



# Enhanced performance in hole transport material free perovskite solar cells via morphology control of $\text{PbI}_2$ film by solvent treatment



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## HIGHLIGHTS

- A simple solvent treatment process is introduced.
- Morphology of  $\text{PbI}_2$  film is modified by the solvent treatment.
- More complete conversion of  $\text{PbI}_2$  to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is observed.
- Enhanced performance and reproducibility is obtained.

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## ABSTRACT

The morphology of  $\text{PbI}_2$  film plays a critical role in determining the quality of the resultant  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film and power conversion efficiency of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cell. Here, we propose a solvent treatment method in the two-step sequential deposition process to control the morphology of  $\text{PbI}_2$  film, which leads to enhanced power conversion efficiency. Hole transport material free perovskite solar cell is chosen as a paradigm to demonstrate this idea. Solvent (isopropanol, chlorobenzene, or ethanol) treated  $\text{PbI}_2$  films exhibit dendrite-like or flake-like morphologies, which facilitate more complete conversion of  $\text{PbI}_2$  to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite in ambient atmosphere with a relative high humidity. Therefore, enhanced performance is obtained with the solvent treated  $\text{PbI}_2$  films. Average power conversion efficiency has been improved from 9.42% in the traditional two-step sequential deposition to 11.22% in solar cells derived from ethanol treated  $\text{PbI}_2$  films.

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## 1. Introduction

Organic-inorganic hybrid perovskites have been demonstrated to be an outstanding class of light harvest materials [1–8]. In a few years, power conversion efficiencies (PCEs) of perovskite solar cells have taken a huge leap forward, from 3.9% in 2009 [9] to a recently reported 20.1% [6]. The perovskites light absorb layer can be easily prepared by cost-effective solution processing method, i.e., one-step spin-coating [10–12] or two-step sequential deposition [13–15]. In one-step spin-coating process, a mixed  $\text{PbX}_2$  ( $X = \text{Cl}, \text{Br}, \text{or I}$ ) and  $\text{CH}_3\text{NH}_3\text{X}$  solution is spin-coated onto the substrate and

annealed. Both evaporation of solvent and crystallization of perovskite take place simultaneously during the spin-coating and subsequently annealing process, thus it is difficult to control the growth and final morphology of perovskite films [12,16]. Usually low quality perovskite films with poor surface coverage and pin-holes are obtained. To prepare high quality perovskite films with controlled morphologies, the two-step sequential deposition method is proposed. In a typical two-step sequential deposition process,  $\text{PbI}_2$  film is first deposited onto substrate by spin-coating, the obtained  $\text{PbI}_2$  film is then dipped into  $\text{CH}_3\text{NH}_3\text{I}$  isopropanol solution. The  $\text{CH}_3\text{NH}_3\text{I}$  molecular will diffuse and intercalate into  $\text{PbI}_2$  crystal and convert it into  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite. However, the intercalation process will expand the  $\text{PbI}_2$  lattice and form a compact  $\text{CH}_3\text{NH}_3\text{PbI}_3$  surface layer. This compact layer will block the further diffusion of  $\text{CH}_3\text{NH}_3\text{I}$  into the inner  $\text{PbI}_2$ , leading to an incomplete conversion of  $\text{PbI}_2$  to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  [17–19]. Too much residual  $\text{PbI}_2$  decreases the PCEs of the perovskite solar cells, and

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the uncontrolled  $\text{PbI}_2$  amount also greatly deteriorates the reproducibility of perovskite solar cells. It has been demonstrated that morphologies of  $\text{PbI}_2$  films play a critical role in determining the conversion of  $\text{PbI}_2$  to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  in two-step sequential deposition process, which influences the morphologies of the resultant perovskite films and their power conversion efficiencies [20,21]. Various methods have been developed to engineer the morphologies of  $\text{PbI}_2$  films, including dissolving  $\text{PbI}_2$  into different solvent (*N,N*-dimethylformamide, or dimethyl sulfoxide, or a mixture of them) [22], using mixed  $\text{PbI}_2$  and  $\text{PbCl}_2$  precursor solution [23], careful thermal annealing treatment [5,24], and adding a small amount of  $\text{CH}_3\text{NH}_3\text{I}$  into  $\text{PbI}_2$  solution [17,18]. All these methods enable a better conversion of  $\text{PbI}_2$  to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite, and better control of the final morphologies of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films, thus enhanced PCEs are observed.

In this manuscript, we have proposed a solvent treatment method to modify the morphologies of  $\text{PbI}_2$  films in the two-step sequential deposition process, in order to ensure more complete conversion of  $\text{PbI}_2$  to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite and better control of the morphologies of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films. The spin-coated wet  $\text{PbI}_2$  films are immediately treated with different solvent, i.e., isopropanol, chlorobenzene and ethanol, before the subsequently thermal drying process. Due to the low solubility of  $\text{PbI}_2$  in these solvent,  $\text{PbI}_2$  would quickly precipitate and crystallize, leading to a dendrite-like or flake-like morphologies with many nano-sized voids. The existence of voids in the  $\text{PbI}_2$  films facilitates the diffusion of  $\text{CH}_3\text{NH}_3\text{I}$ , and the nano-sized  $\text{PbI}_2$  crystal is easily converted into  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite. Thus high quality  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films with controllable morphology and low amount of residual  $\text{PbI}_2$  are obtained. Hole transport material free perovskite solar cells fabricated on these  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films prepared from solvent treated  $\text{PbI}_2$  films exhibit superior PCEs. Average PCE has been improved from 9.42% for the traditional two-step sequential deposition to 11.22% in solar cells derived from ethanol treated  $\text{PbI}_2$  films.

## 2. Experiments

### 2.1. Preparation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film

1.0 M  $\text{PbI}_2$  and 0.2 M  $\text{PbCl}_2$  was dissolved into *N,N*-dimethylformamide (DMF) at 70 °C under stirring overnight. Fig. 1a presents the schematic two-step sequential deposition process to prepare the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films without solvent treatment. At first,

$\text{PbI}_2$  precursor solution was spin-coated onto the mesoporous  $\text{TiO}_2$  film at 6000 rpm for 20 s. The obtained  $\text{PbI}_2$  films were directly dried at 100 °C for 5 min. Then to convert  $\text{PbI}_2$  film into perovskite,  $\text{CH}_3\text{NH}_3\text{I}$  isopropanol solution (7 mg  $\text{mL}^{-1}$ ) was loaded onto the  $\text{PbI}_2$  film for 2 min, and spun at 2000 rpm for 20 s. Fig. 1b presents the two-step sequential deposition process with solvent treatment. Immediately after the first-step spin-coating of the  $\text{PbI}_2$  films, a few drops of solvent, i.e., isopropanol (IPA), chlorobenzene (CB), or ethanol (ET), were dropped onto the wet  $\text{PbI}_2$  film, soaked for 10 s and spun at 2000 rpm, the solvent treated  $\text{PbI}_2$  film was dried at 100 °C for 5 min. The second-step spin-coating process is the same as the procedure in Fig. 1a. The as-prepared  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films were further dried at 100 °C for 15 min.

### 2.2. Fabrication of perovskite solar cells

Solar cells were fabricated under ambient atmosphere with a relative high humidity, usually around 50%. FTO glass was ultrasonic cleaned with ethanol and acetone. A 0.15 M solution of titanium diisopropoxide bis(acetylacetonate) in 1-butanol was spin-coated onto the FTO glass at 3000 rpm for 30 s, and dried at 150 °C for 30 min to form the compact  $\text{TiO}_2$  layer. A homemade P25 paste was prepared by ball milling 2.845 g commercial P25  $\text{TiO}_2$  particles, 1.423 g ethyl cellulose, 11.538 g terpineol and 63.222 g ethanol together for 24 h and was spin-coated onto the compact  $\text{TiO}_2$  layer at 3000 rpm for 30 s, and then annealed at 500 °C for 30 min to form the mesoporous  $\text{TiO}_2$  layer. The  $\text{TiO}_2$  films were further treated with 0.4 M  $\text{TiCl}_4$  aqueous solution at 70 °C for 30 min, then sintered again at 500 °C for 30 min. The  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite film was prepared using two-step sequential deposition method as discussed in the previous context. Finally, a carbon paste was doctor-bladed onto the perovskite film and dried at 100 °C to serve as a counter electrode.

### 2.3. Characterization

X-ray diffraction (XRD) measurements were carried out on a Bruker D8 focus X-ray diffractometer with Cu  $K\alpha$  radiation. Absorption of  $\text{PbI}_2$  films and  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite films were characterized by UV–vis spectrometer (Lambda 650S, PerkinElmer). SEM images were obtained using scanning electron microscopy (SEM, Sirion FEG, USA). J–V characteristics of the perovskite solar cells were measured on a CHI660C electrochemical

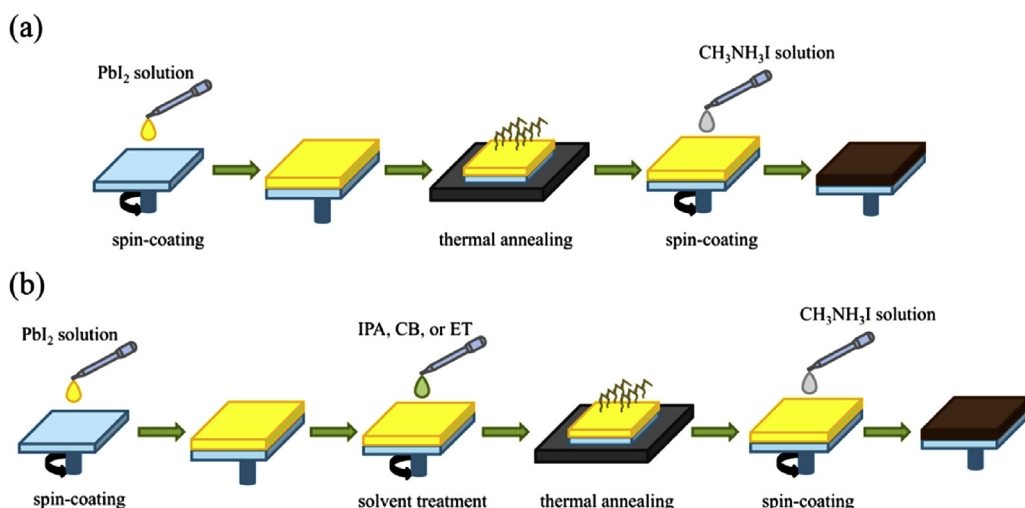


Fig. 1. Schematic two-step sequential deposition process (a) without solvent treatment, and (b) with solvent (IPA, CB, or ET) treatment.

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