



Full paper

Compositional and morphological engineering of mixed cation perovskite films for highly efficient planar and flexible solar cells with reduced hysteresis

Changlei Wang^{a,b}, Dewei Zhao^{b,*}, Yue Yu^b, Niraj Shrestha^b, Corey R. Grice^b, Weiqiang Liao^b, Alexander J. Cimaroli^b, Jing Chen^c, Randy J. Ellingson^b, Xingzhong Zhao^{a,*}, Yanfa Yan^{b,*}

^a Key Laboratory of Artificial Micro/Nano Structures of Ministry of Education, School of Physics and Technology, Wuhan University, Wuhan 430072, China

^b Department of Physics and Astronomy, and Wright Center for Photovoltaics Innovation and Commercialization, The University of Toledo, Toledo, OH 43606, USA

^c School of Electronic Science and Engineering, Southeast University, Nanjing 210096, China

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ABSTRACT

We report on compositional and morphological engineering of mixed methylammonium (MA) and formamidinium (FA) lead triiodide ($\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$) perovskite absorber layers to produce highly efficient planar and flexible perovskite solar cells (PVSCs) with reduced hysteresis. Incorporation of FA into the MAPbI_3 extends the absorption edge of the perovskite to longer wavelengths, leading to enhanced photocurrent of the resultant PVSCs. Moreover, adding a small amount of lead thiocyanate ($\text{Pb}(\text{SCN})_2$) additive into mixed perovskite precursor solutions significantly enlarges the grain size and prolongs the carrier lifetime, leading to improved device performance. With optimal compositional and morphological engineering, the average power conversion efficiency (PCE) improves from $15.74 \pm 0.74\%$ for pure MAPbI_3 PVSCs to $19.40 \pm 0.32\%$ for $\text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3$ PVSCs with 3% $\text{Pb}(\text{SCN})_2$ additive, exhibiting a high reproducibility and small hysteretic behavior. The best PVSC achieves a PCE of 20.10 (19.85)% measured under reverse (forward) voltage scan. Furthermore, the compositional and morphological engineering allowed the fabrication of efficient flexible PVSCs on indium-doped SnO_2 (ITO)/polyethylene terephthalate (PET) substrates, with the best PCE of 17.96 (16.10)% with a V_{OC} of 1.076 (1.020) V, a J_{SC} of 22.23 (22.23) mA/cm^2 and a FF of 75.10 (71.02)% when measured under reverse (forward) voltage scan. Our approach provides an effective pathway to fabricate highly efficient and reproducible planar PVSCs.

1. Introduction

Organic-inorganic metal halide perovskite solar cells (PVSCs) have gained tremendous attention in the past few years, [1–14] and the record power conversion efficiency (PCE) has recently exceeded 22%. [5–7] The bandgap (E_g) of the most commonly studied organic-inorganic perovskite absorber material, methylammonium lead triiodide (MAPbI_3) with $E_g \sim 1.60$ eV, is slightly higher than the optimal E_g range (1.2–1.45 eV) for single junction solar cells per the Shockley - Queisser limit [15,16]. A relatively smaller E_g is desirable for boosting the performance by increasing the portion of photons absorbed, thereby increasing the photogenerated current. Formamidinium lead triiodide (FAPbI_3) perovskite exhibits an E_g of ~ 1.45 eV, [17–20] which is much more suitable for single junction solar cells. However, FAPbI_3 perovskite films often contain a small portion of the undesirable yellow

phase (δ -phase) [7,21,22], which adversely affects the cell performance. Combining different cations has been reported recently to reduce the E_g of perovskite absorbers [4,5,20,21,23–25]. Among these methods, mixing MA and FA cations has shown promising results [5,8,26], but it is challenging to obtain good device reproducibility due to the facile formation of the undesirable δ -phase of FAPbI_3 . [7,21] Mixing MAPbI_3 with FAPbI_3 precursors has been proven to be an effective way to fabricate mixed FA and MA planar PVSCs [26]. However, a significant drawback of this approach is that the resultant ($\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$) perovskite thin films contain rather small grains, hindering the use of relatively thick perovskite absorbers which is needed for maximum light absorption. On the other hand, the high annealing temperature of 150 °C for pure FAPbI_3 hinders its application on flexible substrates, while mixing MA and FA will lower the formation temperature to 100 °C which is more compatible for flexible

* Corresponding authors.

E-mail addresses: dewei_zhao@hotmail.com (D. Zhao), xzzhao@whu.edu.cn (X. Zhao), Yanfa.Yan@utoledo.edu (Y. Yan).

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PVSCs.

High-quality perovskite film is a requisite for fabricating high-efficiency PVSCs. [27–29] PVSCs with small grains and low crystallinity typically exhibit poor fill factors (FF's), because absorber layers exhibit high density of grain boundaries, which could cause charge recombination [30,31]. Therefore, it is highly desirable to reduce the density of grain boundaries [26,31,32] and/or passivate the grain boundaries with other materials, such as (6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM) and PbI₂ [33–35]. Various works have been reported to improve the performance of PVSCs, including perovskite film quality improvement and interfacial engineering of the devices. [36–43] Recently, lead thiocyanate (Pb(SCN)₂) additives have been employed in MAPbI₃ and FA_{1-x}Cs_xPbI₃ perovskite films to enlarge the grains and increase the perovskite crystallinity [24,44]. It was found that Pb(SCN)₂ additives can significantly increase the grain size of perovskite films from about 200 nm to up to several micrometers, and the grain boundaries are passivated with excessive PbI₂ [24,44].

Here, we demonstrate that Pb(SCN)₂ additives can also significantly enlarge the grain size of mixed MA and FA lead triiodide (MA_{1-x}FA_xPbI₃) perovskite thin films and lead to highly efficient planar PVSCs. Mixtures of MA and FA cations extend the absorption edge to longer wavelengths as compared to pure MAPbI₃, leading to enhanced short-circuit current densities (*J*_{SC}'s). Adding a small amount of Pb(SCN)₂ additive into perovskite precursor remarkably increases the grain size of perovskite thin film and thus prolongs the carrier lifetime, which is responsible for the significantly enhanced device performance. With optimal compositional and morphological engineering, the averaged PCE of our PVSCs increases from 15.74 ± 0.74% for pure MAPbI₃ PVSCs (0 wt% Pb(SCN)₂) cells to 19.40 ± 0.32% for MA_{0.7}FA_{0.3}PbI₃ PVSCs with 3 wt% Pb(SCN)₂ additive. The best performing PVSC shows a PCE of 20.10 (19.85) % with an open-circuit voltage (*V*_{OC}) of 1.121 (1.119) V, a *J*_{SC} of 22.85 (22.86) mA/cm² and a FF of 78.46 (77.60) % when measured under reverse (forward) voltage scan, respectively. Furthermore, the compositional and morphological engineering allowed the fabrication of efficient flexible PVSCs on indium-doped SnO₂ (ITO)/polyethylene terephthalate (PET) substrates, with the best PCE of 17.96 (16.10)% with a *V*_{OC} of 1.076 (1.020) V, a *J*_{SC} of 22.23 (22.23) mA/cm² and a FF of 75.10 (71.02)% when measured under reverse (forward) voltage scan. Our results demonstrate that Pb(SCN)₂ additives can be used to effectively increase the crystal quality of the mixed cation perovskite absorbers and improve the photovoltaic performance of planar PVSCs with the regular cell configuration.

2. Experimental section

2.1. Preparation of ESLs

FTO glass (Pilkington, NSG TEC-15) was cleaned with detergent, facilitated by ultrasonication in water, acetone and iso-propanol baths successively before deposition of SnO₂ ESLs. The SnO₂ layer was deposited on the FTO substrates as reported previously.[45] Plasma-enhanced atomic layer deposition (PEALD) process was done with an equipment of Ensure Scientific Group AutoALD-PE V2.0 equipped with a plasma generator. Tetrakis(dimethylamino)-tin(IV) (99%, TDMA-Sn, Strem Chemicals Inc.) was used as the Sn precursor. Oxygen and Argon are used as oxidizer and carrier gases, respectively. The temperature of the reaction is fixed at 100 °C during the deposition process.

2.2. Perovskite precursor preparation

Lead iodide (PbI₂, Alfa Aesar, 99.9985%), methylammonium iodide (MAI, Dyesol), formamidinium iodide (FAI, Dyesol), lead thiocyanate (Pb(SCN)₂, Sigma-Aldrich, 99.5%), dimethyl sulfoxide (DMSO, Sigma-Aldrich, 99.8%) and N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%) are purchased and used without further purification. The

perovskite precursor was prepared using a Lewis acid-base adduct approach with the mixture of MAI, FAI, PbI₂, and DMSO in DMF, where the molar ratio of DMSO and PbI₂ is 1:1 [46,47]. A 45% by weight precursor solution of MAPbI₃ was prepared with PbI₂, MAI and DMSO (molar ratio=1:1:1) in DMF. The solution was stirred for 12 h on a 60 °C hot plate before deposition. The FAPbI₃ precursor solution was made in the same process. The MA_{1-x}FA_xPbI₃ precursor was prepared by mixing two different solutions together with different volume ratio, where the ratio of MAI and FAI is changed from 1:0 to 0:1 (*x*=0, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0). The resulting mixed precursor solution was stirred for one hour on a 60 °C hotplate and then purified using a 0.45 μm filter before spin-coating.

The precursors with Pb(SCN)₂ additives are prepared with fixed amounts of Pb(SCN)₂ with respect to the weight of PbI₂, where the content of Pb(SCN)₂ ranging from 0% to 5%.

2.3. Fabrication of PVSCs

C₆₀-SAM was deposited on PEALD SnO₂ as previously reported [45]. The perovskite precursor solution was spin-coated on the ESL first at 500 rpm for 3 s, and then at 4000 rpm for 60 s using a fast deposition-crystallization technique with diethyl ether as the anti-solvent agent. After spin coating, the perovskite film was annealed at 65 °C for 2 min and then 100 °C for 5 min. All of these processes were carried out in a N₂ filled glove box.

2,2',7,7'-tetrakis(N,N'-di-*p*-methoxyphenylamine)-9,9'-spirobi-fluorene (Spiro-OMeTAD) was used as the HSL and deposited on the perovskite film at 2000 rpm for 60 s. The Spiro-OMeTAD was co-doped using Co-TFSI and Li-TFSI. The Spiro-OMeTAD solution was prepared by dissolving 72.3 mg Spiro-OMeTAD (Shenzhen Feiming Science and Technology Co., Ltd., 99.0%) in 1 mL chlorobenzene (CB) with 28 μL 4-*tert*-butylpyridine (TBP) (Sigma-Aldrich, 96%), 18 μL Li-bis-(trifluoromethanesulfonyl) imide (Li-TFSI) (Sigma-Aldrich, 99.95%) (520 mg/mL in acetonitrile) and 18 μL Co(II)-TFSI salt (FK102, Dyesol) (300 mg/mL in acetonitrile). A layer of 80 nm gold (Au) was then deposited on the top of Spiro-OMeTAD using thermal evaporation. The working area of the devices was 0.08 cm² as defined by a shadow mask during the Au evaporation.

2.4. Characterizations

J-V curves were measured using a Keithley2400 sourcemeter under standard AM 1.5 G illumination using solar simulator (PV Measurements Inc.) with an output intensity of 100 mW/cm². For light intensity dependence test, the light intensity was later adjusted between 1 and 100 mW/cm² using neutral density filters. EQE measurement was carried out with an EQE system (PV Measurements Inc.) using 100 Hz chopped monochromatic light ranging from 300 nm to 900 nm under otherwise near-dark test conditions. The top-view and cross section structures of perovskite films and PVSCs were characterized with a field emission SEM instrument (Hitachi S-4800). Crystallinity and the crystal structure of the perovskite layer were analyzed with an Ultima III X-ray Diffractometer using a Ni-filtered Cu K_α x-ray source (Rigaku Corp.). Absorbance spectra were obtained with a UV-vis spectrophotometer (PerkinElmer Lambda 1050). Sheet resistance was measured using four-point probe method resistivity test system (PRO4-440N, Lucas labs). For steady-state photoluminescence (PL) and time resolved photoluminescence (TRPL) measurements, perovskite films were fabricated by spin-coating perovskite precursors on glass substrates followed by coating another encapsulating layer of polymethylmethacrylate (PMMA) after thermal annealing. PL measurements were performed in ambient air at room temperature. Samples were illuminated through the film side. A 532 nm continuous-wave laser (beam diameter ≈90 μm) at 40 mW/cm² was used as an excitation wavelength for steady-state PL measurement. PL signal was detected via Symphony-II CCD (from Horiba)

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