Combination of Hybrid CVD and Cation Exchange for Upscaling Cs-Substituted Mixed Cation Perovskite Solar Cells with High Efficiency and Stability

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Mixed cation hybrid perovskites such as Cs$_x$FA$_{1-x}$PbI$_3$ are promising materials for solar cell applications, due to their excellent photoelectronic properties and improved stability. Although power conversion efficiencies (PCEs) as high as 18.16% have been reported, devices are mostly processed by the anti-solvent method, which is difficult for further scaling-up. Here, a method to fabricate Cs$_x$FA$_{1-x}$PbI$_3$ by performing Cs cation exchange on hybrid chemical vapor deposition grown FAPbI$_3$ with the Cs$^+$ ratio adjustable from 0 to 24% is reported. The champion perovskite module based on Cs$_{0.07}$FA$_{0.93}$PbI$_3$ with an active area of 12.0 cm$^2$ shows a module PCE of 14.6% and PCE loss/area of 0.17% cm$^{-2}$, demonstrating the significant advantage of this method toward scaling-up. This in-depth study shows that when the perovskite films prepared by this method contain 6.6% Cs$^+$ in bulk and 15.0% at the surface, that is, Cs$_{0.07}$FA$_{0.93}$PbI$_3$, solar cell devices show not only significantly increased PCEs but also substantially improved stability, due to favorable energy level alignment with TiO$_2$ electron transport layer and spiro-MeOTAD hole transport layer, increased grain size, and improved perovskite phase stability.

1. Introduction

Organo-lead-halide perovskite materials have garnered enormous interests in photovoltaic applications in the past few years.[1–9] A power conversion efficiency (PCE) of 22.1% has been certified on single-junction perovskite solar cells (PSCs), almost comparable to that of state-of-the-art crystalline silicon solar cells.[10] Besides the pursuit of an even higher PCE by enhancing perovskite film quality,[11–15] optimizing the device structure and interfaces,[16–18] and adjusting the composition of perovskite films,[19–22] research efforts are also urgently needed to increase the scalability of research findings obtained in research labs and make this technology amenable for industry. There are two main challenges we are still facing.

(1) The first is the stability challenge. At present stability of PSCs is still poorer than inorganic semiconductor based solar cells, for example, crystalline silicon solar cells and thin film copper indium gallium selenide (CIGS) solar cells.[10,23–25] To overcome the instability issue, external protections (e.g., perovskite surface functionalization,[26] utilization of chemically inert electron transport materials, hole transport materials and top electrode, deposition of additional protection layer, etc.) have been attempted.[27–29] Stability of the perovskite layer itself is another key factor.[30] For example, the most widely investigated methylammonium (CH$_3$NH$_3$) or MA lead iodide (MAPbI$_3$) is reported to undergo a phase transition at 54–57 °C[31] and degrade at temperature over 85 °C,[32] suggesting its poor thermal stability.[33] Among other perovskite materials, formamidinium (NH$_2$CH$_2$NH$_3$ or FA) lead iodide (FAPbI$_3$) possesses better thermal stability compared to MAPbI$_3$ and relatively high device performance among various types of perovskites.[34] However, an obvious drawback is its phase stability in the perovskite structure. At room temperature, FAPbI$_3$ tends to form the non-photoactive phase (yellow phase) with a bandgap of 2.48 eV other than 1.53 eV in its photoactive perovskite phase (black phase).[34,35] To maintain FAPbI$_3$ in the black perovskite phase, a mixed perovskite material with 10% FA$^+$ substituted by Cs$^+$, that is, FA$_{0.9}$Cs$_{0.1}$PbI$_3$ has been reported, showing significantly improved phase and device stability.[31] The improved phase stability was interpreted by the optimal effective tolerance factor using mixed cations.[36–38] Following this work, partial substitution of Cs$^+$ has also been demonstrated in other systems, for example, Cs$_{5}$FAM$_{0.3}$Pb$_{0.7}$Br$_{0.3}$, to improve PCE and stability.[39–41] Excellent device stability has been demonstrated on Cs$_{5}$FAM$_{0.3}$Pb$_{0.7}$Br$_{0.3}$, which is the first reported perovskite passing the International Electrotechnical
Commission (IEC) 61215 damp heat test (less than 10% PCE decay at 85 °C and 85% relative humidity for 1000 h), a standard accelerating lifetime testing protocol for crystalline silicon terrestrial photovoltaic modules.[42] The Cs-substituted mixed cation perovskites create a new avenue for development of PSCs with a high potential in solving the intrinsic stability issue.

(ii) The second is the upscaling challenge. Often PCEs of PSCs significantly drop upon increasing the active area of both single solar cells and modules, which are likely due to increase of the sheet resistance and decrease of the film uniformity across large areas.[43] Influence of the sheet resistance increase can be largely overcome by optimizing the device structure for single cells, for example, depositing 100 nm thick Au busbar under the electron transport layer[44] or designing suitable device geometry, for example, tuning the width of the subcells and optimizing the interconnection between subcells for modules.[45] Fabrication techniques such as hybrid chemical vapor deposition (CVD),[46–49] spray coating,[50,51] screen printing,[52,53] and hot casting[54,55] have been developed and shown promising results in achieving large-area uniformity and easy accessibility. However, most large-area single cell/module optimization is based on MAPbI3 and FAPbI3, which are known to suffer from the instability issue. Although significant stability improvement has been demonstrated on the Cs-substituted PSCs by several groups, almost all the high-performing Cs-containing PSCs are prepared by the anti-solvent method on small-area substrates with an active area less than 1.1 cm2.[56–59] To our best knowledge, there are no reports on Cs-substituted perovskite solar modules. Due to the short time window characteristic of the anti-solvent method, it is difficult to apply this method for large-area perovskite cells or modules. For instance, an ultraflat perovskite film without pinholes can be prepared on small substrate (1.5 cm × 1.5 cm) using the anti-solvent method but the film uniformity is severely compromised upon increasing the substrate area to a module size (5 cm × 5 cm or more), possibly due to nonuniform film quality over large area, leading to the significant PCE decrease.[43]

On the other hand, it is also difficult to prepare Cs-substituted perovskite in single or sequential CVD processes, due to the significantly different sublimation temperatures of FAI, PbI2, and CsI. The sublimation and deposition temperatures of CsI are too high that predeposited FAI or PbI2 will resublimate. Therefore, it is urgently needed to develop fabrication methods that are suitable for upscaling of Cs-substituted PSCs, either by large-scale compatible solution processes or vapor deposition.

Ion exchange has been used in perovskites to adjust the bandgap by varying the halide ratio, for example, Br− to I− or the cation ratio, for example, MA+ to FA+ and Pb+2 to Sn+2, Cd+2, Zn+2.[60–65] Here, we propose a method combining hybrid CVD and cation exchange (HCVD-CE) to prepare CsFAxPb1−xI3 mixed perovskite that can take advantage of both enhanced perovskite stability and upscaling compatibility. Because the whole process only uses large-area compatible steps (namely, non-anti-solvent spin-coating, CVD, and cation exchange), it can significantly minimize the effort required for industrialization in the future. Using this method, we are able to precisely control the CsFAxPb1−xI3 film composition with x varying from 0 to 0.24, which includes the optimal Cs+ ratio in the mixture in terms of both device PCE and stability. The solar modules (consisting of six single cells in series) fabricated using Cs0.07FA0.93PbI3 perovskite have an active area of 12.0 cm2 and show a PCE of 14.6%. The PCE loss/area, defined as PCE loss/area = (PCEsmallcell − PCEmodule)/(area_module − area_smallcell) is as small as 0.17% cm−2, demonstrating the advantage of our method toward scaling-up.

In addition to developing the large-area-compatible technique, we also focus on the two remaining questions for the CsFAxPb1−xI3 system. (i) Results show that Cs+ substitution in FAPbI3 can not only improve perovskite phase stability and solar cell stability but also increase PCE. Because the optimal bandgap for a single-junction solar cell is ~1.34 eV, according to the Shockley–Queisser model, it is unlikely that Cs substitution in FAPbI3 should improve the PCE if purely considering the bandgap and absorption. Therefore, the mechanism underlying the PCE improvement needs further investigation. (ii) The optimal ratio of Cs+ in CsFAxPb1−xI3 to achieve the best device performance and stability is still yet to be confirmed.

We find that (I) perovskite grain size first increases as the Cs+ ratio rises from 0 to 10.2% and then decreases as the Cs+ ratio further rises from 10.2 to 16.8%; (II) both electron injection from perovskite to TiO2 and hole injection from perovskite to spiro-MeOTAD are facilitated when the Cs+ ratio is higher than 6.6%, but a Cs+ ratio exceeding 10.2% leads to perovskite phase segregation, which also corroborates with the device PCE; (III) the Cs+ ratio at perovskite surface is 2–3 times higher than the bulk. The Cs-rich perovskite surface layer with a high Cs+ ratio, for example, 15.0% (6.6% in bulk), helps increase the phase stability of the bulk film, possibly due to the prevention of moisture from directly contacting the perovskite bulk. We find that 6.6% Cs+ in bulk is the optimal ratio for achieving both the highest device PCEs and stability.

2. Results and Discussion

2.1. Preparation of the Mixed CsFAxPb1−xI3 Perovskite Films by HCVD-CE

CsFAxPb1−xI3 perovskites with x varying from 0.0 to 0.24 are prepared in this study and details are presented in the Experimental Section. The reaction mechanism can be described by the following equations

\[
PbI2 + xDMA + FAI = FAPbI3 + DMSO \tag{1}
\]

\[
FAPbI3 + xCsCH2COO = CsFAxPb1−xI3 + xFACH2COO \tag{2}
\]

In brief, FAPbI3 perovskite films were deposited on FTO/compact TiO2 (c-TiO2) substrates via a two-step hybrid CVD (HCVD) method slightly modified on the basis of our previous report.[40] A spin-coated PbI2-DMSO film is pre-deposited to convert to FAPbI3 by HCVD with the vapor of formamidinium iodide (FAI) (Figure S1a,b, Supporting Information). The unreacted FAI can be recycled as illustrated in Figure S1c,d.
CsCH$_3$COO solution (using IPA as the solvent), that is, 0, 1, 2, 5, and 10 mg mL$^{-1}$ with the concentration of the CsCH$_3$COO solution, suggesting to obtain Cs$^+$ concentrations for a certain period of time at room temperature to obtain CsPbI$_3$ perovskite films. Cs cation exchange is achieved in Cs$^+$ FAxPb$_{1-x}$I$_3$ mixed perovskite films by cation exchange (Figure 1a). The as-prepared FAPbI$_3$ perovskite film was immersed in the CsCH$_3$COO solution and then annealed to obtain the Cs$_x$FA$_{1-x}$Pb$_3$ perovskite film. Cs cation exchange is achieved in Cs$_x$FA$_{1-x}$Pb$_3$, where $x$ is from 0 to 0.17. The converted films, which were named as A, B, C, D, and E, respectively, were dried and annealed before characterization. The bandgap values of Cs$_x$FA$_{1-x}$Pb$_3$ perovskite films were extracted from UV–vis spectra using Tauc plots. After the cation exchange process, the bandgap value of the perovskite films increases from 1.53 eV for A to 1.56 eV for E (Figure 1b). Because the CsPbI$_3$ perovskite film has a bandgap of 1.73 eV, larger than FAPbI$_3$ perovskite, the increase in bandgap indicates the partial substitution of the FA$^+$ with Cs$^+$. The Cs$^+$ substitution amount is positively correlated with the concentration of the CsCH$_3$COO solution, suggesting that we can obtain various Cs$^+$ ratios in mixed Cs$_x$FA$_{1-x}$Pb$_3$ perovskite films by adjusting the concentration of CsCH$_3$COO solution. Photoluminescence (PL) measurements were performed on the five perovskite films, all of which show strong PL signals. The PL peak position gradually shifts to shorter wavelengths from 819.5 nm (for A) to 805.5 nm (for E), agreeing well with the increase of the Cs$^+$ ratio in these films (Figure 1c). The composition and structure were also characterized by X-ray diffraction (XRD). Diffraction peaks for FAPbI$_3$ at 13.9°, 24.3°, 28.1°, 31.4°, 33.6°, 40.1°, and 42.7° can be assigned to the (−111), (021), (222), (030), (240), and (333) FAPbI$_3$ crystal planes, while the peaks at 26.4°, 37.7°, and 51.5° belong to the FTO substrate (Figure S2, Supporting Information). No diffraction peaks appear at 11.7° (corresponding to the non-perovskite phase of FAPbI$_3$) or 12.6° (corresponding to PbI$_2$), suggesting the good phase purity of the FAPbI$_3$ perovskite films prepared by HCVD. After cation exchange, there are neither changes in peak intensities nor the appearance of additional peaks for all the films, indicating the well-conserved crystal structure during the Cs$^+$ substitution.

Figure 1. a) Schematic drawing for the preparation of the mixed Cs$_x$FA$_{1-x}$Pb$_3$ perovskite films by the HCVD-CE method and Cs$^+$ bulk ratio in the mixed Cs$_x$FA$_{1-x}$Pb$_3$ films. b) UV–vis spectra, c) PL spectra, and d) XRD patterns of Cs$_x$FA$_{1-x}$Pb$_3$ between 27.0° and 30.0°. PbI$_2$-DMSO was spin-coated on an FTO glass substrate, followed by hybrid chemical vapor deposition in FAI vapor for FAPbI$_3$ formation. The as-prepared FAPbI$_3$ perovskite film was immersed in the CsCH$_3$COO solution and then annealed to obtain the Cs$_x$FA$_{1-x}$Pb$_3$ perovskite film. Cs cation exchange is achieved in Cs$_x$FA$_{1-x}$Pb$_3$.
where a parameter decreases as the average Cs to I ratio increase and c parameter increases until Sample D and suddenly decreases for Sample E. Microstrain raises from Samples A to E (Figure S4c, Supporting Information). Minimum crystalline domain size increases from Samples A to D and decrease from D to E (Figure S4d, Supporting Information). To quantify directly the average Cs to I ratio in samples A to E, we performed X-ray fluorescence (XRF) measurements on these samples. Details of the calculation based on XRF results are shown in the Experimental Section. The Cs to I ratios are calculated to be 0% for Sample A, 1.2 ± 0.1% for Sample B, 2.2 ± 0.1% for Sample C, 3.4 ± 0.2% for Sample D, and 5.6 ± 0.3% for Sample E, respectively (Figure S5 and Table S1, Supporting Information). Phase segregation of mixed perovskites has been reported to be detrimental for both device performance and stability.[34,36,39,66] The full width half maximum (FWHM) values of the PL peaks were extracted to show the phase purity on various mixed perovskite samples (Figure S6, Supporting Information). The FWHM values of the peaks in the PL spectra decreased slightly from Samples A to C, but increase substantially from Sample D to Sample E. Because the MCDS value of Sample E is larger than Sample A (Figure S4d, Supporting Information), the FWHM value increases for Sample E is not due to the reduced crystallinity, but due to phase segregation. Further increasing the Cs to I ratio from 16.8 to 24.0% leads to even severe phase segregation or decomposition, as shown in the Experimental Section (Figures S7 and S8, Supporting Information). Therefore, we conclude that CsFA1−xPbI3 perovskite can be mainly in one phase when x is smaller than 6.6%. But when x is larger than 10.2%, Cs−rich CsFA1−xPbI3 is detectable. The phase segregation was also observed on solution-processed CsFA1−xPbI3 films when the Cs+ bulk ratio is higher than 10.2%.[34]

2.2. Performance of the Mixed CsFA1−xPbI3 Perovskite Solar Cells and Modules

First, PSCs fabricated using CsFA1−xPbI3 films with Cs+ ratios varying from 0.0 to 16.8% are prepared by the HCVD-CE method on small area substrates (1.5 cm × 1.5 cm) to evaluate the influence of the Cs+ ratio on the device performance. Planar devices with the structure of FTO/compact TiO2/CsFA1−xPbI3/spiro-MeOTAD/Au were fabricated and photocurrent density versus voltage (J−V) characteristics were measured. PCEs of the CsFA1−xPbI3 champion PSCs with various different Cs+ ratios increase in the following trend: A, B, E, D to C (Figure S9, Supporting Information). Statistical analysis shows that open circuit voltage (Voc) of the CsFA1−xPbI3 PSCs increases when the Cs+ bulk ratio increases from 0.0 to 6.6% and then decreases when the Cs+ ratio further increases to 16.8% (Figure S10a, Supporting Information, Table 1). The increase in Voc from Sample A to Sample C can be ascribed to the following two factors: (I) Bandgap of mixed perovskite increases from 1.52 eV for Sample A to 1.54 eV for Sample C. (II) MCDS of the perovskite films increases from Sample A to Sample C. Variation of the energy level alignment between both TiO2/perovskite and perovskite/spiro-MeOTAD interfaces, which determines both the electron and hole injection efficiency, is another possible reason and will be discussed later. Voc decreases when the Cs+ ratio further increases from 6.6 to 16.8%, which may be related to the decreased crystallite size and/or other reasons, for example, the too high Cs+ ratio at the perovskite surface. Short circuit current density (Jsc) decreases slightly from Sample A to Sample E, which is correlated with the reduced absorption range (Figure S10b, Supporting Information). Changes in fill factor (FF) follow the trend of changes in Voc (Figure S10c, Supporting Information). Because FF is closely related to the photoexcited carrier recombination process,[67,68] the variation of FF could be caused by the charge injection efficiency difference or the different number of the impurities acting as defect states in these films.[64,65] In our work, changes in PCEs are dominated by changes in Voc and FF (Figure S10d, Supporting Information). Specifically, mean PCE is 12.3% for pure FAPbI3 PSCs, which increases to 15.4% for Cs0.07FA0.93PbI3 and then decreases to 13.5% for Cs0.17FA0.83PbI3. Note that J−V hysteresis is observed for all the samples. For example, in the case of a Cs0.07FA0.93PbI3 PSC, PCEs are 15.3% for forward to reverse scan and 13.3% for reverse to forward scan (Figure S11, Table S2, Supporting Information). To assess the device performance more accurately, steady-state measurements were performed by varying voltages to track the maximum power point (MPP), which will be discussed later. The external quantum efficiency (EQE) measurements were performed on champion PSCs with different Cs+ ratios. All the five devices show relatively good EQE with highest efficiency values exceeding 80% (Figure S12a, Supporting Information). The integrated current density

Table 1. Photovoltaic parameters of the mixed CsFA1−xPbI3 perovskite solar cells and modules.

| Device type                | Voc [V] | Jsc [mA cm−2] | FF [%] | PCE [%] |
|---------------------------|---------|---------------|-------|--------|
| A solar cell(8)           | 0.91 ± 0.02 (0.92) | 21.3 ± 0.6 (21.0) | 63.3 ± 4.7 (71.6) | 12.3 ± 0.9 (13.8) |
| B solar cell(8)           | 0.94 ± 0.02 (0.95) | 21.2 ± 0.5 (20.9) | 66.9 ± 4.0 (70.4) | 13.4 ± 0.9 (13.9) |
| C solar cell(8)           | 0.99 ± 0.01 (1.00) | 21.1 ± 0.8 (22.0) | 75.1 ± 2.1 (75.2) | 15.4 ± 0.5 (16.6) |
| D solar cell(8)           | 0.99 ± 0.01 (0.97) | 20.8 ± 0.8 (21.5) | 73.4 ± 2.7 (76.1) | 15.0 ± 0.5 (15.9) |
| E solar cell(8)           | 0.96 ± 0.01 (0.98) | 20.7 ± 0.6 (20.1) | 68.4 ± 4.5 (68.1) | 13.5 ± 0.6 (14.4) |
| C solar module(8)         | 5.80 ± 0.04 (5.84) | 3.68 ± 0.02 (3.67) | 62.4 ± 3.8 (68.1) | 13.4 ± 0.8 (14.6) |
| Cs0.03FA0.97PbI3 solar cell(9)| 0.98 ± 0.02 (1.01) | 21.8 ± 0.5 (22.0) | 68.3 ± 1.7 (70.0) | 14.7 ± 0.4 (15.4) |
| Cs0.03FA0.97PbI3 solar module(9)| 5.01 ± 0.16 (5.06) | 3.50 ± 0.11 (3.65) | 44.8 ± 4.6 (46.6) | 7.7 ± 0.6 (8.6) |

(8) denotes champion cell/module; (9)Prepared by HCVD-CE; (9)Prepared by anti-solvent. Data were collected from forward to reverse scans.
Based on the EQE measurements matches well the $J_{sc}$ values from $J$–$V$ measurement with variations less than 2.0%. When comparing EQE from 780 to 840 nm, we find that EQE edge shifts in sequence from Sample A to Sample E (Figure S12b, Supporting Information). This is attributed to the changes in bandgap, and result in decrease in $J_{sc}$ from Sample A to Sample E as shown in statistics.

After confirming that 6.6% Cs$^+$ is the optimal ratio in terms of PCE, we then fabricated Cs$_{0.07}$FA$_{0.93}$PbI$_3$ perovskite films on large FTO/TiO$_2$ substrates (5 cm × 5 cm) using the HCVD-CE method and the anti-solvent method (as control) to study the fabrication method influence on the film uniformity. Perovskite films prepared by the HCVD-CE method show similar uniform dark color on both small (1.5 cm × 1.5 cm) and module (5 cm × 5 cm) sized substrates, while the uniformity of the perovskite films prepared by anti-solvent method clearly decreased from small area to module sized substrates (Figure 2a,b). When comparing solar modules prepared by
the two different methods, the perovskite film prepared by HCVD-CE is more uniform than that prepared by anti-solvent. To illustrate the uniformity difference at both the macroscopic and microcosmic scales, UV–vis spectroscopy and atomic force microscopy (AFM) measurements were performed on nine points for each of the two perovskite films (Positions P1–P9 are shown in Figure S13, Supporting Information, and raw data are shown in Figures S14–S17, Supporting Information). Perovskite film prepared by the HCVD-CE method shows higher absorbance and much smaller error bars in the wavelength range between 550 and 800 nm than the film prepared by the anti-solvent method (Figure 2c), suggesting that the HCVD-CE method can achieve better photoresponse and higher uniformity at the macroscopic scale. Furthermore, the root-mean-square (RMS) roughness is smaller for the HCVD-CE prepared films (Figure 2d). More interestingly, the RMS variation is almost negligible for the film prepared by HCVD-CE, while significantly higher variations are observed on the film prepared by anti-solvent, suggesting that the HCVD-CE method also improves the uniformity at the microscopic scale. To further demonstrate the scalability of our HCVD-CE method, we prepared a perovskite film on a 10 cm × 10 cm patterned FTO substrate. The perovskite film is of high quality especially in terms of large-area uniformity (Figure S18, Supporting Information). The standard deviation of film thickness is ≈ 5 nm at nine different locations (Figure S19, Supporting Information), which is only 1.4% of the total thickness (Figure S20 and Table S3, Supporting Information). Such a small thickness variation over a large area 10 cm × 10 cm strongly suggests the high quality and uniformity of the film across a large area. We then prepared Cs₀.₀₇FA₀.₉₃PbI₃ perovskite modules with the substrate size of 5 cm × 5 cm using the two methods. A typical module with a total active area of 12.0 cm² includes six single cells, each with an active area of 2.0 cm², which are connected in series. Details of module fabrication, for example, the mask design for patterning individual layers is presented in the Experimental Section (Figures S21 and S22, Supporting Information). The champion module prepared by the HCVD-CE method shows a $V_{oc}$ of 5.84 V, $I_{sc}$ of 44.08 mA, FF of 68.1%, and PCE of 14.6%, which is one of the highest performing perovskite large-area solar module to date (Figure 2e). As comparison, the champion module prepared by the anti-solvent method shows a much lower champion module PCE of 8.6% (Figure 2f). Photograph of a HCVD-CE prepared module is shown in the inset of Figure 2g and the photovoltaic parameters of 1–6 cells in series are listed in Table S4 (Supporting Information). The PCE of one cell in the solar module prepared by the HCVD-CE method is 1.1% higher than the counterpart prepared by the anti-solvent method, which increases to 2.2% for two cells in series, 5.1% for three cells, 4.7% for four cells, 5.2% for five cells, and 6.0% for six cells in series, respectively (Figure 2g). Given that the only difference is the perovskite fabrication method, we assume that the significant different PCE on the whole module is very likely related to the different film uniformity on the large area. Note that $J$–$V$ hysteresis is also observed on the perovskite modules. PCEs are 14.6% for forward to reverse scan and 12.4% for reverse to forward scan for the HCVD-CE prepared module, showing a PCE difference of 15.1% (Figure S23, Table S5, Supporting Information). As for the solar module prepared by the anti-solvent method, PCEs are 8.6% for forward to reverse scan and 5.2% for reverse to forward scan with a PCE difference of 39.5%. The reduced $J$–$V$ hysteresis on the HCVD-CE prepared module could be related to the reduced ion migration rate, the smaller number of defects, etc.[26] But this point still needs further investigation. To qualitatively evaluate that whether a perovskite fabrication method is beneficial for scaling-up, we define a parameter PCE loss/area, which equals to $\frac{(PCE_{small \ cell} - PCE_{module})}{area_{module} - area_{small \ cell}}$. In general, the smaller the PCE loss/area value is, the more potential the method has for upscaling. After a thorough literature survey of reported works on perovskite solar cells and modules, we plot a figure with the PCE loss/area value as the Y-axis and the PCE value as the x-axis. The right bottom corner of the plot is preferred representing higher PCEs and also lower PCE loss/area values. Because at the time of this work there is no report on Cs-substituted perovskite solar modules, we compare our Cs₀.₀₇FA₀.₉₃PbI₃ perovskite solar cells and modules prepared by the HCVD-CE method and the anti-solvent method with MAPbI₃, MAPbI₃, Cl, and FAPbI₃ solar cells/modules in the literature. Three factors are considered when selecting the data point from the literature: (I) both PCE of small cells and modules are shown in the literature in order to extract the PCE loss/area, (II) PCE over 8% is included considering the quality of the module, (III) active area is over 4.0 cm². Details of the solar cell/module parameters are listed in Table S6 (Supporting Information). The champion module prepared by HCVD-CE method not only shows a PCE of 14.6%, which is among the highest performing perovskite modules, but also a PCE loss/area of 0.17% cm⁻², which is among the smallest values according to calculation based on the reported works (Figure 2h). Equally important is that this is the first reported Cs-substituted perovskite module, which shows more potential in terms of the material intrinsic stability than other perovskites. When comparing the perovskite modules prepared by the HCVD-CE and anti-solvent methods, the module prepared by the HCVD-CE method shows much higher PCE and smaller PCE loss/area. Considering these two factors, the HCVD-CE method is promising especially in terms of upscaling. We also observed a slight PCE decrease comparing the small perovskite cells and modules that prepared by the HCVD-CE method, which is likely due to the increased series resistance or poor contact between subcells.[42,70] These issues can be solved with further optimization on the module design and patterning techniques.

### 2.3. Investigation on Morphology of CsₓFA₁₋ₓPbI₃ Perovskite Films

In addition to developing the large-area-compatible Cs-containing perovskite fabrication method, we are also interested in understanding the influence of the Cs⁺ ratio on the device performance and stability of perovskite solar cells based on the Cs₀.₀₇FA₀.₉₃PbI₃ films prepared by the HCVD-CE method. Morphology and the crystallite domain size of the CsₓFA₁₋ₓPbI₃ perovskite layers with various Cs⁺ ratios were investigated using scanning electron microscopy (SEM). All the perovskite films show relatively large crystallite domain.
sizes, suggesting good crystallinity (Figure 3a–e). The crystallite domain size increases from Samples A to D and decreases from Samples D to E, consistent with the Le Bail refinement calculation. Interestingly, changes in the device PCEs follow the trend of the changes of the grain sizes except for sample D. This phenomenon has been found in the research community and interpreted as the different charge extraction processes experienced due to different number of grain boundaries that the photogenerated charges need to pass through.[77] Therefore, we confirm that the grain size variation is one of the reasons for the device PCE increase. On the other hand, no obvious morphology changes can be found for Samples A, B, and C. But for Samples D and E with Cs ratios higher than 10.2%, small crystals with a size less than 100 nm are found at the perovskite surfaces. The number of the small crystals increases as a function of Cs$^+$ concentration increase during the exchange processes. These small crystals are assumed to be the Cs-rich perovskite phase due to increase of the FWHM of PL peaks when Cs$^+$ ratio is increased, which is probably the reason for the device PCE decrease for Samples D and E. To know whether the Cs-rich perovskite phase also appears in the perovskite bulk, a complete PSC based on Sample E is prepared for SEM cross-section imaging. No small crystals can be found in the bulk, suggesting the Cs-rich perovskite impurities are mainly at the film surface rather than in bulk when increasing the Cs$^+$ concentration in the solution during the exchange process.

2.4. Analysis of the Energy Level Alignment of the Mixed Cs$_x$FA$_{1-x}$PbI$_3$ with Electron and Hole Transport Materials

Changes of the Cs$^+$ ratio in HCVD-CE prepared mixed perovskites may also influence the position of perovskite energy levels and thus the device PCE by varying the charge injection efficiency. Therefore, we performed ultraviolet photoemission spectroscopy (UPS) measurements on various Cs$_x$FA$_{1-x}$PbI$_3$ films deposited on FTO/c-TiO$_2$ substrates to understand the influence of the Cs$^+$ ratio on the work function and the valence band edge. The work function and the valence band edge were determined with UPS using a He I (21.22 eV) source. Chamber pressure was below 6.0 × 10$^{-9}$ Torr for XPS and UPS measurements. Element distribution on the film was characterized with XRF (XGT-7000, Horiba). The work function decreases when the Cs$^+$ ratio increases in the films (Figure 4a). The valence band maximum (VBM) shifts toward the Fermi level as the Cs$^+$ ratio increases (Figure 4b). To evaluate energy level alignment on the whole devices for different mixed perovskite, UPS measurements were also conducted on the FTO/c-TiO$_2$ substrate and a doped spiro-MeOTAD film deposited on the FTO/c-TiO$_2$/Cs$_{0.07}$FA$_{0.93}$PbI$_3$ substrate to determine the complete interface energy diagram (Figure 4c, Figures S24 and S25, Supporting Information). The optical bandgap of mixed perovskite films is used to calculate the conduction band minimum (CBM) values. Fermi level alignment instead of vacuum level alignment is used here, and details are explained in the Experimental Section (Figure S26, Supporting Information). The bandgap value of TiO$_2$ is 3.3 eV according to the literature.[16]
and the valence band edge is 3.24 eV, suggesting the Fermi level is strongly pinned to the CBM of TiO$_2$ (Figure S24, Supporting Information). The CBM of FAPbI$_3$ is 10 meV below TiO$_2$. Interestingly, CBM of mixed perovskite increases upon increasing the Cs$^+$ ratio until reaches 6.6%. Specifically, the CBM of Cs$_{0.07}$FA$_{0.93}$PbI$_3$ is 210 meV above that of TiO$_2$, which significantly favors for the electrons injection. Further increase of the Cs$^+$ ratio shows negligible influence on the CBM values.

On the other hand, VBM of mixed perovskite increases as a function of the Cs$^+$ ratio from 1.48 eV for 0.0% to 1.27 eV for 6.6%, then maintains at 1.30 eV until reaches 16.8%. The work function and VBM for spiro-MeOTAD are 3.98 and 1.20 eV, respectively (Figure S25, Supporting Information). Energy difference between VBM of mixed perovskite and spiro-MeOTAD reduces from 280 meV for Sample A to 100 meV for Sample E, also suggesting the improved hole injection from mixed perovskite to spiro-MeOTAD, due to the favored energy level alignment. Both electron and hole injection are facilitated when Cs$^+$ ratio is higher than 6.6%, which is another very important reason for the device PCE increase from Samples A to C. PCE reduction upon further increase of the Cs$^+$ ratio from 6.6 to 16.8% cannot be explained based on the energy level alignment point of view, suggesting that there are other dominating factors determining the device PCE when Cs$^+$ ratio is higher than 6.6%.

To further strengthen our explanation on the device performance enhancement, we performed time-resolved photoluminescence decay (TRPL) measurement on Samples A to E. First, we prepared the perovskite films on the quartz substrates without an electron transporting layer (ETL) or a hole transporting layer (HTL) to evaluate the pure carrier recombination
dynamics (Figure S27, Supporting Information). The carrier lifetimes, defined as the time when the PL intensity decays to 1/e, are extracted and listed in Table S7 (Supporting Information). We then prepared the perovskite films on the FTO/c-TiO2 substrates, which contains ETL. Lifetime parameters are also listed in Table S5 (Supporting Information). It is found that (i) PL decay is faster for all the samples with the structure containing ETL, (ii) the decay is much faster for Samples B–E compared to Sample A with the structure containing ETL. This result suggests that the electron injection from the perovskite to the c-TiO2 layer is facilitated for Samples B–E, which is in agreement with the favorable energy level alignment for Samples B–E compared to Sample A (Figure 4c).

2.5. Analysis of the Cs+ In-Depth and Lateral Distribution on the Mixed CsFAPbI3 Perovskite Film

Because the Cs cation exchange on FAPbI3 is expected to start from the FTO side and then gradually toward the bulk as a result of ion diffusion, Cs+ ratios at the film surface can be different from the bulk. This has been characterized by SEM suggesting that Cs-rich phase appears at the film surface but not in the bulk (Figure 3d–f). Different Cs+ ratios between perovskite surface and bulk could significantly affect the device PCE and stability. High-resolution X-ray photoemission spectroscopy (HRXPS) measurements were performed on the A, B, C, D, and E perovskite films to analyze the element ratios at surface, and then compare with the bulk. Except for Sample A, all other samples show two symmetric peaks at 739.0 and 725.0 eV, which are assigned to the Cs 3d(3/2) and 3d(5/2) peaks, respectively (Figure 5a). The peak intensity at 725.0 eV gradually increases from 0 for Sample A to 278.7 counts for Sample E, suggesting that the Cs+ ratio increases as the Cs+ concentration in the solution rises. Symmetric peaks at 143.4 and 138.5 eV are indexed as the Pb 5/2 and Pb 3/2 peaks (Figure 5b). Compared to Cs+, the intensity of Pb 5/2-related peaks are similar for all the samples. Additional tiny peaks appear at 141.6 and 136.7 eV, which are associated with PbO. These peaks are enlarged by five times to clearly exhibit the trend (Figure 5b inset). We find that the Pb peak intensity increases as a function of Cs+ ratio, suggesting that the amount of metallic lead increases as the Cs+ ratio rises. The peaks at 630.9 and 619.3 eV are attributed to I 3d(3/2) and 3d(5/2) peaks, which show similar positions and intensity for different samples (Figure 5c). Two peaks at 288.5 and 284.9 eV are assigned to C 1s peaks with different chemical states (Figure 5d). The peak at a higher binding energy of 288.5 eV comes from CH(NH2)2, suggesting that the amount of metallic lead increases as the Cs+ ratio rises. The PbO peak intensity increases as a function of Cs+ concentration.

2.6. Stability of the Mixed CsFAPbI3 Perovskite Solar Cells under Different Relative Humidity Conditions

Stability of the series of mixed PSCs prepared by HCVD-CE method is systematically studied to evaluate the influence of Cs+ ratio on the device lifetime. CsFAPbI3 Perovskite PSCs containing different Cs+ ratios were prepared and stored in a dry cabinet with relative humidity of around 18% for aging test. Photos of devices were taken from FTO sides at different storage times to track the color changes. All the fresh prepared CsFAPbI3 PSCs show dark color (Figure S29, Supporting Information). Color of Sample A changes to yellow after 1 d starting from the device edges, which spreads to the whole devices after longer aging time. The fade speed is obvious decreased for Sample B, which shows initial decay until 8 d. Observed yellow color is either from the formation of FAPbI3 non-perovskite phase or from PbI2, evidenced by the appearance of 11.7° and 12.6° XRD peaks (Figure S30, Supporting Information). No color changes are observed for C, D, and E after 32 d, suggesting their significantly improved phase stability. Furthermore, steady-state measurements were performed by applying voltages that tracked the maximum power point (MPP) on A, C, and E to compare their lifetimes under devices working condition. Measurements were first performed in ambient with relative humidity (RH) of ~60%. Similar to the previous report, all the devices experience dynamic stages (designated as stage 1) during the first 1–2 min measurements, and then reach the more stable stages (designated as stage 2) (Figure 6a,b). The appearance of transient behavior in stage 1 was still under investigation, and we focused on the stage 2. In stage 2, both C and E show much slow PCE decay rates compared to A, which can be explained by the improved perovskite phase stability with Cs+ substitution (Figure 6b). When comparing C to E, C shows much...
slower decay. This is correlated to the Cs⁺ ratios at the surface and the bulk of the two perovskite films. The existence of the Cs-rich CsₓFA₁₋ₓPbI₃ layer for C (containing 15.0% Cs⁺) further increase the phase stability of the bulk film (containing 6.6% Cs⁺) due to the prevention of moisture from directly contacting the perovskite bulk, which is the reported decay mechanism for FAPbI₃. While Sample E contains 16.8% Cs⁺ in bulk and 52.8% Cs⁺ at the film surface. Although it has been reported that 15% Cs⁺ in Cs₀.₁₅FA₀.₈₅PbI₃ PSC is thermally stable,[33] such a high Cs⁺ ratio at perovskite surface can lead to obvious phase
segregation and result in device instability. Specifically, 56% PCE from the starting point of stage 2 is maintained for Sample C after 1000 min, which is much better than the solution-prepared Cs0.10FA0.90PbI3 PSCs.[41] These results demonstrate the significant device stability improvement on the Cs-contained perovskite prepared by our HCVD-CE method. To further prove the concept, measurements were then conducted on the three samples in an N2-filled glovebox with RH of ≈5%. Two lifetime stages, that is, stage 1 (dynamic stage) and stage 2 (more stable stage), are also observed (Figure 6c,d). In stage 2, all the three samples show significantly reduced PCE decay rates, demonstrating the improved lifetimes in an inert atmosphere than in ambient. We assume the stability improvement comes from the reduced dynamics on materials, for example, perovskite, spiro-MeOTAD, and the interfaces between different adjacent materials in the inert atmosphere. After 1200 min, 42.6% PCE from starting point of stage 2 is maintained for A, which increases to 56.2% for E. Interestingly, no obvious PCE decrease is observed on C in the whole stage 2 with a stabilized PCE of 14.0%, suggesting the stability of the Cs0.07FA0.93PbI3 PSC prepared by the HCVD-CE method is very promising if proper encapsulation is performed.

3. Conclusions

In summary, a hybrid CVD with cation exchange method is developed for preparation of Cs-substituted mixed cation perovskite films. This technique shows a high potential toward scaling-up the Cs-substituted perovskite from lab solar cell scale (1.5 cm × 1.5 cm sized substrate) to module scale (5 cm × 5 cm sized substrate) with a high module PCE of 14.6% (12.0 cm² active area) and small PCE loss/active area of 0.17% cm⁻². Cs0.07FA0.93PbI3 perovskite solar cell prepared by this method shows 14.0% PCE after 1200 min steady-state measurement by tracking the maximum power point in an N2-filled glove box (≈5% RH), demonstrating the promising device stability achieved by this perovskite fabrication technique.

Supporting Information

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

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