Enhancing the thermal stability of the carbon-based perovskite solar cells by using a Cs$_x$FA$_{1-x}$PbBr$_x$I$_{3-x}$ light absorber†

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Despite the impressive photovoltaic performance with a power conversion efficiency beyond 23%, perovskite solar cells (PSCs) suffer from poor long-term stability, failing by far the market requirements. Although many efforts have been made towards improving the stability of PSCs, the thermal stability of PSCs with CH$_3$NH$_3$PbI$_3$ as a perovskite and organic hole-transport material (HTM) remains a challenge. In this study, we employed the thermally stable (NH$_2$)$_2$CHPbI$_3$ (FAPbI$_3$) as the light absorber for the carbon-based and HTM-free PSCs, which can be fabricated by screen printing. By introducing a certain amount of CsBr (10%) into PbI$_2$, we obtained a phase-stable Cs$_x$FA$_{1-x}$PbBr$_x$I$_{3-x}$ perovskite by a "two-step" method and improved the device power conversion efficiency from 10.81% to 14.14%. Moreover, the as-prepared PSCs with mixed-cation perovskite showed an excellent long-term stability under constant heat (85 °C) and thermal cycling (−30 °C to 85 °C) conditions. These thermally stable and fully-printable PSCs would be of great significance for the development of low-cost photovoltaics.

Introduction

The study of organic–inorganic hybrid lead halide perovskite solar cells (PSCs) has been a hot topic in recent years owing to the meteoric rise of their power conversion efficiency (PCE) from 3.8% to over 23%. Such a high PCE value together with the low-cost and easy fabrication process have prompted PSCs to be a strong competitor to commercial silicon solar cells. For a marketable solar device, passing the standard accelerated aging tests (IEC standard) is the basic guarantee for a device lifetime of 20–25 years. Unfortunately, PSCs are still struggling to pass these aging tests, including thermal cycling, damp heat, UV preconditioning and outdoor exposure. It is well known that organic–inorganic hybrid lead halide perovskites are very sensitive to water and oxygen. For example, the CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) perovskite could easily react with H$_2$O in humid air and decompose into PbI$_2$, CH$_3$NH$_2$ and HI. Theoretically, high-sensitivity encapsulation could protect the perovskite from moisture-related corrosion. Hence, more and more researchers have focused their study on the intrinsic stability problems of perovskites, which are hard to solve using an encapsulating strategy. The thermal stability of the organic–inorganic hybrid lead halide perovskites has been widely reported and is considered as one of the most important intrinsic stability issues for the practical application of PSCs. Outdoors, the temperature of the installed solar cell panels can easily reach up to 85 °C, especially during the day time in a desert region. However, the MAPbI$_3$ perovskite goes through a phase change from tetragonal to cubic phase at around 54 °C. Moreover, the formation energy of the MAPbI$_3$ perovskite is 0.11–0.14 eV, which is very close to 0.093 eV, suggesting a possible degradation at 85 °C. Obviously, the “soft” MAPbI$_3$ perovskite is the vulnerable point in the device’s long-term stability. Nowadays, replacing the CH$_3$NH$_3^+$ cation by [NH$_3$]CH$^+$ (FA) or the Cs$^+$ cation, which has a high thermal tolerance capability, is a common strategy for enhancing the thermal stability of PSCs. Nevertheless, a thermally stable perovskite light absorber is a necessary but not a sufficient condition for a stable PSC device. At the same time, we also need to take into account the other parts of PSCs, such as hole-transport materials (HTM), electron-transport materials (ETM), and the counter electrode (CE). Spiro-OMeTAD and Au are usually used as HTM and CE, respectively, in PSCs with normal structure. So far, the Spiro-OMeTAD and Au-based PSCs have shown superior performance in terms of PCE values than other types of PSC devices; however, both the Spiro-OMeTAD and Au are suffering from various stability problems. It has been widely reported that...
lithium salts could accelerate the thermal degradation of Spiro-
OMeTAD.\textsuperscript{12} Moreover, the Au back contact also could easily
diffuse into the Spiro-OMeTAD layer when the temperature is
above 70 °C,\textsuperscript{13} which can create deep trap states within the films.
Hence, from the perspective of stability, the hole-conductor-free
PSCs with a carbon electrode (carbon-based PSCs) possess
a huge advantage.

The typical carbon-based PSCs mainly consist of three meso-
porous inorganic layers (TiO\textsubscript{2}, ZrO\textsubscript{2} and carbon), which can be
prepared by screen printing. Obviously, the non-use of organic
HTM and Au electrode makes the carbon-based PSCs not only low-
cost but also stable. Since the first report of carbon-based PSCs,\textsuperscript{14}
more and more researchers have shown their interest on such PSCs
with a special mesoporous structure.\textsuperscript{15,18–20} However, most of them
have still focused on how to enhance the PCE of the device. Several
strategies including solvent engineering,\textsuperscript{18} post-treatments\textsuperscript{17} and
adding the halide component\textsuperscript{18,21–23} into the perovskite precursor have been
developed to optimize the crystallization of the MAPbI\textsubscript{3}
perovskite. Up to now, the champion PCE of carbon-based PSCs
with the MAPbI\textsubscript{3} perovskite has exceeded 16%.\textsuperscript{19} Although there is
an obvious gap in terms of the PCE value between carbon-based
PSCs and the traditional one with Au electrode, the carbon-based
PSCs actually have huge industrialization potential because of
their easy scaling-up character.\textsuperscript{20} However, as we mentioned above,
the MAPbI\textsubscript{3} perovskite has intrinsic stability problems. Therefore,
introducing a thermally stable FAPbI\textsubscript{3} perovskite into the carbon-
based PSCs would be of great significance.

Herein, we comprehensively investigated the FAPbI\textsubscript{3} perov-
skite as a light absorber for high-performance carbon-based
PSCs. By introducing a certain amount of CsBr into the PbI\textsubscript{2}
precursor, we found that the phase transition of the FAPbI\textsubscript{3}
perovskite from the a phase to the \( \delta \) phase can be successfully
restrained. Thus, the Cs\textsubscript{x}FA\textsubscript{1-x}PbBr\textsubscript{1.5}I\textsubscript{3-x} based device achieved
a PCE value up to 14.14%, which is much higher than that of the
FAPbI\textsubscript{3} version (10.81%). Importantly, the mixed-cation Cs\textsubscript{y}
FA\textsubscript{1-y}PbBr\textsubscript{1.5}I\textsubscript{3-y} perovskite showed a pleasant thermal stability
both under a constant temperature of 85 °C and thermal cycling
condition (−30 °C to 85 °C). To the best of our knowledge, this is
the first study on the thermal cycling performance of the carbon-
based PSCs, which would provide a certain reference value for their practical application.

Experimental

Materials and precursor preparation

Materials. PbI\textsubscript{2}, PbBr\textsubscript{2}, and CsBr were purchased from Xi’an
p-OLED Corp. CsI, N,N-dimethyl formamide (DMF) and iso-
propanol (IPA) were purchased from Sigma-Aldrich. TiO\textsubscript{2} paste
was purchased from NJUKII. ZrO\textsubscript{2} and carbon paste were
prepared as per former reports.\textsuperscript{14}

Precursor preparation. The lead precursor solutions were
prepared by dissolving PbI\textsubscript{2} with different amounts of PbBr\textsubscript{2},
CsI or CsBr into DMF and stirred until a clear solution was
obtained. The concentrations of all the lead precursor solutions
were 1 M. The FAI solution was prepared by dissolving FAI into
IPA solvent at a certain concentration.

Device fabrication

FTO glass was etched by a laser machine into two detached
electrode patterns, followed by ultrasonic cleaning with a deter-
gent solution, deionized water and ethyl alcohol, and then dried
with clean dry air. A compact TiO\textsubscript{2} layer was first deposited on the
FTO glass by a spray pyrolysis method with di-isopropanolami-
nium bis(acetylatedonate) solution at 450 °C. Then, 1 \( \mu \)m mesoporous
TiO\textsubscript{2} layer, 1.5 \( \mu \)m mesoporous ZrO\textsubscript{2} spacer layer and 10 \( \mu \)m
mesoporous carbon layers were successively printed on the FTO
substrate with the TiO\textsubscript{2} compact layer. After sintering, the device
with triple mesoporous layers films was first filled with 5 \( \mu \)L lead
precursor solution on top of the carbon layer and then annealed at
70 °C for 10 min to remove the excess solvent. After cooling down
to room temperature, the films were immersed into the FAI/IPA
solution for a while until the lead precursor turned completely
into perovskite. Then, the IPA solvent was used to wash off the
residual FAI. Eventually, after 10 min of annealing on the hot
plate, we obtained the working devices. All the above-mentioned
procedures were completed in air.

Characterization

The absorption measurements were performed using a UV-vis
spectrophotometer (Lambda 750S, PerkinElmer America). The
composition and microstructure of the carbon-based PSCs were
characterized using X-ray diffraction spectroscopy (XRD, Cu K\textsubscript{α1},
X'Pert PRO-PANalytical) and field-emission scanning electron
microscopy (FE-SEM, Zeiss Ultra Plus). The steady-state photo-
luminescence (PL) and the time-resolved photoluminescence
(TRPL) were recorded on a fluorescence spectrophotometer
(Hitachi F-7000, Hitachi High-Technologies Co., Tokyo, Japan) and
Delta Flex Fluorescence Lifetime System (Horiba Scientific Com.,
Japan). The photocurrent density and voltage curves of the devices
were measured using a solar simulator (Oriel 94023A, 450 W) with
a source meter (Keithley 2400) under a 100 mW cm\textsuperscript{−2} illumination
(AM 1.5G) at a scan rate of 10 mV s\textsuperscript{−1}. All the devices were tested
under standard AM 1.5G sun light with a metal mask of 0.1475
cm\textsuperscript{2}, which is smaller than the active area (0.8 cm\textsuperscript{2}). An external
quantum efficiency (EQE) measurement system (QEX10, PV
Measurements, Inc.) was used to measure the EQE of the devices
across a wavelength range of 300–850 nm. The long-term thermal
stability measurements were performed in an environmental
chamber (Weiss SC3 600 MHG). For the thermal cycling test, a full
temperature cycle was followed, which consisted of heating the
chamber from room temperature to 85 °C at a rate of 3 °C min\textsuperscript{−1},
maintaining the chamber at 85 °C for 25 min, cooling the
temperature down to −30 °C at the same rate of 3 °C min\textsuperscript{−1}, and
maintaining the chamber at −30 °C for 25 min. And heating the
chamber to room temperature at the same rate of 3 °C min\textsuperscript{−1}.

Results and discussion

Carbon-based PSCs were fabricated using a previously reported
procedure.\textsuperscript{14} As shown in Fig. 1a, mesoporous TiO\textsubscript{2}, ZrO\textsubscript{2} and
carbon films were successively deposited on the FTO substrates,
which have been coated with compact TiO\textsubscript{2} beforehand. Subse-
quently, the perovskite was loaded into the devices by a “two-
step” method. Briefly, lead precursors (pure, 5% Br, 10% Br, 15% Br, 5% Cs, 10% Cs, 15% Cs, and 10% Br–Cs) were first infiltrated into the mesoporous films. After drying on a hot plate, the devices were soaked into the FAI/IPA solution for a while until the color of the films changed from yellow to dark brown, indicating the formation of the FAPbI₃-based perovskite (Fig. 1b).

The microstructures of the as-prepared devices can be observed using scanning electron microscopy (SEM) images of the cross-section. We can clearly find that each layer of the device showed well-defined boundaries and a uniform thickness (Fig. 2a). Through the EDS mapping, the triple layers from the top to the bottom can be identified as carbon, ZrO₂, and TiO₂. For the perovskite, Pb, I, Br, and Cs have a uniform distribution in the carbon/ZrO₂/TiO₂ layers, indicating a good deposition method.

To study the influence of the Cs cation and Br ion in the crystal structure of the FAPbI₃ perovskite, we introduced CsI, PbBr₂, and CsBr with different mole ratios into the PbI₂ solution. X-ray diffraction (XRD) measurements were used to identify the crystal structure of the as-prepared perovskite samples. The pure FAPbI₃ exhibited a series of diffraction peaks at 2θ = 13.8°, 20°, 24.2°, 28°, 31°, 40°, and 42.7°, corresponding to the (111), (220), (021), (222), (231), (240), and (333) crystal planes of the α-FAPbI₃ perovskite (Fig. 3). Moreover, a small diffraction peak at 2θ = 11.7° can be detected, indicating the existence of δ-FAPbI₃. With the increase in Br, the δ-FAPbI₃ showed a declining trend. Moreover, when the Br ratio came to 10%, there was no obvious peak of δ-FAPbI₃. Similarly, the introduction of Cs could also restrain the generation of δ-FAPbI₃.

To further investigate the effect of Br and Cs on the stability of the FAPbI₃ perovskite, we stored all the samples in ambient air at 25 °C at a relative humidity (RH) of 50% and measured their XRD patterns every few days (7 days) to record the changes. As shown in Fig. S1a–h, after 7 days, the peak of δ-FAPbI₃ emerged from all of the samples except the one with 10% of CsBr. Moreover, after 14 days, the FAPbI₃–10% CsBr sample still maintained the black α phase, while other samples had an obvious increase in the δ phase.

Hence, we can conclude that though both Cs and Br could inhibit the transformation of the FAPbI₃ perovskite from α phase to δ phase, only the coexistence of Cs and Br could actually enhance the stability of the FAPbI₃ perovskite (Fig. 3).

The optical properties of the FAPbI₃-based perovskite films with different content of Br and Cs were measured by the UV-vis spectra and steady-state photoluminescence (PL) spectra. As shown in Fig. 4a, with the increase in the content of Br, the absorption edge of the samples had an obvious blue-shift, which is in good agreement with the theoretical calculations. Moreover, all the samples exhibited a slight enhancement of light absorption from 650 nm to 750 nm. For the samples with Cs, a slight blue-shift can be observed, manifesting the limited effect of Cs on the band gap of the FAPbI₃ perovskite. Unlike Br, the introduction of Cs could significantly enhance the light absorption of the FAPbI₃ perovskite from 650 nm to 750 nm. Note that the FAPbI₃ perovskite with both Br and Cs showed the strongest absorbance from 650 nm to 750 nm among all the samples (Fig. 4c). Steady-state PL spectra measurements were also obtained for the perovskite samples loaded in the ZrO₂/glass substrate. The emission peak of the Br-based FAPbI₃ perovskite shifted from 807 nm to 798 nm as the Br ratio increased from 5% to 15% (Fig. 4b). Furthermore, the blue shifting of the Cs-based FAPbI₃ perovskite was more

Fig. 1 (a) The schematic of a fully printable HTM-free mesoscopic PSCs with carbon CE; (b) the schematic of a two-step sequential deposition method.

Fig. 2 (a) The cross-sectional view of the SEM image of the carbon-based PSCs; (b) the corresponding EDS mapping.

Fig. 3 XRD pattern of the FAPbI₃-based PSCs.
inconspicuous (from 809 nm to 805 nm as the Cs ratio increased from 5% to 15%) than that of Br (Fig. 4d). These results are in good agreement with the UV-vis results.

Carbon-based PSCs with these different FAPbI$_3$-based perovskites were measured under standard AM 1.5 illumination. After optimization (see Tables S1 and S2†), we found that the device with 10% Br or 10% Cs possessed higher PCE than that with other ratios. To ensure that the improvement of PCE is repeatable, four batches of PSCs (each consists of 15 devices) were fabricated using pristine FAPbI$_3$, FAPbI$_3$ with 10% of Br, FAPbI$_3$ with 10% of Cs and FAPbI$_3$ with 10% of Br–Cs, respectively. The detailed $J$–$V$ performances are presented in Fig. S2,† and we found that the average PCE value of the devices was improved by introducing Br and Cs into FAPbI$_3$.

To find out how Br and Cs affect the performance of the FAPbI$_3$-based PSCs, we compared the champion devices with 10% Br, 10% Cs and 10% Cs–Br. As shown in Fig. 5a, the device with pristine FAPbI$_3$ perovskite possessed an open circuit voltage ($V_{oc}$) of 929 mV, a short circuit current density ($J_{sc}$) of 20.53 mA cm$^{-2}$ and a fill factor (FF) of 0.567, yielding an overall PCE of 10.81%. By introducing 10% of Br, the FAPbBr$_{0.1}$I$_{2.9}$-based device exhibited a slightly higher $V_{oc}$ (958 mV) and FF (0.593) than that of the pristine one, which resulted in a PCE of 11.53%. The Cs$_{0.1}$FA$_{0.9}$I$_{2.9}$-device showed similar $J$–$V$ parameters with the FAPbBr$_{0.1}$I$_{2.9}$-based one. Interestingly, the Cs$_{0.1}$FA$_{0.9}$PbBr$_{0.1}$I$_{2.9}$-device also showed obvious enhancement in $V_{oc}$ (1018 mV), $J_{sc}$ (22.16 mA cm$^{-2}$) and FF (0.627) in comparison to the other devices and exhibited a champion PCE of 14.14% (see Table 1 for the detail fitting parameters), which can be attributed to the better crystal quality. We deduced that the trap state density in pristine FAPbI$_3$ is pretty high because of the phase transition. By introducing Br and Cs into the crystal, the structure of the FAPbI$_3$ perovskite became more stable, and as a result, the trap state density was reduced. Apparently, the Cs$_{0.1}$FA$_{0.9}$PbBr$_{0.1}$I$_{2.9}$ crystal possessed the best phase stability and the lowest trap state density. Moreover, the $J$–$V$ hysteresis of the Cs$_{0.1}$FA$_{0.9}$PbBr$_{0.1}$I$_{2.9}$-device remained at a low level (Fig. 5d), which also can provide evidence for our deduction.‡

The long-term thermal stability measurements of FAPbI$_3$-based PSCs were performed in an environmental chamber (Weiss SC3 600 MHG). At a constant temperature of 85 °C and 20% relative humidity (RH) condition, the device with the pristine FAPbI$_3$ perovskite lost >60% (from 100% to 35.8%) of the initial PCE value after 500 h (Fig. 6a). However, the device with the Cs$_{0.1}$FA$_{0.9}$PbBr$_{0.1}$I$_{2.9}$ perovskite showed a pleasant long-term stability and maintained 90% of its initial PCE value (from 100% to 90.2%). At a RH 50% condition, the Cs$_{0.1}$FA$_{0.9}$PbBr$_{0.1}$I$_{2.9}$-device also showed a strong moisture resistance (see Fig. S4†). To further evaluate the long-term stability of the device under practical thermal stress, we also performed the thermal cycling test on the devices. First, the encapsulated devices were loaded in the environmental chamber and stabilized at 25 °C. Then, the chamber was heated up to 85 °C for 25 min, and chilled down to −30 °C for 25 min. After 100

**Table 1** The photovoltaic parameters of the champion carbon-based PSCs with different perovskites

<table>
<thead>
<tr>
<th>Composition</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>929</td>
<td>20.53</td>
<td>0.567</td>
<td>10.81</td>
</tr>
<tr>
<td>10% Br</td>
<td>958</td>
<td>20.29</td>
<td>0.593</td>
<td>11.53</td>
</tr>
<tr>
<td>10% Cs</td>
<td>970</td>
<td>20.91</td>
<td>0.578</td>
<td>11.72</td>
</tr>
<tr>
<td>10% Br–Cs</td>
<td>1018</td>
<td>22.16</td>
<td>0.627</td>
<td>14.14</td>
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recombination behaviour between the electron and hole in the FAPbI$_3$-based perovskite. In comparison to the pristine FAPbI$_3$ perovskite, other samples with Br or Cs showed a longer electron lifetime (see Table S3† for the detail fitting parameters), which is highly consistent with the RSC Advances Paper view Article Online
cycles, the Cs$_{0.1}$FA$_{0.9}$PbBr$_{0.5}$I$_{2.9}$ device had no obvious decay in the PCE value, manifesting its superior stability under thermal stress.

Conclusions

In summary, we comprehensively studied the effect of the Br and Cs ions on the performance of carbon-based PSCs with the FAPbI$_3$ perovskite. By regulating the content of Br and Cs, we obtained a high PCE up to 14.14% on the PSC device with the Cs$_{0.1}$FA$_{0.9}$PbBr$_{0.5}$I$_{2.9}$ perovskite. Moreover, the as-prepared device exhibited an outstanding stability against humidity and heat. Without encapsulation, the device maintained 87% of its initial PCE under 50% RH after 120 days, and the PCE only decreased by about 10% after 480 h at 85 °C. Thermal cycling tests were also performed on these carbon-based devices. According to the results, the Cs$_{0.1}$FA$_{0.9}$PbBr$_{0.5}$I$_{2.9}$ perovskite showed superior stability than the FAPbI$_3$ and MAPbI$_3$ perovskites in the carbon-based PSCs. This study may provide a certain reference value to the practical application of low-cost, high-efficiency PSCs.

Conflicts of interest

There are no conflicts to declare.

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Notes and references