ conversion voltage and time. By optimizing the CsPbBr₃ film morphology and thickness, an adequate efficiency of up to 7.86% has been achieved so far in the as-prepared PSCs with the $FTO/c-TiO_2/$ m-TiO₂/CsPbBr₃/spiro-MeOTAD/Au structure. What is more, the as-fabricated device has shown quite robust stability even after a long-time exposure of 150 days to natural light and air (RH: 40-50%), which could have been favored by the action of field-induced lattice contraction in the EC process. Such feasibility of fabrication and impressive performance of materials will hopefully give light to the future development of applicable perovskite devices in general.

2. EXPERIMENTAL SECTION

2.1. Materials. The FTO-coated glasses $(15 \ \Omega \cdot sq-1)$, compact-TiO₂ (c-TiO₂) spin-coating pastes, mesoporous-TiO₂ (m-TiO₂) spincoating pastes, and spiro-MeOTAD were purchased from Shanghai MaterWin New Materials Co., Ltd., China. Lead(II)iodide (PbI₂, 99%) was bought from Sigma-Aldrich. Cesium bromide (CsBr) was acquired from Xi'an Polymer Light Technology Corp.

2.2. Material and Device Fabrication. The FTO substrates were ultrasonically cleaned in detergent, deionized water, acetone, isopropanol, and ethanol bath sequentially for 20 min at each step, followed by an ultraviolet ozone treatment of 20 min. The c-TiO₂ layer has been prepared by sequential spin-coating with 0.15 and 0.30 M c-TiO₂ pastes on clean FTO at 4000 rpm for 30 s at each step, with

postannealing at 500 °C for 30 min. The m-TiO₂ layer has been prepared by spin-coating m-TiO₂ pastes (4 wt %) on FTO with annealed c-TiO₂ at 4000 rpm for 30 s and sintered at 500 °C for 45 min. The EC preparation of the CsPbBr3 perovskite layer was carried out in two steps under atmospheric conditions with a Pt sheet of 4 cm² as the counter electrode. The first step was the deposition of Pb onto m-TiO₂/c-TiO₂/FTO with 0.02 M PbI₂ isopropanol solution. The second step was the conversion of Pb into CsPbBr3 perovskite under a positive bias in a methanol solution of CsBr (15 mg·mL⁻¹). The as-fabricated samples were annealed in the muffle furnace at 250 °C for 10 min. The hole-transporting material (HTM) has been prepared by spin-coating the precursor [prepared by dissolving 72.3 mg of spiro-MeOTAD, 28.8 μ L of 4-*tert*-butylpyridine, and 17.5 μ L of acetonitrile solution of lithium bis(trifluoromethylsulfonyl)imide (520 $mg \cdot ml^{-1}$) in 1 mL chlorobenzene] onto the perovskite surface at 4000 rpm for 30 s. The as-fabricated samples were placed into a drying cabinet overnight. Finally, the upper electrode of 80 nm thick gold was deposited on top of the HTM by thermal evaporation.

2.3. Material and Device Characterization. The morphology of the samples has been characterized by field-emission electron scanning microscopy (Zeiss Ultra Plus). The absorption spectrum of perovskite films was characterized using an ultraviolet-visible (UV-vis) spectrophotometer (Lambda 35, PerkinElmer). The crystallinity of the perovskite samples was investigated by X-ray diffraction (XRD) using a polyfunctional X-ray diffractometer (D8 ADVANCE Da Vinci, Bruker). The steady-state photoluminescence (PL) and time-resolved PL (TRPL) spectra were measured using a steady-state and time-resolved fluorescence spectrophotometer (QM/TM/IM, PTI) with excitation lasers of 325 nm and 340 nm, respectively. The J-V curves of CsPbBr₃ solar cells were tested using a solar simulator (2612A, Newport) under standard 1 sun (AM 1.5). EC impedance spectroscopy (EIS) was measured using an EC workstation (CS350H, Corrtest).

3. RESULTS AND DISCUSSION

3.1. Preliminary Results of EC Deposition of CsPbBr₃. As shown in Figure 1a, the two-step EC method is as follows: 1. deposition of lead, where Pb nanoparticles are formed by reduction of Pb²⁺ on the surface of m-TiO₂/c-TiO₂/FTO using the galvanostatic mode; 2. conversion of Pb into a yellow CsPbBr₃ thin film by the cooperation of field-induced drift and thermal diffusion of Cs⁺ and Br⁻ from the CsBr precursor using the potentiostatic mode. Small islands are evenly formed on the TiO₂ surface after step 1 and much larger islands are developed after step 2 that have fully covered the surface. According to XRD patterns in Figure 1b, significant peaks appear at 31.28 and 36.27° after step 1 and peaks at 15.22,



Figure 2. Effects of EC deposition current (I_{Pb}) of Pb: SEM images (a) and statistics of grain sizes (b) for Pb and CsPbBr₃ (Pb was deposited for 300 s and CsPbBr₃ was converted at 3.0 V for 800 s); (c) average grain size $(D_{Pb} \text{ and } D_{PVSK})$ and thickness $(d_{Pb} \text{ and } d_{PVSK})$ of Pb and CsPbBr₃ vs I_{Pb} ; (d) pinhole coverage vs I_{Pb} ; (e) XRD patterns of CsPbBr₃ films vs I_{Pb} ; (f) PL and (g) TRPL spectra of CsPbBr₃ fabricated at different I_{Pb} values; and (h) characteristics of CsPbBr₃ PSCs with different I_{Pb} values.

21.66, 30.72, and 34.54° are observed after step 2, which correspond to (111) and (200) crystal planes of Pb (PDF#01-0972) and $(\overline{100})$, $(\overline{110})$, $(\overline{200})$, and $(\overline{210})$ planes of CsPbBr₃ (PDF#18-0364), respectively. This has clearly proved the effective formation of Pb and CsPbBr3 after steps 1 and 2, respectively. The UV-vis spectrum in Figure 1c indicates a characteristic absorption peak at 520 nm [corresponding to E_{a} ~ 2.33 eV from the fitted $(Ahv)^2 - hv$ plot shown in the inset].^{32,47} Figure 1c presents the PL peak of the as-fabricated CsPbBr₃ film located at 525 nm, which is comparable to its optical band gap. Finally, a power conversion efficiency (PCE) of 2.41% was obtained (exhibited in Figure S1) after integrating the as-fabricated sample into a n-i-p-type PSC (configuration and energetic diagram are shown in Figure 1d,e). Such a low performance compared to representative results^{27,37–39,48} could be due to the large quantity of recombination centers from the pinholes, which makes further modulation necessary.

3.2. Influence of Pb Deposition Current and Time on EC Perovskite. To solve this problem, the first study has been carried out for the influence of physical parameters of the first step on the final products. As shown in Figure 2a, the grain sizes of both Pb and CsPbBr₃ increase with increasing deposition current (I_{Pb}). The statistical results indicate that the average grain size of Pb (D_{Pb}) almost linearly increases from ~140 to ~240 nm with the deposition current (Figure 2b,c). Correspondingly, the average grain size of CsPbBr₃ (D_{PVSK}) also increases from ~450 to ~510 nm. The thickness of as-formed Pb and CsPbBr₃ has also shown similar positive dependence on the increase of Pb deposition current. Moreover, the pinhole coverage of CsPbBr₃ films (defined as

the pinhole area divided by the overall area) decreased with the increase of $I_{\rm Pb}$ and then increased, reaching a minimum at -4mA, less than 0.5%, as presented in Figure 2d.^{49,50} At $I_{\rm Pb} < -4$ mA, the decrease of pinhole density at a lower current density should be due to the higher coverage of Pb particles formed in the first step that can facilitate the full coverage of CsPbBr3 in the second step. At $I_{\rm Pb}$ > -4 mA, bubbles can occur at the TiO₂ surface by some side reaction (reduction of hydrogen), which could significantly deteriorate the formation of a complete film and enhance the pinhole formation again.^{51,52} The XRD patterns in Figure 2e have shown the significant existence of characteristic peaks for CsPbBr₃ at 15.22, 21.66, 30.72, and 34.54° with different current values. What is more, the intensity peak at 21.66° (corresponding to the (110) crystal plane, the main content of CsPbBr₃) varies with the current, with the highest peak intensity and the smallest fullwidth at half-maximum (fwhm) of 0.156 at -4 mA, indicating the best crystallinity of the CsPbBr₃ film under this condition (details can be found in Table S1 in the Supporting Information).³⁹

As for the electro-optical behavior (Figure 2f), all the PL peaks are located at ~525 nm. The maximum PL intensity is achieved at -4 mA, indicating the highest photoinduced carrier yield and weak recombination.³⁷ This is also supported by TRPL curves in Figure 2g, which have been fitted by a biexponential function: $I_{(t)} = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The average carrier lifetime τ_{avg} can be calculated using the formula $\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$, where τ_1 and τ_2 are the fast and slow components of decay times, respectively, and A_1 and A_2 are the fast and slow decay amplitudes, respectively. In the case of insulated samples in this



Figure 3. Effects of EC deposition time (t_{Pb}) of Pb: (a) statistics of average grain size $(D_{Pb} \text{ and } D_{PVSK})$ of Pb and CsPbBr₃ vs t_{Pb} ; (b) average thickness $(d_{Pb} \text{ and } d_{PVSK})$ of Pb and CsPbBr₃ vs t_{Pb} ; (c) XRD patterns of CsPbBr₃ films; (d) PL and (e) TRPL decay curves of the corresponding CsPbBr₃; and (f) J-V statistical graph of PSCs fabricated under increasing t_{Pb} . $(I_{Pb} \text{ is } -4 \text{ mA. CsPbBr}_3 \text{ is converted at 3.0 V for 800 s.})$

experiment, the decay of PL should be mainly induced by the bulk defects and interface recombination, so a longer lifetime corresponds to a better photoelectric quality (details of fitting can be found in Table S2 in the Supporting Information).^{24,53,54} The longest carrier lifetime of 5.15 ns has been obtained at -4 mA, matching well with the PL and XRD results. In summary, with the increase of Pb deposition current, the grain size of perovskite becomes larger, while the coverage and crystal quality of the CsPbBr₃ film are improved. This has also been further represented by the I-V characteristics of PSCs, as shown in Figure 2h (which can also be referred to from Figure S2 and Table S3); the PCE first increases and then decreases with the increase of the Pb deposition current. The drop in the performance at currents larger than -4 mA could be mainly due to the side reactions (e.g., formation of H_2 bubbles at the cathode) in the first deposition that had reduced the uniformity and enhanced the carrier recombination of the film.

Second, the deposition time of the Pb layer (t_{Pb}) could also be an important factor affecting the crystal formation. Figure 3a,b shows a positive and an almost linear dependence of the Pb grain size and thickness on the deposition time, where the grain size and thickness increase, respectively, from ~220 to \sim 290 nm and from \sim 180 to \sim 380 nm with the time increasing from 350 to 500 s. Correspondingly, the variation of the grain size of CsPbBr3 versus time (increases from ${\sim}500$ to ${\sim}525$ nm) appeared to be quite small compared to CsPbBr₃ thickness (increases from ~450 to ~750 nm). This means that the thickness other than the grain size of as-formed perovskite is more strongly influenced by the grain size of Pb precursors. This phenomenon could be due to the significant volume expansion from Pb to CsPbBr₃ in the whole procedure: as also shown in Figure 1a, there has been a significant distance among the Pb particles, but after step 2, the coverage of CsPbBr₃ has become almost 100% on the surface under all conditions (also shown in Figure S3 in the Supporting Information). Therefore, the significant size increase of Pb particles will more likely result in much more significant enhancement of CsPbBr₃ formation along the vertical direction due to the confinement of space in the horizontal direction. Nevertheless, the increase of Pb particle size can still induce other effects in the horizontal direction, that is, certain stress can be generated and therefore more interfacial defects or even

certain film deformation could result (which can be referred to from Figure S4 in the Supporting Information).⁵⁵ Furthermore, some structural change also emerges with the deposition time of Pb, as shown in the XRD pattern in Figure 3c. For t_{Pb} < 400 s, only pure CsPbBr₃ phase is detected. After 400 s, new peaks emerge at 11.6, 18.8, 29.4, and 33.4°, corresponding to the (002), (112), (213), and (310) orientations of the CsPb₂Br₅ phase (PDF#25-0211), respectively. The relative intensity of those peaks increases with further increase of $t_{\rm Ph}$ in the first step, which indicates the increase of the CsPb₂Br₅ content when $t_{\rm Pb}$ > 400 s. Considering the stoichiometry of CsPb₂Br₅ and CsPbBr₃, this phenomenon is likely to be due to the overdosed Pb formed at too long t_{Pb} that could react with more field-transported Br- anions in the solution and thus enhance the formation of $CsPb_2Br_5$ with the relative shortage of Cs^{+.46} As evidence, if more CsBr is added in step 2, all the characteristic peaks of CsPb₂Br₅ will be significantly attenuated, as shown in Figure S5 and Table S4.

As a consequence, the intensity of the steady-state PL of the samples gradually increases with t_{Pb} when $t_{Pb} < 400$ s but drops remarkably with t_{Pb} > 400 s (Figure 3d). This drastic change should be mainly attributed to the emergence of CsPb₂Br₅, which is a PL inactive component with an indirect band gap due to the long-time reaction.^{39,56} Similar evidence can be found in TRPL measurements in Figure 3e. The carrier lifetime also first increases and then decreases with increasing Pb deposition time, reaching a maximum of 10.80 ns at $t_{\rm Pb}$ = 400 s (detailed fitting results can be referred to from Table S5 in the Supporting Information). When $t_{\rm Pb}$ > 400 s, the recombination is mainly caused by bulk defects, while the interface recombination begins to increase with the appearance of CsPb₂Br₅. The as-fabricated perovskites have been integrated into PSCs with J-V characteristics shown in Figure 3f. When the time is shorter than 400 s, both $J_{\rm SC}$ and PCE show an increasing trend, which could be easily understood by the facilitation of higher thickness on the photon absorption.⁴² However, the PCE has shown significant declination at t_{Pb} > 400 s. This behavior may be induced by the same origin for the XRD, PL, and TRPL results. When the deposition time is 400 s, the average thickness of the perovskite film is 525 nm (close to the theoretically calculated optimal value of 500 nm^{57}), showing the best performance ($\eta \sim 6.00\%$, $V_{\rm OC}$ = 1.38 V, $J_{\rm SC}$ = 6.93 mA cm⁻², and FF = 0.63).



Figure 4. Influence of CsPbBr₃ perovskite conversion voltage (U_{PVSK}) in step 2 (all Pb deposited at -4 mA for 400 s). (a) SEM images of CsPbBr₃ converted at different U_{PVSK} ; (b) statistical graph of the average grain size of CsPbBr₃; (c) XRD patterns of CsPbBr₃ films; (d) PL and (e) TRPL decay curves of the corresponding CsPbBr₃; (f) EIS Nyquist plots; and (g) PCE statistic graph of PSCs prepared under different U_{PVSK} .

3.3. Effect of Conversion Voltage and Time on the **Perovskite.** Furthermore, the voltage amplitude (U_{PVSK}) in step 2 can also significantly influence the as-formed perovskite. As shown in Figure 4a,b, the average grain size of perovskite has first shown a rising and then a descending trend with increasing voltage, with the maximum value of ~624 nm achieved at \sim 2.5 V. The surface of the product is quite uniform when U_{PVSK} is below 2.5 V. However, a significant etching effect has appeared at some positions for voltages higher than 2.5 V (indicated by the circles in Figure 4a). This change in uniformity can be possibly due to distortion of the electric field induced by surface roughness that can magnify the variation of local field intensity at higher voltages.^{58,59} When the local field intensity is too high, certain EC etching effect will be generated at certain sites with a higher curvature.^{46,60-62} As a result, smaller grains and more boundaries can be generated at those positions. Furthermore, the microstructures of samples have also been investigated by XRD. As shown in Figure 4c, when the U_{PVSK} is small, typical characteristic peaks of CsPbBr₃ (15.2, 21.7, and 30.8°) are detected in the perovskite films. As the U_{PVSK} gradually increases to 3.0 V, CsPb₂Br₅ diffraction peaks (11.6, 29.2, and 33.2°) begin to appear. Noticeably, the intensity of the diffraction peak with the (110) crystal plane (21.7°, main content in the perovskite) first rises with increasing voltage, reaches maximum at 2.5 V, and then decreases again, with the corresponding fwhm following the opposite trend (detailed in Table S6). This indicates that the perovskite film converted at 2.5 V has the best crystallinity.³⁹ The emergence of CsPb₂Br₅ could be mainly due to the faster reaction speed caused by the higher voltage, which enhances the consumption of Cs⁺ and Br⁻ near the substrate. The higher field intensity accelerates the drift of Cs⁺ to the counter electrode and leaves a Br-enriched layer near the substrate. Like the modulation on the Pb-deposition step, this effect can also be diminished by the addition of CsBr in step 2 (see Figure S6 in the Supporting Information). As another interesting consequence of this operation, the peak width of CsPbBr₃ will also become narrower (see Table S7 in the

Supporting Information), corresponding to larger crystal domains and better crystallinity.

Consequently, this evolution has induced significant influence on the electro-optic properties of materials. The PL spectrum also illustrates a curve that first rises and then descends (in Figure 4d), which is mainly due to the appearance of CsPb₂Br₅ phase.^{41,56} The PL of the sample at 3.5 V has shown a blue shift from 525.3 nm (at 2.5 V) to 523.8 nm, mainly owing to the appearance of $CsPb_2Br_5$ with a wider band gap of 3.45 $eV_{7}^{37,39,63}$ which also leads to a significant quenching effect. Similar behavior is also indicated by TRPL. The lifetime of the perovskite film increases from 12.06 ns at 2.0 V to 12.50 ns at 2.5 V and then drastically decreases to 1.5 ns at 3.5 V. The positive dependence of lifetime at lower voltages could be due to the positive dependence of crystallinity on the voltage under this condition. According to previous discussion, when the voltage is too high (>2.5 V), certain etching effect begins to appear and can lead to a significant increase of the interfacial recombination and a drastic decrease in the lifetime (detailed fitting results can be found in Table S8). In addition, EIS has been performed in the dark environment at a bias close to $V_{\rm OC}$ to further study the charge-interface transport. As shown in Figure 4f, only the high-frequency region of the Nyquist plots can be observed, which is mainly related to the recombination processes.^{64,65} As is commonly known, the intercept on the horizontal axis and the arc are related to the serial resistance R_s and the recombination resistance R_{rec} , respectively. A smaller intercept and a larger arc radius indicate the lower serial resistance and higher recombination resistance, respectively, which lead to a better performance of the material in devices. As demonstrated in Figure 4f and Table S9, the recombination resistance $R_{\rm rec}$ increases first and then decreases with the increase of voltage, with the maximum achieved at 2.5 V. This indicated 2.5 V as the more optimal condition for the as-fabricated product as interfacial recombination is a more dominant factor that influences the device performance than the serial resistance.^{36,66,67} Furthermore, the time of conversion step also

influences the formation of the final product. When the conversion time is less than 400 s, there has been some existence of $CsPb_2Br_5$, which will gradually vanish with increasing time, until it completely disappears at 800 s (the corresponding details can be found in Figure S7 and Table S10 in the Supporting Information). No significant change can be observed for the reaction time longer than 800 s. Finally, the perovskite thin films converted under different voltages are integrated into PSCs. The optimal U_{PVSK} appears to be around 2.5 V, according to photovoltaic characteristics exhibited in Figure 4g (see details in Figure S8 and Table S11 in the Supporting Information).

3.4. Performance and Stability of EC CsPbBr₃ in Solar Cells. Figure 5a exhibits the statistics of PCE of all PSCs with



Figure 5. Performance of EC CsPbBr₃ in photovoltaic devices: (a) PCE histogram of PSCs with CsPbBr₃ prepared under optimal conditions; (b) J-V curves measured under forward and reverse scans for the best cell; (c) stability of CsPbBr₃ cells without encapsulation in ambient air with RH 40–50% at 25 °C; and (d) comparison of the water droplet contact angle of the CsPbBr₃ layer prepared by the traditional spin-coating method and the EC method (insets show the samples with the maximal contact angle).

CsPbBr₃ fabricated under optimized conditions (step 1: -4 mA for 400 s; step 2: 2.5 V for 800 s), indicating quite good reproducibility of the electrochemical fabrication for CsPbBr₃. The J-V curve of the champion device is presented in Figure 5b, showing η of 7.86% (with $V_{\rm OC}$ = 1.43 V, $J_{\rm SC}$ = 8.85 mA cm^{-2} , and FF = 0.62) by reverse scanning. To further study the stability of the cells, the samples have been tested via the ISOS-LC-1 protocol,⁶⁸ which had been stored under natural light in air (RH 40-50%, 25 $^{\circ}\mathrm{C})$ without encapsulation and tested under AM 1.5 (1 sun) by a solar simulator. As shown in Figure 5c, the device had shown no significant degradation of PCE during the storage of 150 days (the degradation is just about 0.3% against its original value). Such robust stability could be due to significant lattice contraction compared to normal CsPbBr₃ (details can be found in Table S12 in the Supporting Information) by certain field-induced annealing effect.^{46,69} According to the previous literature, as a ferroelectric material, the crystal undergoes electrostriction under the action of an external electric field and the corresponding lattice constant and unit cell volume will change to reduce the electrical strain. Therefore, the unit cell volume of the obtained CsPbBr3 film will reduce.^{70,71} Compared to the standard sample, the unit cell volume of EC CsPbBr₃ (step 1: under -4 mA for 400 s; step 2:

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at 2.5 V for 800 s) is reduced from 200 Å³ of the standard sample to 197.47 Å³ in the EC sample, which is a reduction of 1.3%. In addition, the EC CsPbBr₃ has shown a much more hydrophobic surface than the traditional spin-coated ones, which partly explains its tolerance to the ambient conditions without encapsulation (Figure 5d).⁷²

4. CONCLUSIONS

In summary, the direct EC synthesis method has been successfully applied in all-inorganic CsPbBr₃ perovskite films. The thickness and grain size of the products can be well controlled by simply tuning the physical parameters (current, voltage, and time) during the process. Consequently, the optoelectronic properties of the material can be effectively influenced and optimized. The emergence of an additional phase $(C_{s}Pb_{2}Br_{5})$ could also be formed by a side reaction or too high voltage, which could be easily controlled by some simple chemical operation. As a result, so far the highest PCE of 7.86% has been achieved in typical n-i-p PSCs, with a $V_{\rm OC}$ of 1.43 V, a J_{SC} of 8.85 mA cm⁻², and a FF of 0.62. Furthermore, the unencapsulated perovskite cell still maintained ~99.7% of its original PCE even after 150 days of storage in air (40-50 RH % and RT) under natural light, showing quite impressive tolerance to the environment and long-term stability. Hopefully, this work could offer some facilitative light in the development toward more ideal and applicable devices with high efficiency, robust stability, and low cost.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c14816.

J-V characteristic curves; SEM images of CsPbBr₃ films; XRD patterns and data; and fitting results of TRPL decay (PDF)

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Author Contributions

X.W. and H.L. jointly completed the experimental plan, experiments, data analysis, and manuscript writing. S.A., D.Z., J.W., Y.W., and Z.C. participated in related discussions and aided the experiments. This project was completed under the guidance and supervision of W.S. and H.L. All authors have approved the final version of the manuscript.

Notes

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ABBREVIATIONS

PSCs, perovskite solar cells PCE, power conversion efficiency V_{OC} , open-circuit voltage J_{SC} , short-circuit current density FF, fill factor c-TiO₂, compact TiO₂ m-TiO₂, mesoporous TiO₂ EC, electrochemical method TS, traditional spin-coating method SEM, scanning electron microscopy XRD, X-ray diffraction PL, photoluminescence TRPL, time-resolved photoluminescence fwhm, full-width at half-maximum RT, room temperature

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