



# Pinhole-free mixed perovskite film for bending durable mixed perovskite solar cells



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## ABSTRACT

Methylammonium (MA) and formamidinium (FA) mixed perovskites have been widely utilized in invert planar perovskite solar cell (PSC) applications due to their great potentials such as solution processing, high power conversion efficiency, high absorption, and low cost. To commercialize the PSCs, further improving the device performance without detrimentally changing the device configuration is important at present. Herein, small amount (5%) of CsI is introduced to form a pinhole-free mixed perovskite light absorption layer in a flexible photovoltaic system with enhanced main photovoltaic parameters of the device, resulting in a  $\sim 36\%$  enhancement of power conversion efficiency (PCE) from 8.9% to 12.1% (from 11.3% to 14.6% for rigid device). The origins of the enhancement have been studied by exploring the crystal structures, optical absorption, and crystal morphologies of the synthesised perovskite layers and charge carrier behaviors of the devices. Through small perturbation transient photovoltage (TPV) measurements, the lifetime of the charge carriers are found remarkably increased after the small amount of CsI doping. These characteristics make cation doping of the mixed perovskite layer a promising method in facile tuning of the film quality of the perovskite layer for efficient charge carriers transporting and further boosting the PCE of the devices.

## 1. Introduction

The power conversion efficiency (PCE) of the organic-inorganic lead halide perovskite solar cells (PSCs) has experienced a rapid growth from only 3.9% to exceed 22% in just 7 years [1–10]. The formula of  $\text{APbX}_3$  [A = Cs (cesium), MA ( $\text{CH}_3\text{NH}_3$ , methylammonium), or FA ( $\text{NH}=\text{CHNH}_3$ , formamidinium); X = Cl, Br and I] has been utilized to represent the organic-inorganic lead halide perovskites, which are widely used in various optoelectrical and thermoelectrical applications [11–16]. PSCs have been broadly recognized as a strong competitor to traditional silicon solar cells and III–V solar cells for the future sustainable power supply due to the unique optoelectrical properties of these perovskites such as tunable optical properties and long charge carriers diffusion length, as well as ease of fabrication and cost efficiency [2,3,9,14].

At present, lots of resources and efforts have been invested in the fabrication of mesoporous  $\text{TiO}_2$  based rigid (fluorine doped tin oxide glass substrate is often used as transparent conductive electrode) PSC

[7,8,10,17,18]. However, the energy consumption for  $\text{TiO}_2$  electron transport layer fabrication (heating up to 500 °C), noble metals (gold and silver) usage for electrode deposition, and brittle property of glass substrate may suppress their massive production for commercial application [17–19]. Thus, researchers' attention has turned to flexible and planar PSC since this type of device can easily solve these mentioned problems of  $\text{TiO}_2$  based rigid PSCs because of the usage of polymer-based flexible substrates [such as indium tin oxide (ITO) on polyethylene naphthalate (PEN) and ITO on polyethylene terephthalate (PET)], economic Al electrode and solution processed interfacial materials for the device fabrication under low temperature ( $\leq 120$  °C) [20–25]. Meanwhile, mixed perovskites have attracted growing attention due to their great potential in fabrication of efficient and stable PSC by replacing the traditional pure perovskites such as  $\text{MAPbX}_3$ ,  $\text{FAPbX}_3$ , and  $\text{CsPbX}_3$  that have shown lots of drawbacks such as low PCE for single functional layer device ( $\text{MAPbX}_3$ ,  $\text{FAPbX}_3$ , and  $\text{CsPbX}_3$ ), structural ( $\text{MAPbX}_3$ ,  $\text{FAPbX}_3$ ) and thermal stability ( $\text{CsPbX}_3$ ) problems [7,8,10,18,23]. However, after a preliminary study, we found that this

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mixed perovskite layer is not good for a compact (pinhole-free) light absorption layer formation in the invert planar structure PSC with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as hole transport layer and phenyl-C71-butyric acid methyl ester (PCBM) as electron transport layer. And the overall performance of this PSC based on low quality perovskite film (with lots of pinholes) is not good, which may reduce their potential in photovoltaic applications [23,25]. Thus, a simple method without dramatically changing the device configuration is urgently needed at present to form a pinhole-free perovskite layer and further enhance the device performance of the PSCs, at the same time, without increase the overall cost of the device fabrication. Further cation doping of the mixed perovskite should be a good choice to solve this problem [10,18].

Herein, the pinhole-free CsI doped mixed-cation perovskite films have been introduced for more efficient and stable invert planar PSC fabrication with an optimized low-temperature process. PCEs as high as 12.1% and 14.6% have been obtained in the flexible and rigid devices, respectively. And the originates of the device performance enhancement is investigated through the small perturbation TPV measurements, prolonged charge carrier lifetime has been observed in the 5% CsI doped device. The longer carrier lifetime benefits for the efficient carrier injection/transport and leads to enhanced overall performance of the PSC. In addition, preliminary stability study shows that CsI doping can be a facile method to increase the quality of the perovskite film and stability of the invert flexible device. The bending durability test shows that the prepared devices can maintain ~ 94% of their initial PCE after 400 times bending with a small radius of 4 mm.

## 2. Methods

### 2.1. Materials

Unless specified otherwise, all materials were purchased from Sigma-Aldrich. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was purchased from Clevious. Phenyl-C71-butyric acid methyl ester (PCBM) was purchased from Nano-C. Methylammonium iodine (MAI), formamidinium iodine (FAI), methylammonium bromide (MABr), and  $\text{PbI}_2$  were purchased from Tokyo Chemical Industry Co., Ltd.

### 2.2. Device fabrication

Indium tin oxide polyethylene naphthalate substrate (ITO PEN, < 15  $\Omega$ /sq, Xinyan Technology Ltd.) was cleaned with detergent (2% Hellmanex® III solution), deionized (DI) water, isopropanol (Sigma-Aldrich) and treated with UV ozone treatment at 100 °C for 10 min. The patterned ITO glass substrate (< 15  $\Omega$ /sq, Xinyan Technology Ltd.) was cleaned with detergent, DI water, acetone (Sigma-Aldrich), isopropanol and treated with UV ozone treatment at 100 °C for 10 min. The ITO PEN substrate was etched with diluted HCl (2 M, Sigma-Aldrich) and zinc powder. The etched ITO substrate was fixed on a plain glass substrate by double side tape in order to deposit functional layers easily. A ~ 30 nm PEDOT:PSS layer was deposited on top of the ITO substrate by spin-coating the precursor solution at 4000 rpm for 30 s. The PEDOT:PSS precursor solution was filtered through a syringe filter (0.45  $\mu\text{m}$  pore size) to remove the large particles. Then, it was heated at 120 °C for 10 min in a  $\text{N}_2$  filled glovebox. Next, perovskite film was deposited on the substrate by a spin-coating process in the glovebox. First, 2000 rpm for 10 s; second, 6000 rpm for 30 s, then anhydrous chlorobenzene (0.11 mL, Sigma-Aldrich) was dropped in 8–10 s during the second spin-coating process. The precursor solution was prepared by dissolving 0.265 g  $\text{PbI}_2$  (TCI), 0.037 g  $\text{PbBr}_2$  (Sigma-Aldrich), 0.011 g MABr (TCI) and 0.094 g FAI (TCI) in 0.4 mL anhydrous N,N-dimethylformamide (Sigma-Aldrich) and 0.1 mL anhydrous dimethylsulfoxide (Sigma-Aldrich). The substrate was then heated at 100 °C for 30 min. As for the Cs doped mixed perovskites,

corresponding amount of CsI (Sigma-Aldrich) was added to achieve the desired triple cation composition. PCBM (Nano-C) was deposited by spin-coating at 1000 rpm for 30 s. The PCBM solution was prepared by dissolving 20 mg PCBM in 1 mL anhydrous chlorobenzene. Finally, 80 nm of aluminum was deposited as an electrode by thermal evaporation.

### 2.3. Characterization

Current density-Voltage (*J-V*) characteristics were measured in the glovebox with a solar simulator (SAN-EI Electric XES-301S 300 W Xe Lamp JIS Class AAA) and a Keithley 2400 sourcemeter. The flexible solar cells were masked with metal apertures to define the active areas which were typically 0.2 and 1  $\text{cm}^2$ , the rigid solar cells based on patterned ITO substrates were fabricated with a active area of 0.09  $\text{cm}^2$ . IPCE was recorded with a Keithley 2400 sourcemeter combined with an Oriel 300-W Xe lamp, an Oriel Cornerstone 130 monochromator and a SRS 810 lock-in amplifier (Stanford Research Systems). A calibrated Si diode was used as the reference. For the stability test, the samples are stored in the  $\text{N}_2$  fill glovebox at room temperature without encapsulation. The surface and cross section morphologies of the samples were investigated by a SEM (JEOL JSM-7001F) at 10 kV. XRD experiments were conducted by a Bruker AXS (D8 ADVANCE) X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The optical absorption spectra were measured on a PerkinElmer Lambda 950UV/VIS/NIR spectrometer and the samples for this study were prepared with the same procedures of device fabrication. A 532 nm Nd:YAG pulsed laser (NT341A-10-AW, pulse duration shorter than 4 ns and 1 Hz repetition frequency) was used as excitation light source in the small perturbation TPV experiments. Neutral density filters were used to afford a small perturbation of the cell photovoltage (below 20 mV). A white light halogen lamp was employed to fix the back illumination level. The TPVs were monitored by a digital oscilloscope (Agilent 54845A).

## 3. Results and discussion

The device structure of the flexible devices is shown in Fig. 1a, with the device configuration of flexible transparent conductive electrode [ITO on PEN]/hole transporting material (PEDOT:PSS)/sunlight absorber (perovskite)/electron transporting material (PCBM)/top electrode (Al). Fig. 1b shows the energy levels of different device components [17,26]. When light enters the device, the perovskite layer absorbs light and generates free holes and electrons. The free electrons are transported through the PCBM layer to the Al electrode while the free holes are extracted through the PEDOT:PSS layer and collected by the ITO electrode. In Fig. 1c, we show the fabrication processes of the flexible device. A thin (~ 30 nm) and compact PEDOT:PSS film is firstly deposited on top of a clean ITO substrate by spin-coating at 4000 rpm for 30 s and then heated at 120 °C for 10 min inside a glovebox. After that, a ~ 450 nm thick perovskite layer is spin-coated on top of the substrate with a two-step spin-coating process. After heating at 100 °C for 30 min inside the glovebox, a ~ 30 nm PCBM film is deposited on top of the substrate by spin-coating a 2% PCBM (20 mg/mL) in chlorobenzene solution and then an 80 nm Al electrode is thermal evaporated on top of the PCBM layer to complete the device fabrication.

CsI has been utilized to partially replace MA/FA in the mixed perovskite  $[\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3]$  light absorber and the quantitative effect of CsI doping on the perovskite film formation and charge carrier transport within the flexible PSC has been carefully studied. For convenience, Cs-x has been utilized to represent the different types of mixed perovskites with a formula  $\text{Cs}_x(\text{FA}_{0.81}\text{MA}_{0.15})_{100-x}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ , where *x* is the percentage of CsI. The X-ray diffraction (XRD) patterns of the prepared perovskites with different amounts of CsI doping, as shown in Fig. 2a, are in agreement with some recent results [18,27,28]. A small peak at 12.6° corresponding to the cubic  $\text{PbI}_2$  derived from the incomplete transformation of the perovskite

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