Slow halide exchange in CsPbIBr₂ films for high-efficiency, carbon-based, all-inorganic perovskite solar cells

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ABSTRACT Halide exchange offers a versatile way to modify the properties of halide perovskites, but it is particularly challenging to slow the reaction rate to restrain defect growth in the products. Herein, we propose a slow halide exchange strategy to simultaneously fine-tune the optical and microstructural characteristics of CsPbIBr₂ films by physically pairing CsPbIBr₂ and CH₃NH₃PbI₃ films. Once a proper heating treatment is applied, halide exchange of Br[−] and I[−] ions between the films is activated, and the reaction rate can be well-controlled by the heating recipe, in which a high temperature can accelerate the exchange reaction, while a low temperature slows or stops it. By using an optimal halide exchange temperature (110°C) and time (2 h), the parent CsPbIBr₂ film was transformed into high-quality CsPbI_{1+x}Br_{2−x} film, featuring an extended absorption onset from 590 to 625 nm, coarsened grains, improved crystallinity, reduced surface roughness, suppressed halide phase segregation, and identical stability to the pristine film. Accordingly, the efficiency of a carbon-based, all-inorganic perovskite solar cell (PSC) was boosted to 10.94%, which was much higher than that of the pristine CsPbIBr₂ film (8.21%). The CsPbI_{1+x}Br_{2−x} PSC also possessed excellent tolerance against heat and moisture stresses.

Keywords: halide exchange, slow reaction rate, CsPbIBr₂, defects, all-inorganic perovskite solar cells

INTRODUCTION

As an emerging photovoltaic technology, perovskite solar cells (PSCs) have achieved noticeable progress in the past decade [1–3]. In particular, their power conversion effi-

ciencies (PCEs) are now comparable to silicon solar cells, with a record value of 25.4% [4]. However, the inherently poor operational stability of conventional PSCs with a typical configuration of fluorine-doped tin oxide (FTO)/electron-transport layer (ETL)/hybrid perovskite/hole-transport layer (HTL)/metal electrode seems to hinder their further commercialization prospects [2,5]. This issue primarily stems from the chemical instability and decomposition tendency of hybrid perovskite films, as well as the degradation of the HTL/metal electrode interface [6,7]. Alternatively, carbon-based, all-inorganic PSCs have been proposed in which a hybrid perovskite is replaced by a more stable all-inorganic one, and the HTL and metal electrode are substituted with a cheap, inert carbon electrode prepared by well-established screen-printing technology [8–11]. The resulting carbon-based, all-inorganic PSCs are endowed with superior stability, low cost, and easy fabrication.

Among the various inorganic perovskites explored for carbon-based, all-inorganic PSCs, Br-rich CsPbIBr₂ has a bandgap of 2.05–2.10 eV and superior thermal stability, making it a better choice than others, such as CsPbBr₃, CsPbI₂Br and CsPbIBr₂ [12–18]. Liang *et al.* [19] reported the first carbon-based, all-inorganic CsPbIBr₂ PSC with a PCE of 8.25%. Guo *et al.* [13] achieved an enhanced PCE from 4.73% to 7.00% and a high open-circuit voltage (*V*_{oc}) of 1.31 V for a similar CsPbIBr₂ PSC by treating the SnO₂ ETL with an SnCl₄ solution. Tan *et al.* [20] reported a CsPbIBr₂ PSC with a PCE of 9.25% by incorporating Li⁺ ions into a CsPbIBr₂ lattice. More recently, we found that interfacial voids can boost the *V*_{oc} of a CsPbIBr₂ PSC to

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1.338 V, coupled with a PCE of 10.20% [21].

Despite this considerable progress, the PCEs achieved to date for carbon-based, all-inorganic CsPbIBr₂ PSCs are still low [16,22], primarily for two reasons. One is that the wide bandgap of CsPbIBr₂ confines its light absorption to below ~600 nm, causing a low short-circuit current density (J_{sc}) of the final PSC. The other reason is the poor electronic features of solution-processed CsPbIBr₂ films, such as a high defect density, large degree of electronic disorder, and unmatched band energy [23–25]. Modifying CsPbIBr₂ films with a low-bandgap organic semiconductor/dye [26,27] or doping it with Sn²⁺ ions to form a CsPb_{1-x}Sn_xIBr₂ alloy [19,28] was demonstrated to extend the film's absorption range, which improved the J_{sc} . Some other innovative strategies, such as intermolecular exchange [12], ionic incorporation [29,30], and interface modification [31,32], have also been used to regulate the growth of CsPbIBr₂ films. The improved quality of CsPbIBr₂ films effectively suppresses the non-radiative recombination of charge carriers, leading to an increased fill factor (FF) and/or V_{oc} in the resulting PSCs. Although these attempts have been successful, the simultaneous modification of the absorption characteristics and crystal quality of CsPbIBr₂ films to improve both the J_{sc} and FF/ V_{oc} toward highly efficient PSCs has rarely been studied. Moreover, the above-mentioned strategies to extend the absorption range of CsPbIBr₂ films inevitably introduce extra organic modification layers or Sn²⁺ ions that are prone to oxidation to Sn⁴⁺ in ambient air [19,26–28], which causes additional stability issues for the PSCs.

Since the first report of exchange behavior on the anion sites of halide perovskites [33,34], much attention has been paid to tailor the composition and/or microstructure of perovskite materials *via* halide exchange [35–39]. In principle, it is also applicable for CsPbIBr₂ films to modify their composition and/or microstructure, and thus boost their absorption properties and crystal quality. However, previous studies have demonstrated that the halide exchange reaction is extremely fast in perovskite materials [33,34,36,38,40,41]. For example, Solis-Ibarra *et al.* [34] found that the transformation of CH₃NH₃PbI₃ to CH₃NH₃PbBr₃ or CH₃NH₃PbX₃ (X=I or Br) to CH₃NH₃-PbCl₃ is complete in 5–8 min. Luo *et al.* [40] reported that the parent CsPbI₃ film changed into CsPbBr₃ within a few seconds during a Br₂-vapor-assisted halide-exchange process. Even for centimeter-sized perovskite single crystals, complete halide exchange can be achieved after a few days [42,43]. Rapid halide exchange not only interferes with the fine-tuning capability of the optical and crystalline properties, but also generates many structural

defects in CsPbIBr₂ films, leading to inferior performance of the resulting PSCs.

Herein, we propose a halide exchange strategy that offers remarkable controllability over the reaction rate to simultaneously modulate the optical and microstructural properties of CsPbIBr₂ films. This strategy involves the face-to-face pairing of CsPbIBr₂ and CH₃NH₃PbI₃ films. With proper heat treatment, the halide exchange between these two films is activated and proceeds concurrently, with Br⁻ diffusing toward the CH₃NH₃PbI₃ film and I⁻ diffusing toward the CsPbIBr₂ film. In this manner, the halide exchange rate can be well-controlled by changing the heating parameters, wherein a higher temperature can accelerate the halide exchange, while a lower temperature effectively slows down or stops it. By using an optimal halide exchange temperature (110°C) and time (2 h), a high-quality CsPbI_{1+x}Br_{2-x} film can be obtained, which holds an extended absorption onset from 590 to 625 nm, coarsened grains, improved crystallinity, decreased surface roughness, and reduced halide phase segregation. The film maintains these properties without sacrificing the excellent stability of the pristine CsPbIBr₂ film. The carbon-based, all-inorganic PSC fabricated with the optimal CsPbI_{1+x}Br_{2-x} film yielded a superior PCE of 10.94%, together with excellent operational stability at high temperatures in ambient air.

EXPERIMENTAL SECTION

Materials

CsI (ultra-dry, 99.998%), PbI₂ (ultra-dry, 99.998%), and PbBr₂ (ultra-dry, 99.999%) were received from Alfa-Aesar. Dimethylsulfoxide (DMSO, anhydrous, 99.8+%) and *N,N*-dimethylformamide (DMF, anhydrous, 99.8+%) were purchased from Sigma-Aldrich. CH₃NH₃I (purity, 99.8+%) was received from Xi'an Polymer Light Technology Corp. Conductive carbon paste was bought from Shanghai MaterWin New Materials Co., Ltd., China. FTO substrates (8 Ω sq⁻¹) were received from Yingkou OPV Tech New Energy Co., Ltd.

Preparation of CsPbIBr₂ and CH₃NH₃PbI₃ films

The FTO substrate was ultrasonically cleaned in deionized water, acetone, and ethanol, followed by ultraviolet-ozone (UVO) treatment for 10 min. TiO₂ colloidal solution was then spin-coated onto the FTO substrate (3500 rpm for 30 s) and annealed at 480°C for 60 min in the air to form a compact TiO₂ (c-TiO₂) layer. To obtain a CsPbIBr₂ film, the CsPbIBr₂ precursor solution was first prepared by dissolving 367 mg PbBr₂ and

260 mg CsI in 1 mL DMSO. Then, the precursor was spin-coated on the FTO/c-TiO₂ substrate at 1500 rpm for 30 s and 5000 rpm for 60 s, after which it was heated at 60°C for 5 min and further annealed at 280°C for 20 min. The CH₃NH₃PbI₃ film was prepared by a solvent-engineering assisted one-step spin-coating route. Specifically, 60 μ L CH₃NH₃PbI₃ precursor obtained by mixing 160 mg CH₃NH₃I, 461 mg PbI₂, 78 mg DMSO, and 600 mg DMF was dripped onto the FTO/c-TiO₂ substrate, and then the substrate was spun at 4500 rpm for 20 s. Within the first 6 s of spinning, 0.5 mL anhydrous diethyl ether was dripped continuously onto the substrate. After the annealing treatment at 100°C for 10 min, a crystalline CH₃NH₃PbI₃ film was obtained.

Halide exchange treatment

First, the as-obtained CsPbIBr₂ and CH₃NH₃PbI₃ films were face-to-face paired. Then, the samples were placed on a hotplate and heated at a specific temperature, such as 110°C. During this stage, the halide exchange between Br[−]

ions in CsPbIBr₂ film and I[−] ions in CH₃NH₃PbI₃ film proceeded slowly. By controlling the heating treatment time, the desired CsPbI_{1+x}Br_{2−x} film was obtained.

Fabrication of carbon-based, all-inorganic PSC

Commercial carbon paste was screen-printed onto the CsPbI_{1+x}Br_{2−x} film, which was further heated at 125°C for 15 min in ambient air to solidify the carbon electrode. The area of the carbon electrode was confined to 0.09 cm².

The details for the characterization of CsPbI_{1+x}Br_{2−x} films and carbon-based, all-inorganic PSCs can be found in our previous work [12,23].

RESULTS AND DISCUSSION

The key procedure for achieving a slow halide exchange is shown schematically in Fig. 1a, wherein the CsPbIBr₂ and CH₃NH₃PbI₃ films were face-to-face paired. With the proper heating treatment, the I[−] ions in the CH₃NH₃PbI₃ film tended to vaporize and penetrate into the CsPbIBr₂

Figure 1 (a) Schematic illustration of the halide exchange strategy with a slow reaction rate. (b) Photographs and (c) UV-vis absorption spectra of CsPbI_{1+x}Br_{2−x} films prepared with different halide exchange temperatures of RT, 90, 110, 130, 150, and 170°C, respectively. (d) XRD patterns and (e) UV-vis spectra of CsPbI_{1+x}Br_{2−x} films formed with different halide exchange durations of 0, 1, 2, and 3 h, respectively.

film, during which the Br^- ions in CsPbIBr_2 film concurrently diffused into the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film [39]. Thus, the halide exchange of I^- and Br^- ions occurs between CsPbIBr_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, producing $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films, respectively. In this case, the halide exchange rate is dominated by the release rate of I^- ions in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. Therefore, it can be well-controlled by the heating recipe, in which a higher temperature accelerates the halide exchange, but a lower temperature will effectively slow down or even stop it, as described below.

Fig. 1b presents the photographs of a series of samples prepared under different halide exchange temperatures, including room temperature (RT), 90, 110, 130, 150, and 170°C, respectively. The colors of the films formed at RT and 90°C showed negligible changes after halide exchange, while the colors tended to deepen for the others upon increasing the halide exchange temperature. The color changes of the samples were well-supported by their ultraviolet-visible (UV-vis) absorption spectra in Fig. 1c. The films prepared at RT and 90°C yielded a similar absorption onset of 590 nm, which corresponds to a bandgap of 2.10 eV and is in line with that of CsPbIBr_2 films reported previously [14,31]. By comparison, the absorption onsets shifted to 603, 615, 637, and 655 nm for the samples prepared at 110, 130, 150, and 170°C, respectively. The greater red-shift in the absorption onset was generally accompanied by a greater portion of I^- in the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ film [44]. Therefore, the above results indicate that when the heating temperature reaches 110°C, the halide exchange is activated, and a higher temperature increases the exchange rate. Since a slower halide exchange rate is expected to form a $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ film with fewer defects, we chose 110°C as the optimized halide exchange temperature in subsequent experiments. Indeed, as exhibited in Fig. S1, the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ film prepared at 110°C exhibited a more intense photoluminescence (PL) peak than the one obtained at 150°C, indicating fewer non-recombination sites and, thus, structural defects in the former. Hereinafter, the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ film with a halide exchange time of 0 h represents the parent CsPbIBr_2 film, which is adopted as a control sample.

Fig. 1d gives the X-ray diffraction (XRD) patterns of the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films prepared at 110°C with different halide exchange times of 0, 1, 2, and 3 h, respectively. The clear diffraction peaks of the (001)/(100), (110), and (002)/(200) crystal planes for cubic perovskite $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ were observed in all samples, while no impurity phase was identified [37]. This indicates that

halide exchange has little impact on the crystal phase of the as-investigated films. Upon prolonging the halide exchange time, the dominant diffraction peaks, such as those of the (100), (110), and (200) planes, progressively shifted towards low diffraction angles, which was ascribed to the increased I^- portion in $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films [36,37]. Meanwhile, the intensity of the dominant XRD peak increased following the same trend. We ascribe this phenomenon to the improved crystallinity of the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films upon increasing the halide exchange time. That is to say, a slow halide exchange reaction repaired crystal defects in the parent CsPbIBr_2 film. The UV-vis absorption spectra in Fig. 1e show that the absorption onsets are 590, 607, 625, and 636 nm for $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films with halide exchange durations of 0, 1, 2, and 3 h, respectively. These results indicate a higher I^- portion in the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films prepared with a longer halide exchange time, in good accordance with the XRD results.

The morphology characteristics of the as-prepared $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The SEM images in Fig. 2a₁–d₁ show that all $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films have a full surface coverage to ensure effective light absorption and prevent the possible formation of shuttling shuttling paths in the final carbon-based, all-inorganic PSCs. Meanwhile, the average grain sizes were estimated to be 0.64, 0.68, 0.79, and 0.90 μm for the films obtained with halide exchange durations of 0, 1, 2, and 3 h, respectively (Fig. S2). The increase in the average grain size with the halide exchange time can be assigned to the organic CH_3NH_3^+ ions from the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. These ions can promote the grain coarsening in the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ film *via* the Ostwald ripening mechanism, as proposed in previous studies [45,46]. The AFM images in Fig. 2a₁–d₁ support the SEM results. The root-mean-square (RMS) roughness values were evaluated to be 22.3, 19.4, 18.7, and 15.5 nm for $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films with halide exchange durations of 0, 1, 2, and 3 h, respectively. This indicates that the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ film surface became flatter upon prolonging the halide exchange time. Taken together, all of the above results indicate that a slow halide exchange reaction rate produces pure-phase $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films with a narrower bandgap, improved crystallinity, enlarged grains, and reduced surface roughness. Moreover, such characteristics become increasingly better upon extending the halide exchange time.

Further, the influence of halide exchange on the photophysical properties and composition of $\text{CsPbI}_{1+x}\text{Br}_{2-x}$

Figure 2 (a₁–d₁) SEM images and (a₂–d₂) AFM images of CsPbI_{1+x}Br_{2-x} films with halide exchange durations of 0, 1, 2, and 3 h, respectively. All scale bars represent 1 μm.

Figure 3 (a) Steady-state PL and (b) TRPL spectra of the CsPbI_{1+x}Br_{2-x} films with halide exchange durations of 0 and 2 h, respectively. Both samples were grown on insulated glass substrates. (c, d) Steady-state TRPL spectra of the CsPbI_{1+x}Br_{2-x} films with halide exchange durations of 0 and 2 h, respectively. The CsPbI_{1+x}Br_{2-x} films were prepared on FTO/c-TiO₂ substrates.

films were investigated by taking films with halide exchange durations of 0 and 2 h as examples. Fig. 3a presents the steady-state PL spectra of the films grown on insulated glass substrates. The film with a halide exchange duration of 0 h, namely the parent CsPbIBr₂ film, exhibited a PL peak at ~574 nm, consistent with those of CsPbIBr₂ materials reported previously [12,14,32]. By

comparison, the PL peak of the CsPbI_{1+x}Br_{2-x} film with a halide exchange duration of 2 h underwent a red-shift to 611 nm, indicating its narrower bandgap. Its PL intensity is much stronger than that of the parent film. Since both films were deposited on insulated glass substrates, a more intense PL peak indicates weaker non-radiative recombination of charge carriers in the related

CsPbI_{1+x}Br_{2-x} film. The time-resolved RL (TRPL) spectra in Fig. 3b show that the CsPbI_{1+x}Br_{2-x} film with a halide exchange time of 2 h exhibits slower PL decay, in line with the steady-state PL results [47]. In particular, the average PL lifetime (τ_{ave}) values were fitted to be 10.8 and 20.9 ns for the CsPbI_{1+x}Br_{2-x} films with halide exchange times of 0 and 2 h, respectively.

In terms of Br-rich, mixed-halide inorganic perovskites, the Pb–Br bond is stronger than the Pb–I bond and, thus, can spontaneously drive I[−] out to generate a Br-rich domain phase. Such a process easily forms small-bandgap I-rich domains and large-bandgap Br-rich domains, causing undesired halide phase segregation [48]. To gain insight into such a phenomenon in the CsPbI_{1+x}Br_{2-x} films, their steady-state PL spectra after being illuminated with a 478-nm laser (30 mW cm^{−2}) for different durations were recorded. Both films were deposited on FTO/c-TiO₂ substrates to coincide with carbon-based, all-inorganic PSCs. As shown in Fig. 3c, the PL peak underwent a clear red-shift, and its intensity increased with the illumination time for the CsPbI_{1+x}Br_{2-x} film with a halide exchange time of 0 h. These results indicate unavoidable halide phase segregation, as frequently observed in previous CsPbIBr₂ films [12,28,48,49]. By contrast, the changes in the PL peak during continuous illumination were greatly reduced for the CsPbI_{1+x}Br_{2-x} film with a halide exchange time of 2 h, as exhibited in Fig. 3d. Namely, the halide exchange strategy with a slow reaction rate can effectively suppress undesired halide phase segregation in CsPbIBr₂ films.

Fig. 4a provides the core-level N 1s X-ray photoelectron spectroscopy (XPS) spectra of CsPbI_{1+x}Br_{2-x} films with halide exchange durations of 0 and 2 h. Similar to the parent sample, no N atoms were detected in the film after halide exchange. That is to say, despite the exchange of Br[−] and I[−] between the parent CsPbIBr₂ and CH₃NH₃PbI₃ films, CH₃NH₃⁺ cations were not present in the final CsPbI_{1+x}Br_{2-x} film. Fig. 4b–e provide the corresponding core-level Cs 3d, Pb 4f, I 3d, and Br 3d XPS spectra. Their binding energies are similar to those of CsPbI_{1+x}Br_{2-x} films reported earlier [12,23]. The slight differences in the binding energies between CsPbI_{1+x}Br_{2-x} films with halide exchange durations of 0 and 2 h were mainly related to their different compositions [12,23,50]. In addition, from the core-level I 3d, and Br 3d XPS spectra, the relative atomic ratios of [I]/[Br] were estimated to 0.46 and 1.35 for the CsPbI_{1+x}Br_{2-x} films with halide exchange durations of 0 and 2 h, respectively, verifying again the increased portion of I[−] ions in the film after halide exchange.

Next, we studied the effects of slow halide exchange on

the performance of carbon-based, all-inorganic PSCs with a layer stacking of FTO/c-TiO₂/CsPbI_{1+x}Br_{2-x}/carbon. Fig. 5a gives the cross-sectional SEM image of a typical PSC, with each of the functional layers clearly visible. The thickness of the CsPbI_{1+x}Br_{2-x} film was approximately ~400 nm. To obtain a reliable conclusion, 20 independent PSCs based on the CsPbI_{1+x}Br_{2-x} films with halide exchange durations of 0, 1, 2, and 3 h were fabricated from four batches. Fig. S3a presents the statistical PCEs of all the as-fabricated CsPbI_{1+x}Br_{2-x} PSCs. The average PCEs were evaluated to be 7.67%, 8.36%, 9.86%, and 6.82%, respectively. These results make it clear that the halide exchange strategy with a slow reaction rate and suitably long reaction time is an effective method to produce carbon-based, all-inorganic PSCs with improved performance, particularly at the optimal halide exchange time of 2 h. Furthermore, the corresponding statistical J_{sc} , FF, and V_{oc} results in Fig. S3b–d indicate that the improved PCEs mainly come from the enhanced J_{sc} and FF values.

The current density *versus* voltage (J - V) curves of the best-performing carbon-based, all-inorganic CsPbI_{1+x}Br_{2-x} PSCs with halide exchange durations of 0, 1, 2, and 3 h are provided in Fig. 5b. The PSC based on the CsPbI_{1+x}Br_{2-x} film with a halide exchange time of 0 h—the parent CsPbIBr₂ film—shows a PCE of 8.21%, together with a J_{sc} of 10.43 mA cm^{−2}, an FF of 0.64, and a V_{oc} of 1.230 V. By comparison, the PSCs with halide exchange times of 1 and 2 h exhibit much improved performances. In particular, the PCE of the latter improved to 10.94%, for which its J_{sc} , V_{oc} , and FF were 12.30 mA cm^{−2}, 1.186 V, and 0.75, respectively. However, when the halide exchange time was extended to 3 h, the PCE of the resultant CsPbI_{1+x}Br_{2-x} PSC decreased to 7.79%. Further comparisons revealed that such an inferior PCE was mainly related to the low V_{oc} and FF. We attribute this phenomenon to the degraded stability of the CsPbI_{1+x}Br_{2-x} film prepared with a halide exchange time of 3 h. As shown in Fig. S4, the film was partially decomposed after the deposition of the carbon electrode in ambient air. Therefore, it appears that the optimal halide exchange time is around 2 h, which ensures the superior performance of CsPbI_{1+x}Br_{2-x} PSCs.

The external quantum efficiency (EQE) spectra of the best-performing CsPbI_{1+x}Br_{2-x} PSCs were also measured, as given in Fig. 5c. The photocurrent onsets were determined to be ~590, 607, 625, and 636 nm for those with halide exchange durations of 0, 1, 2, and 3 h respectively, which are consistent with the bandgaps of the corresponding CsPbI_{1+x}Br_{2-x} films. Furthermore, as provided in Fig. S5, the integrated J_{sc} of the EQE spectra are 8.42,

Figure 4 (a) N 1s, (b) Cs 3d, (c) Pb 4f, (d) I 3d, and (e) Br 3d core-level XPS spectra of typical $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films prepared with halide exchange durations of 0 and 2 h, respectively. (f) The corresponding relative atomic ratio of I and Br obtained from the core-level XPS results.

9.81, 11.29, and 10.64 mA cm^{-2} for the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs obtained using films with halide exchange durations of 0, 1, 2, and 3 h, respectively. They are in accordance with those derived from the light J - V curves. The slight discrepancy mainly resulted from the spectral mismatch between the EQE light source and the solar simulator [15,29,45,48]. In addition, one can see that the EQEs are higher for the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs prepared from films with halide exchange times of 1 and 2 h, revealing their superior photoelectric conversion.

The stability characteristics of the typical champion $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs were also studied. Fig. 5d gives the stabilized current density outputs near the maximum power points of the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs with halide exchange times of 0 and 2 h, respectively. It is clear that

during the test period, both $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs showed negligible photocurrent degradation in ambient air with continuous AM 1.5G illumination, suggesting their superior operational stability. Stable PCEs can also be derived from Fig. 5d, which are 7.73% and 9.96% for the PSCs with halide exchange times of 0 and 2 h, respectively. These values are slightly smaller than those obtained from the J - V curves in Fig. 5b, manifesting that general J - V hysteresis also occurs in our carbon-based, all-inorganic $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs [31,48,49].

Additionally, the thermal stability of the PSCs was evaluated in a glovebox atmosphere at 85°C for 15 h. As seen from Fig. 5e, the performance degradation of the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs with halide exchange times of 0 and 2 h did not exceed 6%, revealing their similar thermal

Figure 5 (a) Cross-sectional SEM image of a typical all-inorganic carbon-based, CsPbI_{1+x}Br_{2-x} PSC. (b) Light J-V curves, (c) EQE spectra, and (d) stabilized current density outputs near maximum power points for the optimized PSCs based on CsPbI_{1+x}Br_{2-x} films with halide exchange durations of 0 and 2 h, respectively. (e, f) The corresponding relative PCE evolutions for CsPbI_{1+x}Br_{2-x} PSCs in a glove box and ambient air atmosphere, respectively.

stability. In addition, the long-term storage stability of the as-obtained CsPbI_{1+x}Br_{2-x} PSCs was monitored in ambient air with a controlled temperature of $25 \pm 3^\circ\text{C}$ and relative humidity (RH) of $40\% \pm 10\%$. The results in Fig. 5f indicate that the CsPbI_{1+x}Br_{2-x} PSC fabricated with a halide exchange time of 0 h retained 85% of its initial PCE after being tested for 45 d. As for the CsPbI_{1+x}Br_{2-x} PSC obtained with a halide exchange time of 2 h, its performance degradation was below 20%, which is comparable to that of the former. The above stability investigations make clear that, despite an increased I⁻ portion due to slow halide exchange, the stability of the resulting CsPbI_{1+x}Br_{2-x} PSCs is still satisfactory. In par-

ticular, the one fabricated with a halide exchange time of 2 h displayed similar stability features as the PSC based on the parent CsPbIBr₂ film.

Overall, the halide exchange strategy with a slow reaction rate can transform pristine CsPbIBr₂ films into CsPbI_{1+x}Br_{2-x} ($0 < x < 2$) films that possess narrower bandgaps, improved crystallinity, enlarged grains, reduced surface roughness, and suppressed halide phase segregation. Moreover, by optimizing the halide exchange parameters, a carbon-based, all-inorganic PSC with a much-improved PCE and similarly superior stability can be obtained. The modified PCE has an improved J_{sc} due to the narrower bandgap of the CsPbI_{1+x}Br_{2-x} film after

the halide exchange treatment. The enhanced crystalline quality of the $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films may help reduce the non-radiative recombination of charge carriers, which can ultimately result in an enlarged FF and/or V_{oc} [23–25,51]. To validate this speculation, the kinetic characteristics of charge carriers in typical $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs with halide exchange times of 0 and 2 h were studied by photocurrent/photovoltage (TPC/TPV) and electrochemical impedance spectroscopy (EIS), respectively. Fig. 6a, b provide the TPC and TPV curves of the typical carbon-based, all-inorganic $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs with halide exchange times of 0 and 2 h, respectively. The PSC with a halide exchange time of 2 h has a faster TPC decay and a slower TPV decay than the one with a halide exchange time of 0 h. For example, its TPC and TPV average lifetime (τ_{ave}) values were fitted to be 1.54 μs and 1.06 ms, respectively, while the corresponding values were 2.81 μs and 0.47 ms for the other. These results reveal the more effective interfacial extraction and reduced non-radiative recombination of charge carriers in the

Figure 6 (a) TPC and (b) TPV curves, as well as the (c) Nyquist plots of the EIS results for the typical carbon-based, all-inorganic $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs with halide exchange durations of 0 and 2 h.

$\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSC with a halide exchange time of 2 h [12,23,45,50]. Fig. 6c presents the Nyquist plots of the as-investigated $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSCs, in which the clear arcs are related to the interfacial recombination of charge carriers, labeled by the recombination resistance (R_{rec}). The $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSC with a halide exchange time of 2 h has a much larger R_{rec} indicating its weaker non-radiative recombination [12,15,23,45,50]. The TPC/TPV and EIS results support this speculation.

CONCLUSIONS

The halide exchange happens between the CsPbIBr_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ films physically paired together, which proceeds with a slow reaction rate that could be well-controlled by changing the heat treatment temperature. It thus offers the ability to simultaneously finely modulate the optical and microstructural characteristics of CsPbIBr_2 films. By optimizing the halide exchange temperature and time, the parent CsPbIBr_2 film could be transformed into high-quality $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ films that exhibited an extended absorption onset from 590 to 625 nm, coarsened grains, improved crystallinity, suppressed halide phase separation, but without degradation of the thermostability and moisture resistance, in contrast to the parent film. The carbon-based, all-inorganic PSC based on the optimized $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ film (halide exchange temperature and time of 110°C and 2 h) showed a PCE of 10.94%, which is much higher than the best-performing one fabricated with the parent CsPbIBr_2 film that yielded a PCE of 8.21%. The $\text{CsPbI}_{1+x}\text{Br}_{2-x}$ PSC possessed comparable stability to the CsPbIBr_2 film-based PSC, and it retained up to 96% or 80% of its initial PCE after being tested at 85°C for 15 h in a glovebox at $25 \pm 3^\circ\text{C}$ and $40\% \pm 10\%$ RH for 45 days in ambient air.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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基于缓慢卤素交换处理CsPbIBr₂薄膜制备高性能碳基全无机钙钛矿太阳能电池

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摘要 卤素交换反应为调变卤化物钙钛矿材料的光电学性质提供了一种通用途径。但是, 如何降低此类反应的速率, 进而抑制缺陷的生长, 仍然是一个突出难题。本研究中, 我们提出了一种缓慢的卤素交换策略, 通过将已制备的CsPbIBr₂和CH₃NH₃PbI₃薄膜面对面放置于热台上以进行卤素交换反应, 其中Br⁻和I⁻各自向CH₃NH₃PbI₃和CsPbIBr₂薄膜扩散。实验研究发现通过改变反应参数如温度、时间等, 可以精细控制薄膜间的卤素交换速率。例如, 较高的温度可以加速卤素交换反应, 而较低的温度则可使之减缓或使之完全停止。因此, 通过优化卤素交换温度和时间分别为110°C和2 h时, 制得了高质量的CsPbI_{1+x}Br_{2-x}薄膜。薄膜的光吸收截止边由590 nm红移至625 nm, 有效地拓宽了薄膜的光吸收范围。同时, CsPbI_{1+x}Br_{2-x}薄膜的结晶质量也得到了明显改善, 其晶粒尺寸有所增加、结晶性提高、表面粗糙度降低、相分离得到抑制, 并且仍然保持原有薄膜优异的湿、热稳定性。因此, 基于此类CsPbI_{1+x}Br_{2-x}薄膜制备的碳基全无机钙钛矿太阳能电池的效率高达10.94%, 远优于基于原始CsPbIBr₂薄膜组装的器件(8.21%)。另外, 制备的高效率电池在85°C氮气环境中加热15小时后, 可保持其初始效率的96%; 在温、湿度分别为25±3°C和40%±10%的环境中放置45天可保持其初始效率的80%。表明基于缓慢卤素交换策略制备的碳基全无机钙钛矿太阳能电池也具有优异的湿、热耐受能力。