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Efficient and photostable $CsPbI_2Br$ solar cells realized by adding PMMA

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Organic–inorganic hybrid perovskite materials demonstrate promising applications in high-efficiency perovskite solar cells (PSCs) with a certified power conversion efficiency (PCE) of 25.5% (https://www.nrel.gov/pv/cell-efficiency.html). However, intrinsically volatile and thermally unstable nature of the organic cations result in poor thermal stability of organic–inorganic hybrid perovskite materials, hampering the commercialization of organic-inorganic hybrid PSCs[1]. All-inorganic $CsPbI_{3-x}Br_x$ (x = 0–3) perovskites have been attracting great attention in recent years because of their higher thermal stability[2]. Among the reported $CsPbI_{3-x}Br_x$ perovskites, $CsPbI_2Br$ bears a reasonable balance between bandgap and phase stability, thus becomes the most extensively studied material[3–15]. Though there are many works aiming at achieving high-efficiency $CsPbI_2Br$ PSCs, improving the photostability of $CsPbI_2Br$ PSCs is another key for commercialization of all-inorganic PSCs. Intriguingly, it has been reported that $CsPbI_2Br$ is susceptible to make light-induced phase segregation, i.e. severe segregation of $CsPbI_2Br$ to low-bandgap I-rich and wide-bandgap Br-rich domains *via* ion diffusion, leading to obvious current–voltage hysteresis and decrease of stabilized power output (SPO)[16–20]. Such a light-induced phase segregation can be suppressed by optimizing the interface between perovskite layer and charge-transport layer[18, 19]. For example, Tian *et al.* improved the photostability of $CsPbI_2Br$ PSCs through modifying SnO_2 electron-transport layer by PN4N and incorporating dopant-free PDCBT hole-transport layer[18]. Xiao *et al.* developed a new dopant-free hole-transport layer PSQ2 to substitute Spiro-OMeTAD, and found that PSQ2-based devices had less SPO loss[19]. Despite of the effectiveness of suppressing light-induced phase segregation *via* such interfacial modification, whether the phase segregation is induced merely by light illumination or already exists in the crystallization of $CsPbI_2Br$ remains unclear yet. Another open question is whether the photostability of $CsPbI_2Br$ can be improved by eliminating light-induced phase segregation of $CsPbI_2Br$ via modulating the crystallization process of $CsPbI_2Br$.

Here, we introduced poly(methyl methacrylate) (PMMA) additive into $CsPbI_2Br$ to modulate the crystallization process of perovskite films. We found that phase segregation occurs during crystallization of $CsPbI_2Br$ especially under fast crystallization rate and low annealing temperature, and this intrinsic phase segregation exacerbates light-induced phase segregation. With PMMA additive, $CsPbI_2Br$ solar cells gave an enhanced PCE of 15.88%, and the photostability was improved.

We added PMMA *via* anti-solvent dripping (Fig. S1)[21]. The $CsPbI_2Br$ film with PMMA exhibited slow color change from transparent to brown-yellow during annealing (Fig. S2), indicating that PMMA incorporation leads to slower crystallization of $CsPbI_2Br$ and larger grain with reduced root-mean-square (RMS) roughness. (Fig. 1(a), Figs. S3 and S4). The crystallinity and crystalline orientation of $CsPbI_2Br$ film were also optimized. XRD shows that $CsPbI_2Br$ film with 0.05 mg/mL PMMA has strongest (100) and (200) diffraction peaks (Fig. S5). The GIXRD patterns reveal the improved orientation of $CsPbI_2Br$ crystal with (100) and (200) planes parallel to the substrate (Figs. S6 and S7). PMMA incorporation improves the crystalline orientation of $CsPbI_2Br$ along plane (100) (Fig. 1(b)).

We studied the trap-state density (n_t) of $CsPbI_2Br$ layer by using space charge limited current (SCLC) method based on an electron-only device with a structure of ITO/SnO_2/ZnO/perovskite/PCBM/Ag (Fig. 1(c))[22]. n_t can be calculated by equation:

$$n_t = \frac{2\varepsilon\varepsilon_0}{eL^2} \times V_{TFL},$$

where ε_0 is the vacuum permittivity, ε is the relative dielectric constant of $CsPbI_2Br$[13], e is the elementary charge, and L is the thickness of perovskite film. The trap-filled limit voltage (V_{TFL}) is the bias voltage at the kink point. The n_t decreased from 1.09×10^{16} to 8.18×10^{15} cm^{-3} after PMMA incorporation. Low trap density favors to reduce charge recombination. The carrier lifetimes (τ) of $CsPbI_2Br$ films measured by time-resolved photoluminescence (TRPL) were 6.68 and 10.34 ns for the control film and the film with PMMA, respectively (Fig. S8, Table S1)[23]. The prolonged carrier lifetime sug-

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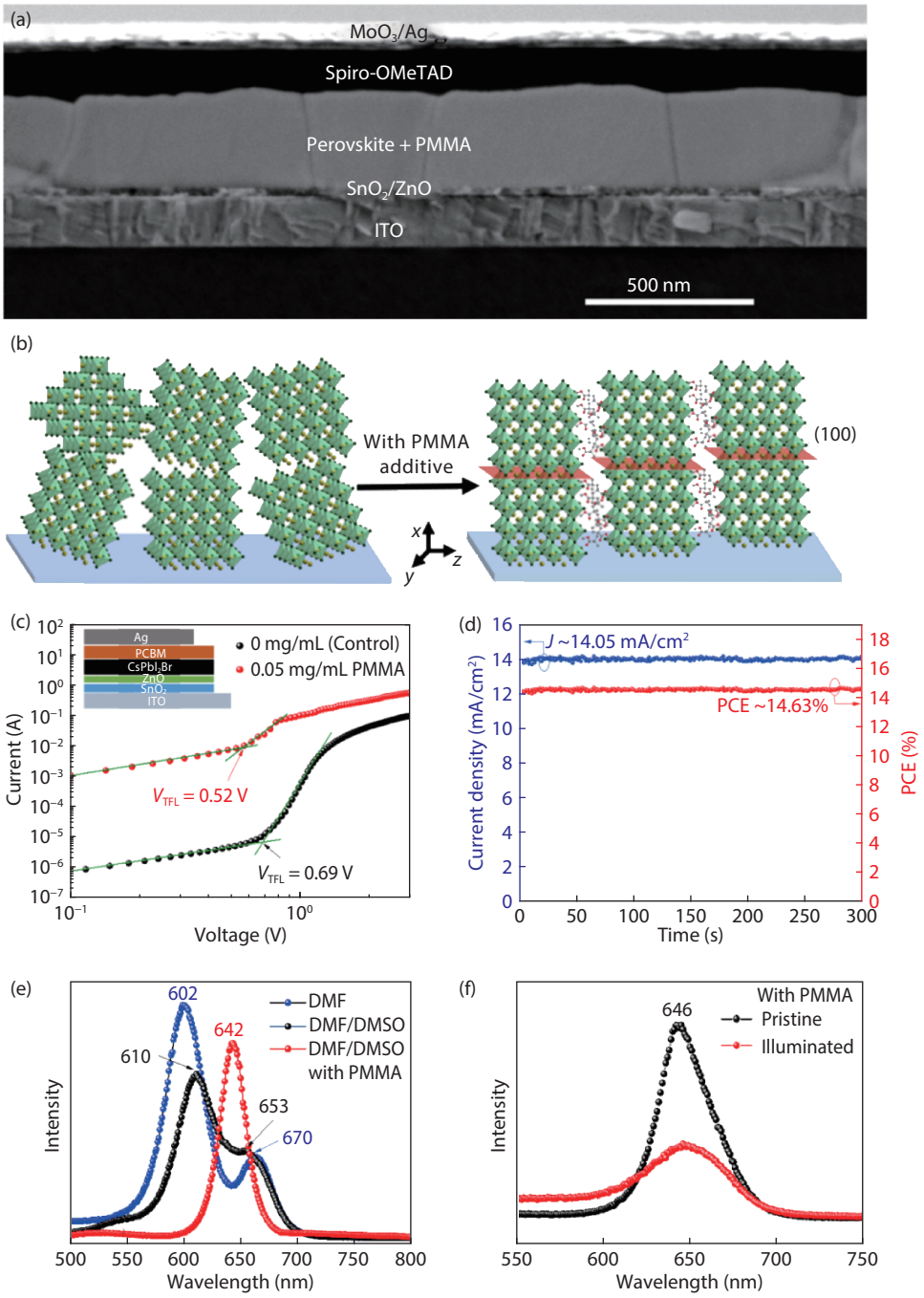

Fig. 1. (Color online) (a) Cross-section SEM image for $CsPbI_2Br$ solar cell. (b) Schematic illustration of perovskite crystal with and without PMMA. (c) Dark current–voltage curves for the electron-only devices with and without PMMA. (d) Stabilized power output (SPO) of $CsPbI_2Br$ device with PMMA. (e) Steady-state PL spectra for $CsPbI_2Br$ films from different fabrication process (annealed at 100 °C). (f) Steady-state PL spectra for $CsPbI_2Br$ films with PMMA before and after illumination.

gests that PMMA can passivate trap states. The higher intensity of the PL peak for $CsPbI_2Br$ film (Fig. S9), smaller ideal factor (ε) obtained from V_{oc} vs light intensity plots (Fig. S10), and decreased R_{ct} (charge transfer resistance) obtained from EIS (Fig. S11 and Table S2) all suggest suppressed non-radiative decay in $CsPbI_2Br$ film with PMMA.

PSCs with a structure of ITO/SnO_2/ZnO/$CsPbI_2Br$/Spiro-OMeTAD/MoO_3/Ag were made. The photovoltaic performances for the devices with and without PMMA were compared (Fig. S12, Fig. S13 and Table S3). The PCE increased from 14.42% to 15.88% after adding 0.05 mg/mL PMMA. The negligible change of J_{sc} is verified by external quantum efficiency (EQE) measurements (Fig. S14). The PCE enhancement for the device with PMMA results from the increases of V_{oc} (1.124 to 1.216 V) and FF (67.77% to 75.28%), which can be attributed to decreased trap states in $CsPbI_2Br$ film with PMMA. The devices with PMMA have smaller hysteresis index (Fig. S15 and Table S4) and less degradation of SPO (Fig. 1(d) and Fig. S16(a))[18, 19]. The existence of hysteresis and SPO degradation suggest the occurrence of light-induced phase segregation of $CsPbI_2Br$[19, 20]. The smaller hysteresis and SPO degradation suggest that PMMA can suppress light-induced phase segregation of $CsPbI_2Br$.

Without PMMA, the phase segregation of $CsPbI_2Br$ takes

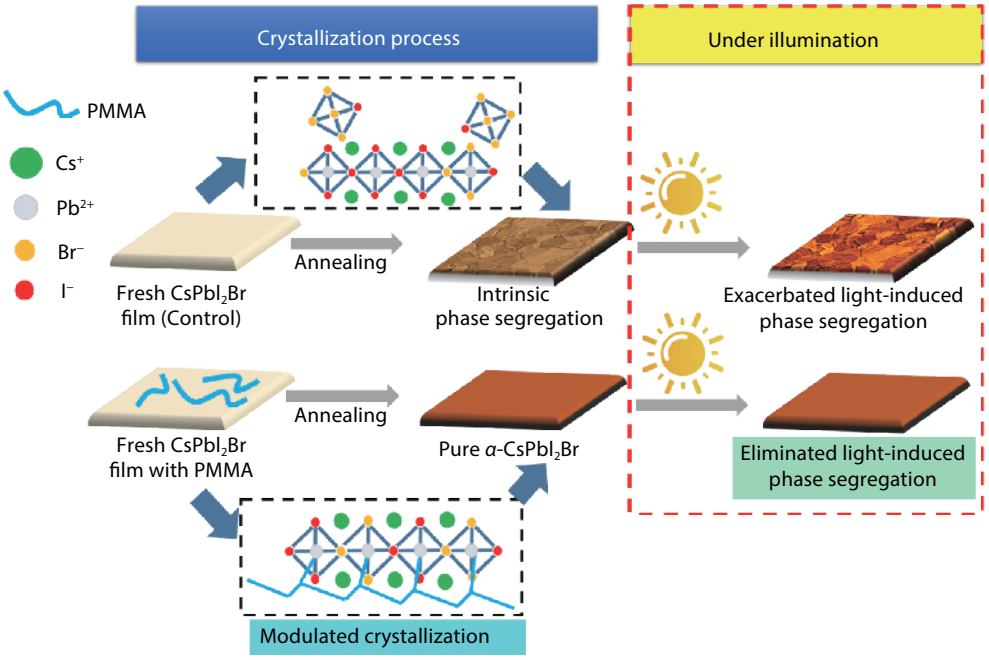

Fig. 2. (Color online) The proposed mechanism for the elimination of phase segregation in $CsPbI_2Br$ film by PMMA.

place during the formation of $CsPbI_2Br$ film, and we call it intrinsic phase segregation. On the one hand, intrinsic phase segregation occurs more easily at low annealing temperature. The best devices we discussed above were all made at 240 °C. However, $CsPbI_2Br$ PSCs made under 100 °C exhibit more serious degradation of SPO (Fig. S16(b)) and larger hysteresis index (Table S4), indicating more severe phase segregation. Low annealing temperature does not favor the growth of homogeneous inorganic perovskite films, which are commonly made at high temperature. But, with PMMA incorporation, hysteresis and SPO degradation (Fig. S16(c)) were suppressed effectively even at low temperature. On the other hand, insufficient components diffusion could occur at fast crystallization rate, which results in phase segregation eventually. Usually, perovskite precursors with DMF solvent exhibit fast crystallization rate, while DMSO could slow down the crystallization[24]. When using DMF/DMSO mixed solvent, PL peak split indicates that phase segregation becomes less obvious. PMMA retards the crystallization (Fig. S2), leading to single PL peak, suggesting the elimination of intrinsic phase segregation (Fig. 1(e)).

Light-induced phase segregation is caused by ion migration, and the smaller Br^- ions are easier to migrate than I^-. With higher Br content, the phase segregation takes place easily[25]. Intrinsic phase segregation generates I-rich phase and Br-rich phase, and this uneven composition will exacerbate phase segregation. According to SEM images (BSE mode) (Fig. S17), more uniform grain color reveals suppressed phase segregation. After 45 min illumination, no PL peak split and GIXRD (200) diffraction peak were observed for $CsPbI_2Br$ film with PMMA (Fig. 1(f), Fig. S18 and Fig. S19)[9], indicating that light-induced phase segregation was suppressed by PMMA. We further evaluated the photostability of $CsPbI_2Br$ devices under continuous illumination (unencapsulated in N_2 glovebox). A ~36% PCE drop was observed for the control device after 400 h operation, while for PMMA-containing device, the PCE droped by ~17% (Fig. S20(b)). The improved photostability was due to the elimination of phase segregation.

We propose a mechanism for the elimination of phase segregation in $CsPbI_2Br$ film by using PMMA (Fig. 2). The coordination interactions between C=O groups in PMMA and Pb^{2+} in $CsPbI_2Br$ (Fig. S21 and Fig. S22) lead to lowered crystallization rate, making uniform distribution of I^- and Br^- anions[21]. The intrinsic phase segregation is eliminated at low annealing temperature and this prohibition effect is expected to exist under light illumination as well, resulting in suppressed *J–V* hysteresis and eliminated light-induced phase segregation.

In summary, PMMA was added into $CsPbI_2Br$ layer to modulate the crystallization and eliminate the phase segregation. PMMA can also passivate the trap states. The $CsPbI_2Br$ solar cells delivered an enhanced PCE of 15.88% and an improved photostability.

Acknowledgements

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Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/1674-4926/42/5/050501.

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