

NANO EXPRESS

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Realizing Full Coverage of Stable Perovskite Film by Modified Anti-Solvent Process

Long Ji¹, Ting Zhang¹, Yafei Wang¹, Peng Zhang¹, Detao Liu¹, Zhi Chen^{2*} and Shibin Li^{1*}

Abstract

Lead-free solution-processed solid-state photovoltaic devices based on formamidinium tin triiodide (FASnI₃) and cesium tin triiodide (CsSnI₃) perovskite semiconductor as the light harvester are reported. In this letter, we used solvent engineering and anti-solvent dripping method to fabricate perovskite films. SnCl₂ was used as an inhibitor of Sn⁴⁺ in FASnI₃ precursor solution. We obtained the best films under the function of toluene or chlorobenzene in anti-solvent dripping method and monitored the oxidation of FASnI₃ films in air. We chose SnF₂ as an additive of CsSnI₃ precursor solution to prevent the oxidation of the Sn²⁺, improving the stability of CsSnI₃. The experimental results we obtained can pave the way for lead-free tin-based perovskite solar cells (PSCs).

Keywords: Lead-free perovskite solar cells, Solvent engineering, Anti-solvent dripping

Background

Organic-inorganic halide perovskite solar cells have attracted great attention in recent years. The general formula for perovskite is ABX₃ (A cation, B cation, X anion). In 2012, the first all-solid-state solar cell [1] was introduced with a power conversion efficiency (PCE) of 9% [1] which is now increasing up to 22% [2]. These perovskite solar cells are mainly based on methylammonium lead iodide (MAPbI₃) [3–8] and formamidinium lead iodide (FAPbI₃) [9, 10]. Different halogens are used as anions (I, Br, Cl) [11] and inorganic cesium (Cs) is also used as cation with methylammonium (MA) and formamidinium (FA) in perovskite solar cells (PVCs) [12]. All of these materials have toxic lead, which is harmful to human health. This limits the commercial use of perovskite solar cells. Scientists have been looking for a non-toxic elements to replace lead in perovskites [16–26]. Some tried to mix the bivalent cations Sn²⁺ and Pb²⁺ as CH₃NH₃Sn_xPb_(1-x)I₃ [13, 14] and others mixed the monovalent A cations along with mixed bivalent cations, i.e. FA_{0.8}MA_{0.2}Sn_xPb_{1-x}I₃ [15], but these perovskites are still toxic. In 2014 [16] Snaith and co-workers first

developed complete lead-free perovskite solar cells based on methylammonium tin triiodide (CH₃NH₃SnI₃) and achieved a PCE around 6%. In the same year, Kanatzidis and co-workers [17] investigated CH₃NH₃SnI_{3-x}Br_x and received almost the same PCE. MASnI₃ is very unstable in air according to previous reports [16]. Later, researchers attempted to use formamidinium tin triiodide (FASnI₃) with the additive of SnF₂ to delay the oxidation of Sn²⁺ to Sn⁴⁺ [18, 19]. They found that FASnI₃ was more stable than MASnI₃. Recently, Seok and co-workers [20] obtained a smooth and dense FASnI₃ perovskite layer using SnF₂-pyrazine complex as an additive. With SnF₂ additives and diethyl ether dripping in a solvent engineering process to synthesize FASnI₃ perovskite thin films [21], Dewei Zhao and co-workers [21] achieved an improved PCE up to 6.22% for lead-free Sn-based perovskite solar cells.

Similar as FASnI₃, CsSnI₃ also shows perovskite phase at room temperature. CsSnI₃ has four phases at different temperatures [22], but only the black orthorhombic phase B-γ-CsSnI₃ is the perovskite phase. Kumar et al. [23] fabricated solar cells using CsSnI₃ as the perovskite layer between a TiO₂ electron transfer layer and a Spiro-OMeTAD hole transfer layer and achieved a PCE of 2%. Zhou et al. [24] modulated B-γ-CsSnI₃ grain sizes by employing different annealing temperatures and chose the optimal architecture for perovskite solar cells. They achieved a PCE of 3.31%. Marshall et al. [25] proved that

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the existence of SnCl_2 resulted in higher film stability and they achieved a PCE of 3.56% from PSCs without any hole-selective interfacial layer. CsSnI_3 can be used as the perovskite absorption layer as well as the active region in lead-free perovskite infrared LEDs [26]. Generally, Spiro-OMeTAD is used as a hole transport material (HTM), which typically contains acetonitrile and lithium (Li) and/or cobalt (Co) salts that may change the morphology of Sn-based perovskite films and form the undesirable Cs_2SnI_6 polymorph [21, 22].

While SnF_2 -pyrazine complex [20] and SnF_2 [21] have been used as additives into FASnI_3 solution and resulted in good performance on stability and efficiency, SnCl_2 also can be used as an alternative additive. The mechanism is similar to other tin halides (SnF_2 , SnCl_2 , SnBr_2 , SnI_2) additives which are chosen in CsSnI_3 -based perovskite photovoltaics [25]. In this report, we chose SnCl_2 as an additive of FASnI_3 solution and SnF_2 as an additive of CsSnI_3 solution to investigate the stability of the perovskite films, respectively. The measurement of the evolution of absorption spectra at different time courses and other experimental results (SEM, photos etc.) showed that the stability of the films was improved by both additives. With different anti-solvent dripping during spin-coating, we obtained some new findings about the surface morphology and obtained complete coverage of perovskite films.

Methods

The synthesis method of FASnI_3 follows reference [21]: 372 mg of SnI_2 (Sigma-Aldrich) and 172 mg of formamminium iodide (FAI) were dissolved in 800 μl anhydrous dimethylformamide (DMF, Sigma-Aldrich) and 200 μl anhydrous dimethyl sulfoxide (DMSO, Sigma-Aldrich). For this precursor solution, 10 mol% SnCl_2 was added and then stirred. Via spray pyrolysis at 500 $^\circ\text{C}$, a compact layer of TiO_2 substrate was deposited on FTO glass. The films were annealed at 500 $^\circ\text{C}$ for 15 min and then cooled down to room temperature. The mesoporous TiO_2 scaffold was spin-coated at 4500 rpm for 20 s and then heated at 500 $^\circ\text{C}$ for 1 h. FASnI_3 films were synthesized by spin-coating the precursor solution with SnCl_2 additives at 4000 rpm for 60 s in a glove box. During the process of spin-coating, the anti-solvent (diethyl ether, toluene, chlorobenzene) was dripped and then the perovskite films were annealed at 70 $^\circ\text{C}$ for 20 min.

The synthesis method of CsSnI_3 is described in a previous paper [23]: 0.6 M of CsSnI_3 that contained equimolar quantities of CsI and SnI_2 without or with 10 mol% SnF_2 additives, respectively, was added to DMSO and stirred overnight at 70 $^\circ\text{C}$. Sixty microliters of the precursor solution was spin coated onto the TiO_2 substrate at 4000 rpm. The substrates were then annealed at 70 $^\circ\text{C}$ for 10 min, and mirror-like black perovskite films were formed.

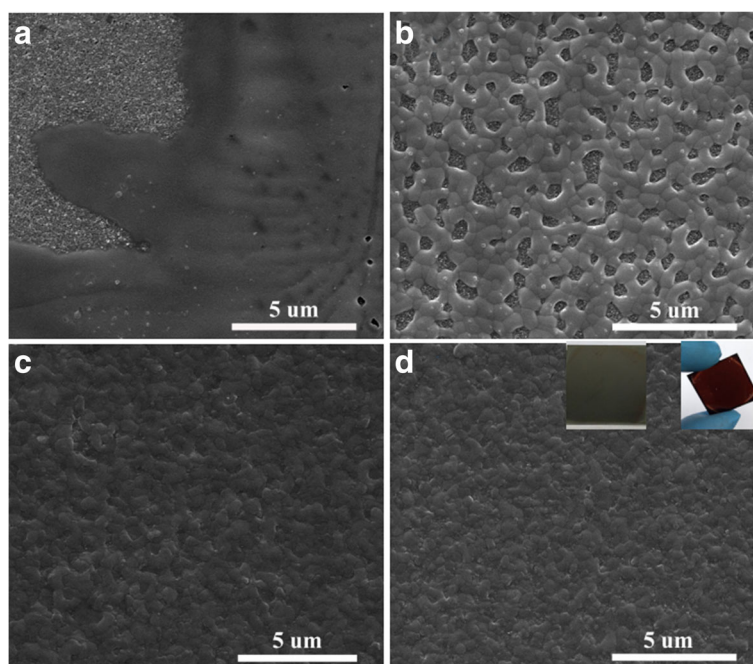


Fig. 1 SEM images of perovskite films prepared (a) without anti-solvent dripping, (b) with diethyl ether dripping, (c) with toluene dripping, and (d) with chlorobenzene dripping

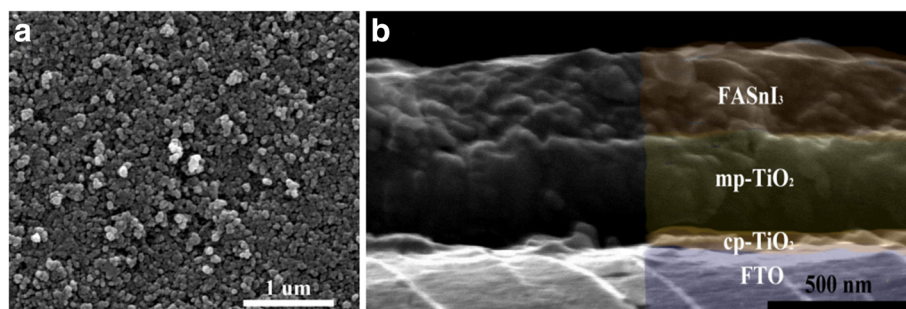


Fig. 2 XRD patterns of FASnI₃ perovskite films under different anti-solvents dripped

Results and Discussion

Under the effect of different anti-solvent dripping, the FASnI₃ films with 10 mol% SnCl₂ additives exhibit different film morphologies. Figure 1 shows the SEM images of FASnI₃ perovskite films on TiO₂ with different anti-solvents dripped. Figure 1a shows discontinuous nucleation, partial coverage and the presence of pinholes on the surface of the FASnI₃ film without (w/o) any anti-solvent dripped. Dripping with diethyl ether (Fig. 1b), the formed FASnI₃ film likes a net which has a lot of holes on it and spreads on the TiO₂ substrate. Dripping with toluene or chlorobenzene (Fig. 1c and d, respectively), the surface morphology of the FASnI₃ film has been further improved, and the film is highly uniform and dense with full coverage on the substrate. Using toluene as the anti-solvent, the average size of crystal particles is bigger than that of films fabricated by using chlorobenzene as the anti-solvent. These results are consistent with those reported in other articles [20, 21]. Without anti-solvent dripped, the film does not change color during spin-coating, and after continuous annealing at 70 °C, the film turns to black immediately and leads to the formation of a rough surface. When the film is dripped with diethyl ether, toluene or chlorobenzene, it changes into a reddish color immediately. After thermal annealing at 70 °C for 20 min, the film turns whitish with diethyl ether dripping and black (the left insert in Fig. 1d) with toluene or chlorobenzene dripping. No matter what kind of anti-solvent is dripped, films from the back view of the FTO glasses are brownish red (the right insert in Fig. 1d).

To investigate whether the anti-solvents dripping would lead to any crystal phase transition or not, we measured the XRD patterns. As shown in Fig. 2, all of the FASnI₃ films that were formed on TiO₂ crystallize in the orthorhombic structure and random orientation, which is consistent with other reports [20, 21].

Figure 3a shows the scanning electron microscopy (SEM) images of TiO₂ substrates. The cross-sectional SEM image (Fig. 3b) of a structure of FTO/compact

TiO₂/mesoporous TiO₂/FASnI₃ clearly displays the stacked layers. From the figure, the thickness of FASnI₃ is about 250 nm.

The optical absorption spectra of the FASnI₃ perovskite thin film with 10 mol% SnCl₂ additives under the effect of different anti-solvent dripping are shown in Fig. 4a. The absorption onset occurs at 900 nm, and this result is consistent with that reported by other groups [21]. As shown in Fig. 4, there are various absorption peaks of the films prepared by dripping with different anti-solvents. The absorption strength can indirectly reflect the quality of perovskite films. It is known that FASnI₃ can automatically degrade to FA₂SnI₆ in air, [18, 21] and the absorption coefficient of the latter in the visible spectrum is smaller than that of the former. Degradation of the film in air with respect to time can be measured from absorption spectra. As shown in Fig. 4b, UV-vis absorption as a function of time was measured. The changed intensity of absorption reflected the process of degradation. Note that, relative humidity of the environment was

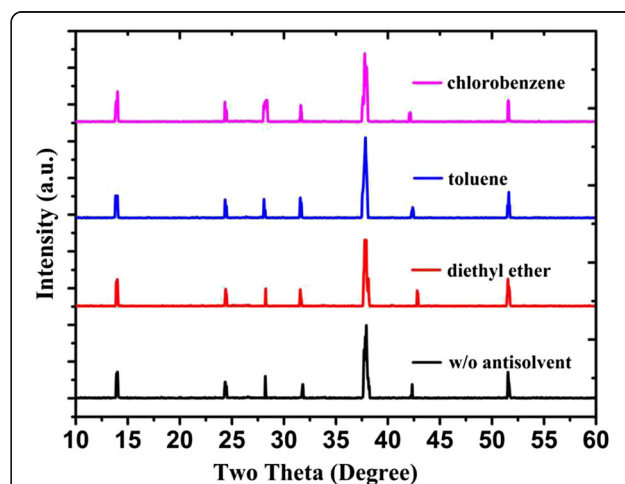
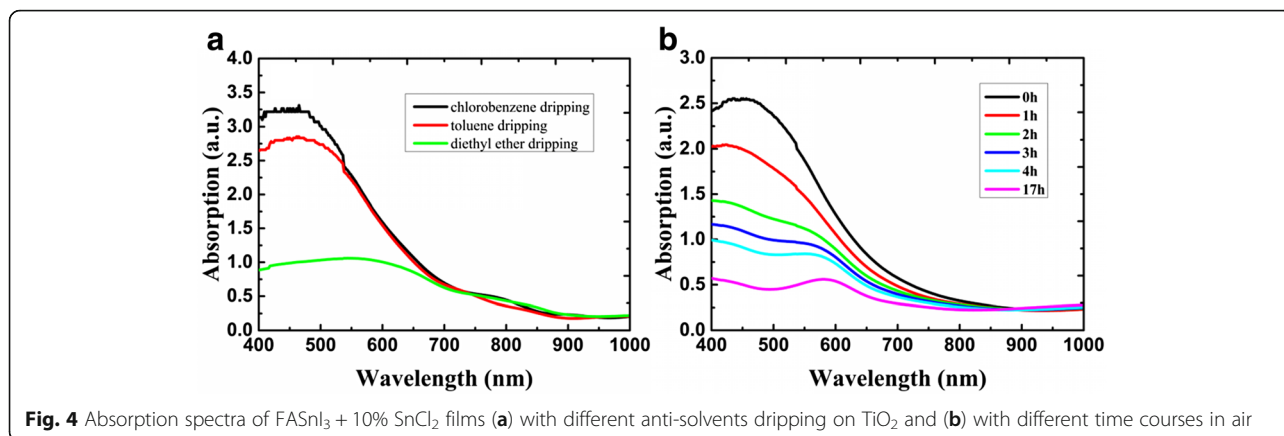


Fig. 3 a SEM top view of TiO₂ surface. b The cross-sectional SEM image of a structure of FTO/compact TiO₂/mesoporous TiO₂/FASnI₃



about 46% and the room temperature was 15 °C. From optical pictures, we can see that FASnI₃ degrades quickly during the first few hours. After 17 h, the absorption peak corresponding to FA₂SnI₆ becomes obvious. This result confirms that FASnI₃ can degrade to FA₂SnI₆ in air.

Figure 5a shows a cross-sectional SEM image of the FASnI₃ PSCs with a structure of FTO/cp-TiO₂/mp-TiO₂/FASnI₃/Spiro-OMeTAD/Au. Figure 5b shows the J-V curves measured with different anti-solvent effects. Although the PCEs of these PSCs are quite low, some characteristics still offer new insights of the fabrication of lead-free perovskites. From Fig. 1a, we know that the nucleation of the film without anti-solvent dripping is discontinuous, which leads to nano-radiative recombination of electrons and holes and causes a large leakage current between TiO₂ and FASnI₃. The result of the films used diethyl ether as the anti-solvent was approximately the same as the untreated sample. The leakage current is large, but the coverage of the film is improved. With toluene and chlorobenzene as anti-solvents, the coverage of

the film has been further improved, and larger crystal particles can create less grain boundaries to enhance the charge separation and collection of electrons and holes, thus leading to the highest PCE.

There are several challenges that hinder performance improvement of CsSnI₃ perovskite solar cells: (1) Sn²⁺ oxidizes to Sn⁴⁺ easily, which seriously affects the photoelectric properties of CsSnI₃ perovskite solar cells. (2) It is difficult to synthesize uniform and fully covered lead-free Sn-based thin films. Even with different additives, there are many pinholes existing on the crystallite surface which may short electron transfer layer and hole transport layer, leading to an enormous leakage current. (3) Lead-free Sn-based PSCs are often prepared in regular cell structures [18, 23]. In the following content, we have made some preliminary studies on the CsSnI₃ films.

Without any additives, the color of CsSnI₃ precursor solution was more yellowish than the solution with 10 mol% SnF₂ additive, as presented in Fig. 6. This indicates that oxidation occurred more easily for pure CsSnI₃.

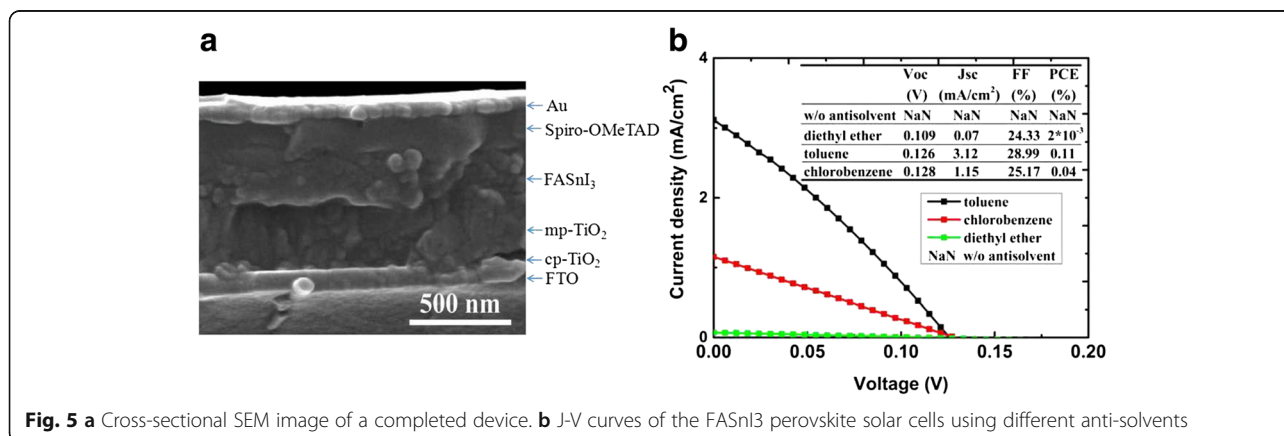


Fig. 5 a Cross-sectional SEM image of a completed device. b J-V curves of the FASnI₃ perovskite solar cells using different anti-solvents

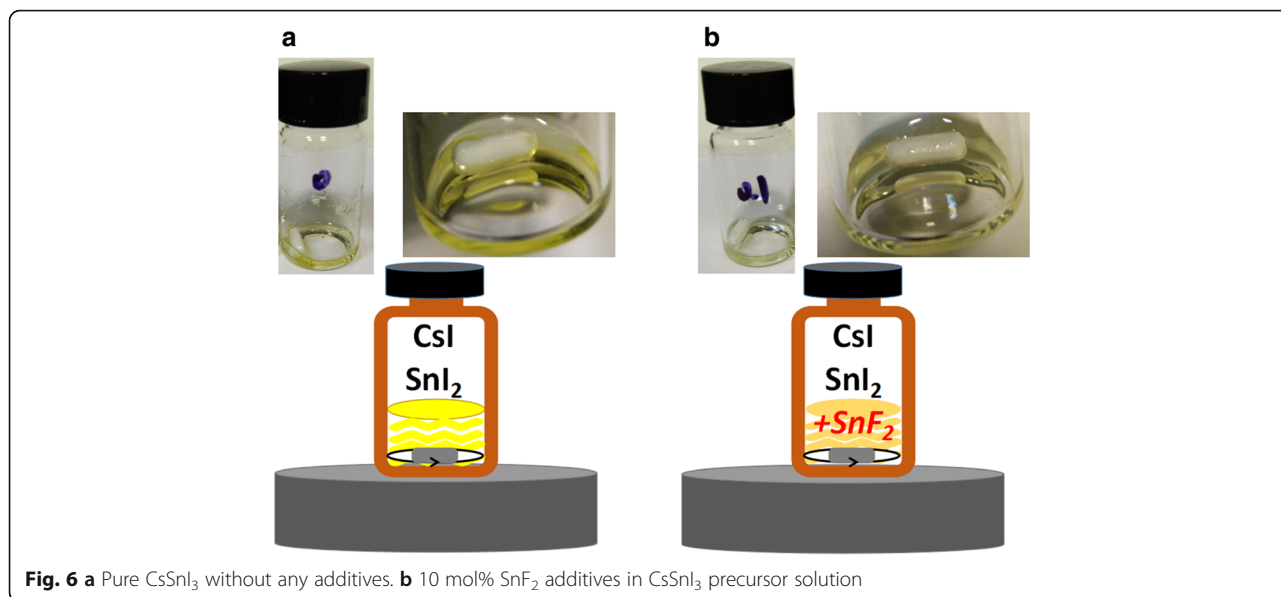


Fig. 6 **a** Pure CsSnI₃ without any additives. **b** 10 mol% SnF₂ additives in CsSnI₃ precursor solution

We also plotted the evolution of absorption spectra at different time courses to investigate the degradation of CsSnI₃ thin films with and without additives in air. As shown in Fig. 7, the black vertical line indicates the direction of change with increasing time in ambient air. Without additives, the CsSnI₃ thin films degraded quickly when it was exposed to air at relative humidity of 57% and temperature of 13 °C. The degradation rate of the film was very fast in the beginning, but it slowed down a lot after 1 h. The degeneration process of CsSnI₃ with 10 mol% SnF₂ additive showed some difference. During the first few minutes, the film was quite stable and no oxidation occurred. Meanwhile the absorption peaks were at the same position. Few minutes later the oxidation rate accelerated and slowed down after an hour. Therefore, it can be deduced that the stability of the film is improved by the addition of SnF₂.

Conclusions

In summary, we have studied the different morphology characteristics of FASnI₃ films prepared by using different anti-solvents and 10 mol% SnCl₂. The aforementioned experimental results show that toluene and chlorobenzene are the best anti-solvents for improving the quality of the films and allow the film to completely cover the substrate. Using toluene as anti-solvent, we can gain the highest PCE of PSCs. The stability of FASnI₃ can be kept for several hours, while CsSnI₃ can only be stable for few minutes. So if we want to develop alternative Pb-free Sn-based perovskite films, the most critical issue is to stabilize the material, namely, suppressing the oxidation of Sn²⁺ within the crystal. This will enhance the long-term stable operation of perovskite films. This technique may offer a promising approach to fabricate the high efficiency of Pb-free Sn-based perovskite solar cell over the next few years.

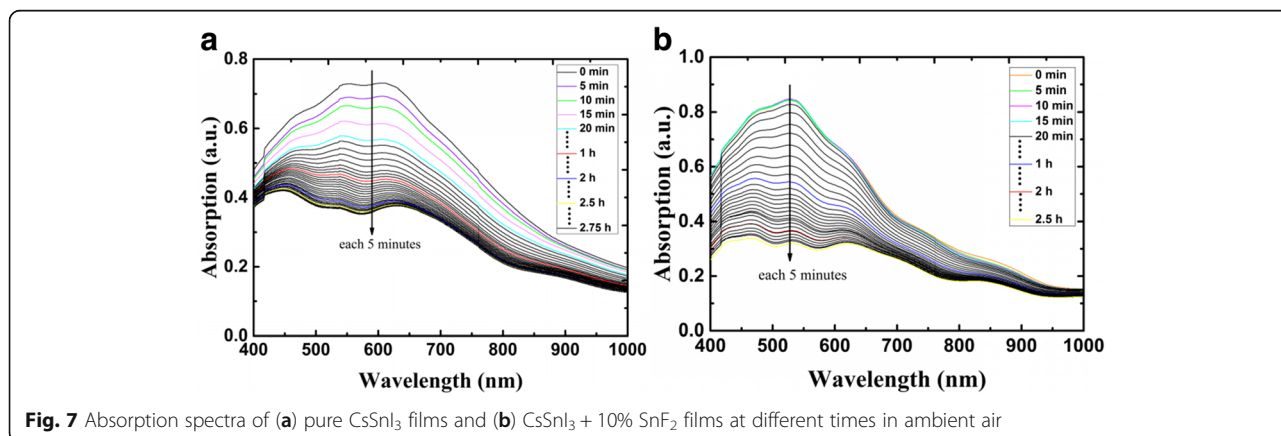


Fig. 7 Absorption spectra of **(a)** pure CsSnI₃ films and **(b)** CsSnI₃ + 10% SnF₂ films at different times in ambient air

Acknowledgements

This work was supported by National Natural Science Foundation of China under Grant Nos. 61421002, 61574029, and 61371046. This work was also partially supported by University of Kentucky.

Authors' Contributions

LJ, TY, and YW were mainly responsible for the experimental operation. The main work of PZ and DL were material analysis and characterization. SL and ZC helped to draft the manuscript. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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Received: 9 March 2017 Accepted: 26 April 2017

Published online: 22 May 2017

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