Antisolvent engineering for mixed tin-lead inorganic perovskite solar cells

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Abstract. Recently, inorganic perovskite has been a research hotspot due to its thermal stability and promising photovoltaic performance. Here, we demonstrate the antisolvent engineering can assist the fabrication of the mixed tin-lead inorganic perovskite films. The treated devices exhibit enhanced stability in atmosphere air. The champion perovskite solar cells (PSCs) treated with anisole exhibits a power conversion efficiency of 9.3% with an open-circuit voltage over 0.8 V.

1. Introduction
Inorganic perovskite solar cells (CsPbX₃, X=I, Br, Cl) are attracting lots of attention due to the promising charge-carrier mobilities and high thermal stability[1,2]. Recently, the power conversion efficiency (PCE) of inorganic perovskite solar cells has surpassed 20%[3]. However, the high fabrication temperature hinders their further application and commercialization[4]. Besides, the bandgap over 1.6 eV limits their photovoltaic performance due to Shockley-Queisser limit, which predicts an ideal bandgap of 1.2-1.4 eV. Therefore, reducing the bandgap of inorganic perovskites to the ideal bandgap and minimizing the fabricating temperature is quite necessary.

Partially replacing Pb with Sn is able to reduce the bandgap of perovskites[5]. In addition, the phase transition temperature of tin-based perovskites is always lower than that of lead-based perovskites[6]. Hence, it is vital to fabricate high-performance low-bandgap inorganic perovskite solar cells. Here, we explore 3 antisolvents and demonstrate that anisole is the best antisolvent to prepare high-quality CsPb₀.₆Sn₀.₄I₃ films. The antisolvent treated PSC has enhanced stability than the control one. The best inverted planar device shows a PCE of 9.3%.

2. Results and discussion
A 0.8M CsPb₀.₆Sn₀.₄I₃ precursor solution was prepared by stirring corresponding molar CsI, PbI₂, SnI₂ and SnF₂ (SnI₂ :SnF₂ = 10:1 in molar ratio) in mixed anhydrous solvents of DMSO and DMF for 3 hours. We use a simple one step method combining with an antisolvent engineering to fabricate inorganic perovskite films. To explore the effect of antisolvents on the mixed tin-lead inorganic perovskite films, we choose three different antisolvents chlorobenzene (CB), toluene (Tol) and anisole (Ani). All the antisolvents were dripped onto the film 10 s before the end of the spin-coating and then the films were annealed at 70 ℃ for 10 min. The scanning electron microscopy (SEM) images of the obtained perovskite films treated with different antisolvents were shown in Figure 1 (a) - 1 (d). After treated with antisolvents, the number of pinholes on the surface is reduced, while the grain sizes remained unchanged. However, all the films had small pinholes, which would lead the decrease of the devices’ short-circuit current density (Jsc) and fill factors (FF).
The optical property of the films were further tested by Ultraviolet-visible (UV-Vis). All the films were measured without encapsulation. As shown in Figure 1 (e), the obtained film without antisolvent degraded, while the films treated with antisolvents all showed normal absorption across the spectrum. The film treated with Ani showed the highest absorption, which is good for the improvement of the Jsc of the devices. Besides, all the films treated with antisolvents showed similar bandgap (1.39 eV) due to the UV-Vis measurements.

The X-ray diffraction (XRD) pattern of the control and ani-treated perovskite films were shown in Figure 2 (a). Obviously, the control film degraded to a nonperovskite phase. In contrast, the ani-treated film showed the characteristic peaks at 14.48°, 20.36°, 29.08° and 36.02°, assigning to the (110), (200), (220) and (312) planes of the orthorhombic CsPb$_{0.6}$Sn$_{0.4}$I$_{3}$ structure[7]. The result of the XRD also proved the good quality of the antisolvents treated films. The bad stability of the control film arising from the bad film morphology would restrict the performance of the devices. As shown in Figure 2 (b), the ani-treated device can maintain a good stability in atmosphere air, while the control device degraded in a few hours. The enhanced stability can attribute to the improved film morphology and good crystal quality.

Figure 2. (a) XRD patterns of the control film and anisole treated film. (b) The photograph of the devices based on the perovskite films treated without and with anisole stored in atmosphere air for 2 hours.
Tin-based perovskites prefer the inverted structure to construct solar cells than the normal structure, because traditional metal oxides have oxygen vacancies to accelerate tin oxidation, which will deteriorate the performance of the PSCs[8]. In addition, the hole transport layer (HTL) of the normal devices always need additions to oxidize the material, which will also oxidize the perovskite layer. Therefore, we employ the inverted structure to fabricate PSCs (Figure 3 (a)). Figure 3 (b) presented statistic PCE data of 64 devices. The performance of the devices were measured in air atmosphere without any encapsulation. The PSCs based on the films treated with Ani showed the highest PCE, which matched well with the results of the morphology and absorption. The control devices showed an average PCE less than 4%. This poor performance may result from the bad morphology and instability when measured in air atmosphere. The champion device exhibited a PCE of 9.3% with an open-circuit voltage (Voc) of 0.81 V, Jsc of 18.9 mA/cm² and FF of 61.2% (Figure 3 (c)). In contrast, the control device only showed a low PCE of 4.4%.

3. Conclusion
In summary, an antisolvent engineering for mixed tin-lead inorganic perovskites is demonstrated. The morphology and absorption of CsPb0.6Sn0.4I3 films treated with 3 different antisolvents are discussed. After treated with antisolvents, the perovskite films show better film morphology and enhanced absorption. Through comparing the performance of the PSCs based on the treated perovskite films, anisole is proved to be an effective antisolvent to fabricate high-quality tin-lead inorganic perovskite films. As a result, the optimized device delivers a PCE of 9.3% with a Voc of 0.81 V. The results provide a great promise for the application of the mixed tin-lead perovskite solar cells.

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