CsPbCl$_3$-Driven Low-Trap-Density Perovskite Grain Growth for >20% Solar Cell Efficiency

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Charge recombination in grain boundaries is a significant loss mechanism for perovskite (PVK) solar cells. Here, a new strategy is demonstrated to effectively passivate trap states at the grain boundaries. By introducing a thin layer of CsPbCl$_3$ coating before the PVK deposition, a passivating layer of PbI$_2$ is formed at the grain boundaries. It is found that at elevated temperature, Cl$^-$ ions in the CsPbCl$_3$ may migrate into the PVK via grain boundaries, reacting with MA$^+$ to form volatile MACl and leaving a surface layer of PbI$_2$ at the grain boundary. Further study confirms that there is indeed a small amount of PbI$_2$ distributed throughout the grain boundaries, resulting in increased photoluminescence intensity, increased carrier lifetime, and decreased trap state density. It is also found that the process passivates only grain surfaces, with no observable effect on the morphology of the PVK thin film. Upon optimization, the obtained PVK-film-based solar cell delivers a high efficiency of 20.09% with reduced hysteresis and excellent stability.

In improving the performance of PSCs, a series of strategies have been studied, such as interface material fabrication,[15–18] crystal-growth engineering,[19–23] optical engineering,[24–27] and composition engineering.[28–31] Significant achievements have been made in these areas. More recently, trap state passivation has also been found to be a key factor because the trap states in the PVK layer, especially in the grain boundaries,[34–37] can induce serious charge carrier recombination for reduced PSC performance. Unfortunately, these trap passivation methods usually trigger uncontrollable nucleation sites in the film, resulting in deteriorated PVK grain growth and crystallinity.[38–41] Hence, it is imperative to develop an effective method to passivate the grain boundary defects without affecting the crystallinity of the PVK film.

Herein, we demonstrate a new strategy to effectively passivate trap states at the grain boundaries. By introducing a thin layer of CsPbCl$_3$ before the PVK deposition, a passivating layer of PbI$_2$ is formed at the grain boundaries. It is found that the CsPbCl$_3$ layer has no effect on the morphology of the PVK thin film beyond passivating the trap states at the grain boundaries. As a result, the compact PVK film has uniform morphology without pinholes, allowing us to fabricate high-performance PSCs with efficiency of 20.09% and superior stability.

To study device performance, the planar structure (FTO/TiO$_2$/PVK/spiro-OMeTAD/Au) was employed using (FAPbI$_3$)$_{0.85}$ (MAPbBr$_3$)$_{0.15}$ as an active PVK absorber material because of its optimized bandgap and phase stability.[42] For the material preparation, CsPbCl$_3$ quantum dots (QDs) were sandwiched between TiO$_2$ and PVK precursor layers. Figure 1a schematically details the formation process of the CsPbCl$_3$-QDs-driven low-trap grain-boundary FA$_{0.85}$MA$_{0.15}$PbI$_{2.55}$Br$_{0.45}$ thin film. It is expected that the PVK thin film with high defect density was first produced by annealing the liquid FA$_{0.85}$MA$_{0.15}$PbI$_{2.55}$Br$_{0.45}$ precursor at 150 °C for 15 min. During the process, the Cl$^-$ ions in the CsPbCl$_3$ QDs diffuse into the PVK film via the grain boundaries, reacting with MA$^+$ to form volatile MACl, which sublimes at the elevated temperature and leaves a surface layer of PbI$_2$ that passivates the grain boundaries.[43]

It should be noted that when a suitable amount of CsPbCl$_3$ QDs is used to form just a surface layer of PbI$_2$, the optimum passivation effect is observed. Any superfluous CsPbCl$_3$ QDs will generate too much residual PbI$_2$, thus inhibiting the charge transfer and collection.[44] The energy level diagram of the PSCs

Organic–inorganic lead halide perovskite (PVK), with its outstanding photophysical properties and versatility in low-temperature solution processes,[1–8] is considered one of the most promising materials for thin-film solar cells.[9–11] In just the few years since its invention, the power conversion efficiency (PCE) of the organic–inorganic hybrid PVK solar cell (PSC) based on mixed cations and halides has been rapidly increased to as high as 22.7%.[12–14]
is shown in Figure 1b, and the photogenerated carrier transport is illustrated as well. The comparison of the cross-sectional scanning electron microscopy (SEM) images (Figure 1c) of the devices with and without the CsPbCl$_3$ QDs treatment indicates that the CsPbCl$_3$ QDs have no obvious effect on the PVK grain growth beyond the surface passivation.

SEM, atomic force microscope (AFM), and energy-dispersive X-ray (EDX) are utilized to further investigate the composition and morphological evolution of the PVK films treated with different amounts of CsPbCl$_3$ (0, 5, 20, and 50 mg mL$^{-1}$). The SEM images of the representative PVK films are exhibited in Figure 2a–d. All the obtained films display compact and uniform morphology without observable pinholes. Note that in the SEM images, components with different conductivities are displayed in different shades of gray. The control film made without the CsPbCl$_3$ QDs shows essentially all dark grains throughout the image, indicating only PVK grains without PbI$_2$. When the CsPbCl$_3$ QDs were introduced, white edges appeared around the PVK grain boundaries, indicating formation the PbI$_2$ surface layers. The more CsPbCl$_3$ QDs is used, the more PbI$_2$ is observed. The white PbI$_2$ phase covers almost half of the film when the CsPbCl$_3$ concentration is increased to 50 mg mL$^{-1}$. It is clear that the formation of PbI$_2$ originated from the reaction of CsPbCl$_3$ QDs with the PVK grain surfaces. Meanwhile, a similar phenomenon is also observed in the MAPbI$_3$ film, as shown in Figures S1 and S2 and Table S1 in the Supporting Information.

To understand the effect of Cl$^{-}$ on the PVK films, XPS measurements were performed for CsPbX$_3$-driven (X = Cl, Br, I) PVK films. Compared with the pristine reference, the 3d peaks of Cs still exist for all the samples, whereas the 2p peaks of Cl disappear. Consistent with the speculation and findings of Figure 2, these results indirectly demonstrate the formation of volatile MACl. To further clarify whether Cs and Pb or Cl in the QDs play an important role in the passivation of PVK films, the performance of CsPbX$_3$ (X = Cl, Br, I) QDs-driven PVK-based PSCs are illustrated and compared in Figures S4 and S5 in the Supporting Information.

In order to study the effect of the CsPbCl$_3$ QDs concentration on the structural and optical properties of PVK films, four representative samples with different contents of CsPbCl$_3$,
Figure 2. a–d) The SEM images and e–h) AFM images of PVK thin films (FA0.85MA0.15PbI2.55 Br0.45) formed using different amounts (0, 5, 20, and 50 mg mL\(^{-1}\), respectively) of CsPbCl\(_3\). i–l) The EDX elemental mappings and m,n) EDX spectra of PVK film using 50 mg mL\(^{-1}\) CsPbCl\(_3\) QDs at different locations.

Figure 3. a) The XPS spectra of TiO\(_2\)/FTO and CsPbCl\(_3\) QDs/TiO\(_2\)/FTO film. b) The XPS spectra of pristine PVK thin films (FA0.85MA0.15PbI2.55 Br0.45) and films formed using 50 mg mL\(^{-1}\) of different components (CsPbCl\(_3\), CsPbBr\(_3\), and CsPbI\(_3\)).
(0, 5, 20, and 50 mg mL\(^{-1}\)) were selected as the research objects. To maintain identical test conditions, all the samples were prepared with the structure PVK/CsPbCl₃/TiO₂/FTO. The X-ray diffraction (XRD) patterns (Figure 4a) clearly confirm that the amount of PbI\(_2\) phase increases with increasing CsPbCl₃, with is ascribed to the sublimation of MACl. These XRD results are coincident with those of the corresponding SEM images in Figure 2. The elemental proportions of Cs, Pb, Br, and I from the XPS measurements (Figure 4b) also indicate increasing PbI\(_2\) with increasing CsPbCl₃, which is in agreement with the results of XRD and SEM.

Figure 4c,d provides the absorption and photoluminescence (PL) spectra, respectively, of the pristine PVK films and those formed using different amounts of CsPbCl₃. The observable bandgap widening and PL blueshift with increasing CsPbCl₃ content mainly result from the existence of the PbI\(_2\) phase.\[^{[44]}\] It has been reported that the PbI\(_2\) could passivate the surface and grain boundaries of the PVK layer;\[^{[49,50]}\] therefore, the PL intensity was remarkably increased with increasing CsPbCl₃ content. Figure 4e compares the time-resolved photoluminescence (TRPL) decay curves of the representative samples. The TRPL decay curves were fitted using a biexponential decay function [times (\(\tau_i\)) and amplitudes (\(A_i\))], with the relevant key parameters listed in Table S3 in the Supporting Information. The average recombination lifetime (\(\tau_{ave}\)) was estimated using\[^{[51–53]}\]

\[
\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}
\]

The lifetime is significantly prolonged from 0.13 to 1.24 \(\mu s\) with the increase of CsPbCl₃ content, confirming that the PbI\(_2\) indeed passivates the defects in the grain boundaries in PVK films. The defects are considered recombination centers;\[^{[54]}\] and a longer lifetime is beneficial for extracting the photogenerated carriers.

Finally, the performances of different devices are compared to investigate the beneficial role of CsPbCl₃ in the PSCs. Figure 5a depicts the current density–voltage (\(J–V\)) curves of the devices fabricated without and with different CsPbCl₃ contents. As the reference, the pristine device shows a PCE of 18.86%, with open-circuit voltage (\(V_{oc}\)), short-circuit current density (\(J_{sc}\)), and fill factor (FF) of 1.082 V, 22.87 mA cm\(^{-2}\), and 76.2%, respectively. With the introduction of the CsPbCl₃, the device performance improved gradually with increasing QDs concentration. Even with the use of a small amount of CsPbCl₃ QDs (5 mg mL\(^{-1}\)), the device performance is improved significantly to a PCE of 19.35%, with the corresponding \(V_{oc}\), \(J_{sc}\), and FF improved to 1.101 V, 23.11 mA cm\(^{-2}\), and 76.1%, respectively. When the CsPbCl₃ content reached 20 mg mL\(^{-1}\), the PCE jumped to 20.09%. It is worth noting that both the \(J_{sc}\) and \(V_{oc}\) increased substantially. Given the prolonged lifetime, it is reasonable to attribute the improvement of the device performance to passivation of the traps by PbI\(_2\). However, further increasing the amount of CsPbCl₃ QDs until there are too many CsPbCl₃ QDs is not favorable to device performance, which is due to the wide bandgap (2.3 eV) of the resulting excess PbI\(_2\).\[^{[55]}\] The detailed parameters from the \(J–V\) curves are summarized in Table 2.

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**Figure 4.** The structure and optical properties of PVK thin films (FA\(_{0.85}\)MA\(_{0.15}\)PbI\(_{2.55}\)Br\(_{0.45}\)) formed using different amounts of CsPbCl₃ (0, 5, 20, and 50 mg mL\(^{-1}\)): a) XRD patterns, b) XPS elemental spectra, c) absorption spectra, d) PL spectra, and e) TRPL decay curves.
The typical external quantum efficiency (EQE) spectra of the devices are shown in Figure 5b. In the visible region, the EQE is highest for the device formed using 20 mg mL⁻¹ CsPbCl₃ QDs. The results further indicate that the CsPbCl₃ QDs can enhance the device performance. It should be noted that the \( J_{SC} \) values calculated using the EQE curves are consistent with those from the \( J-V \) measurements (errors less than 5%), indicating that the latter is well calibrated. The trap state densities (\( n_t \)) in all the representative devices were estimated from the dark current–voltage (\( I-V \)) curves (Figure 5c). The applied voltage at the kink point, where the current increases and becomes nonlinear, is defined as the trap-filled limit voltage (\( V_{TFL} \)), which is determined by the defect density. The following equation relates \( V_{TFL} \) to \( n_t \) [56]:

\[
V_{TFL} = \frac{en_tL^2}{2\varepsilon\varepsilon_0}
\]

where \( e \) is the elementary charge, \( L \) is the film thickness, \( \varepsilon \) is the relative dielectric constant, and \( \varepsilon_0 \) is the vacuum permittivity. The calculated values of \( n_t \) are shown in Table 1 for devices based on the pristine PVK films and those based on PVK films formed using different CsPbCl₃ QDs contents. Distinctly, the trap state

![Figure 5.](image)

**Table 1.** Performance comparison of the PSCs based on different PVK films (extracted from Figures 4 and 5).

| CsPbCl₃ [mg mL⁻¹] | \( J_{SC} \) [mAcm⁻²] | \( V_{OC} \) [V] | FF [%] | PCE [%] | \( J_{SC(EQE)} \) [mAcm⁻²] | \( \tau_{ave} \) [µs] | \( V_{TFL} \) [V] | \( n_t \) [cm⁻³] | \( \tau_t \) [µs] |
|-------------------|------------------------|----------------|--------|---------|------------------------|----------------|----------------|----------------|----------------|
| 0                 | 22.87                  | 1.082          | 76.2   | 18.86   | 21.76                  | 0.13           | 1.24           | 1.37 × 10¹⁷    | 45.3           |
| 5                 | 23.11                  | 1.101          | 76.1   | 19.35   | 22.11                  | 0.31           | 1.05           | 1.16 × 10¹⁷    | 71.2           |
| 20                | 23.45                  | 1.122          | 76.4   | 20.09   | 22.55                  | 1.07           | 1.02           | 1.13 × 10¹⁷    | 140.2          |
| 50                | 23.27                  | 1.121          | 76.6   | 19.46   | 22.13                  | 1.24           | 0.97           | 1.07 × 10¹⁷    | 276.5          |
density decreases with increasing CsPbCl₃ QDs amount. The reduced trap state density demonstrates the considerable improvement of the PVK film quality, resulting in the enhancement of the device performance. In parallel, the reduced trap state density is consistent with the prolonged lifetime in Figure 4e.

To further elucidate the role of CsPbCl₃ on the improved performance of PSCs, the carrier transport process and recombination behaviors are investigated by electronic impedance spectroscopy (EIS). The Nyquist plots for the devices without and with different CsPbCl₃ concentrations measured in the dark are shown in Figure 5d. The equivalent circuit model comprised of the series resistance ($R_s$), the recombination resistance ($R_{rec}$), and capacitance ($C_{oc}$) is depicted in the inset of Figure 5d. In the high-frequency region, the X-axis intercept is the equivalent $R_s$. The main arc is associated with the recombination process. The EIS parameters from the Nyquist plots are summarized in Table S4 in the Supporting Information. Clearly, the value of $R_s$ is decreased from 11.2 to 9.6 $\Omega$ after the CsPbCl₃ modification. The reduced $R_s$ indicates that the introduction of the CsPbCl₃ QDs facilitates the carrier transport. However, when the concentration of CsPbCl₃ QDs is 50 mg mL⁻¹, the $R_s$ is increased to 11.7 $\Omega$, which is due to the excess PbI₂ induced by the CsPbCl₃. For $R_{rec}$, the increasing values with increasing amount of CsPbCl₃ mean that the carrier recombination is reduced. Given the identical conditions for all the PSCs, the increased $R_{rec}$ could be mainly ascribed to the microstructure evolution resulting from the effect of the CsPbCl₃ addition. Meanwhile, from the complex plane curves, the effective lifetimes ($\tau_{n}$) were extracted as the reciprocals of the frequencies corresponding to the peaks of the semicircles in the Cole–Cole plots. The $\tau_{n}$ for the optimized device (140.2 $\mu$s) is considerably longer than that of the pure PVK (45.3 $\mu$s), indicating that photogenerated carriers have more time to transport to the anode before possible recombination.

Hysteresis is a notorious behavior for planar PSCs. Figure 5e shows typical $J$–$V$ curves of the devices measured both reverse and forward scan directions, with key device parameters listed in Table 2. It should be noted that $J$–$V$ hysteresis was substantially eliminated by the addition of CsPbCl₃, while the reference cell showed obvious hysteresis. The hysteresis index of the devices was defined by

$$\text{Hysteresis index} = \frac{\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}}}{\text{PCE}_{\text{reverse}}}$$

Clearly, the hysteresis index for the optimized device is 0.027, lower than 0.055 for the reference formed without CsPbCl₃ addition.

Table 2. Static figures of merit for the reference and CsPbCl₃ QDs optimized devices.

| Device     | Scanning mode | $J_{SC}$ [mAcm⁻²] | $V_{OC}$ [V] | FF [%] | PCE [%] | Hysteresis index |
|------------|---------------|--------------------|--------------|--------|---------|-----------------|
| Reference  | reverse       | 22.87              | 1.082        | 76.2   | 18.86   | 0.055           |
|            | forward       | 22.76              | 1.071        | 73.1   | 17.83   |                 |
| Optimized  | reverse       | 22.45              | 1.122        | 76.4   | 20.09   | 0.027           |
|            | forward       | 22.34              | 1.100        | 76.2   | 19.55   |                 |

To ensure the $J$–$V$ measurement is reliable, the PCEs of the devices were recorded as a function of time with the cells biased at their respective $V_{MP}$ (voltage at the maximum power point, in this case 0.88 V for the reference and 0.90 V for the optimized device), as shown in Figure 5f. Clearly, the optimized device shows stable performance, while for the reference one, it exists some fluctuations which should be caused by the process of filling the uncertainty traps among grain boundaries under illumination. In general, both the stabilized PCE values are very close to those obtained by the direct $J$–$V$ measurements. To confirm the process reproducibility, 50 individual devices (each) were fabricated from the reference and optimized films using the same procedure, with the statistical distribution of the key $J$–$V$ parameters ($V_{OC}$, $J_{SC}$, FF, and PCE) presented in Figure S6 in the Supporting Information. All the key parameters exhibited fairly narrow distributions, indicating that the process was reproducible.

In summary, we adopted a thin CsPbCl₃ QDs film to finely control the PbI₂ content in planar PSCs, and we found that moderate residual PbI₂ could result in stable and high-efficiency solar cells. By fine-tuning the residual PbI₂ in the PVK layer accordingly, we have achieved a stable and high PCE of 20.09% with reduced hysteresis. We believe that more efficient and stable planar PSCs can be obtained in the future by employing interface engineering, crystal-growth engineering, optical engineering, and compositional engineering.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

CsPbCl₃, grain boundaries, perovskites, solar cells, trap density
