SHORT COMMUNICATION

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Stabilizing black-phase $CsPbI_3$ under over 70% humidity

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Recently, all-inorganic perovskites have attracted attention due to good thermal stability[1–12]. Among them, $CsPbI_3$ has the most desirable optical bandgap (~1.7 eV) for applications in optoelectronic devices[13–16]. In general, making black-phase $CsPbI_3$ film requires a high-temperature annealing up to 320 °C[17, 18], which inevitably raises energy consumption. Though being made at high temperature, the resulting black-phase (α or β phase) $CsPbI_3$ film still suffers from an undesirable phase transition under ambient conditions[19, 20]. Several strategies have been developed to lower the annealing temperature (90–100 °C)[20–26], it is still challenging to stabilize black-phase $CsPbI_3$ under ambient condition with high humidity and without a tedious annealing process. Herein, we developed a simple crystal redissolution (CR) strategy to make stable black-phase $CsPbI_3$ film in ambient air with high humidity and without post-annealing. 4-N,N-dimethylamino-4′-N′-methyl-stilbazolium tosylate (DAST) can chemically interact with $CsPbI_3$ to reduce the formation energy of black-phase and inhibit $CsPbI_3$ to undergo black-to-yellow phase transition.

Fig. 1(a) shows the CR approach. By using the perovskite precursor consisting of PbI_2, CsI and HI, a light-yellow film was obtained in ambient air, which is due to the existence of both yellow-phase δ-$CsPbI_3$ and PbI_2, as evidenced in XRD pattern (Fig. 1(b))[22]. In contrast, by using CR-derived perovskite precursor (Fig. S1), a mirror-like black $CsPbI_3$ film was obtained even under 70% relative humidity, which uniformly covered the entire substrate (inset in Fig. 1(c)). Compared with the control sample (Fig. 1(b)), there is no PbI_2 signal (12.6°) in XRD pattern (Fig. 1(c))[27], which is due to a more direct conversion and rapid self-assembly from $CsPbI_3$ crystals to $CsPbI_3$ film, rather than the complicated competition among Pb^{2+}, Cs^+, I^- ions and solvent molecules[27, 28]. The diffraction peaks at 14.98° and 29.20° are the typical (100) and (200) planes of black-phase β-$CsPbI_3$. Meanwhile, the absorbance of the control film sharply declined after 450 nm, while CR-derived black $CsPbI_3$ film presents an absorption onset at 733 nm (Fig. S2), which agrees with the previous report on β-$CsPbI_3$ film[12]. For the control film, inferior surface coverage was observed (Figs. S3(a) and S3(c)). And CR-derived film shows better surface coverage (Figs. S3(b) and S3(d)).

Black-phase $CsPbI_3$ film gradually degraded and underwent phase transition when stored in air for one week, as evidenced by the gradual decrease of absorbance (Fig. S4). To further improve phase stability and optoelectronic properties of β-$CsPbI_3$ film prepared by CR strategy, we introduced the DAST additive (Fig. 1(d)). DAST not only maintains black-phase $CsPbI_3$ structure, but also slightly enhances the crystallinity and promotes the crystal growth orientation along (100) and (200) planes (Fig. S5). DAST also helps to reduce the grain sizes (100–200 nm) and improve the surface coverage of the resultant β-$CsPbI_3$ film (Fig. S6). DAST molecules can interact with $CsPbI_3$ *via* robust bidentate coordination, thus impeding grain growth due to the steric hindrance effect (Fig. 1(e))[11]. The interaction between DAST molecule and β-$CsPbI_3$ was studied by FTIR (Fig. S7). The pure DAST shows characteristic signals at 1023 and 1666 cm^{-1}, corresponding to C=C bond and benzene group, respectively. DAST-modified $CsPbI_3$ film also shows similar peaks, but with a slight shift, suggesting possible interaction between zwitterion and ions in perovskites[20]. The DAST-modified $CsPbI_3$ film was stored at room temperature in air with a relative humidity of ~35%. There was no obvious degradation observed even after one month, as proved by XRD pattern (Fig. 1(f)).

In short, by using the CR strategy, we successfully stabilized the black-phase $CsPbI_3$ film in ambient air with >70% humidity. DAST can further stabilize the black phase. The approaches in this work will be useful for developing efficient perovskite solar cells.

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Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1088/1674-4926/43/3/030501.

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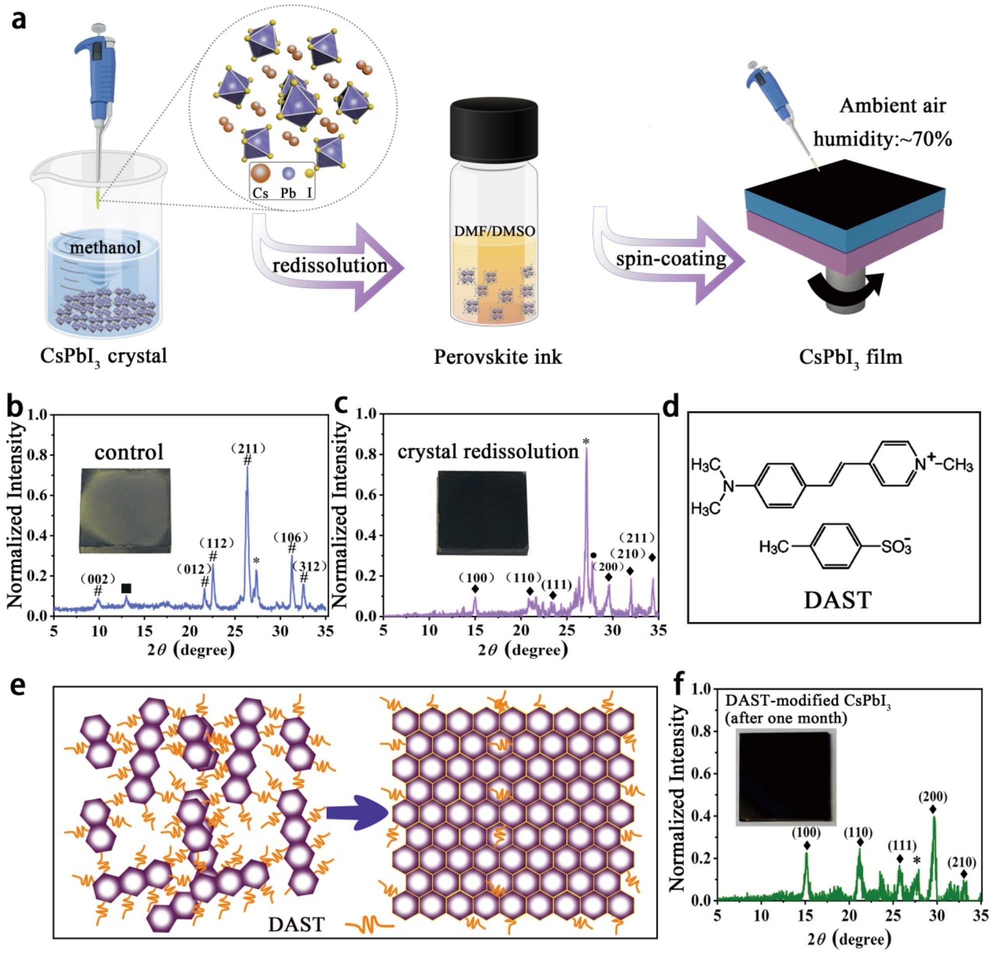

Fig. 1. (Color online) (a) The ambient air-processed black-phase $CsPbI_3$ film *via* CR strategy. The XRD patterns of the control (b) and CR-derived $CsPbI_3$ film (c). Note: the hash key represents the signal from δ-$CsPbI_3$; the square symbol represents the signal from PbI_2; the diamond symbol represents the signal from β-$CsPbI_3$; the circular pattern represents the signal from CsI and the asterisk represents the signal from FTO glass substrate. (d) The structure of DAST. (e) Schematic for the molecular interaction and $CsPbI_3$ film formation. (f) The XRD pattern for DAST-modified $CsPbI_3$ film after being stored in air for one month.

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