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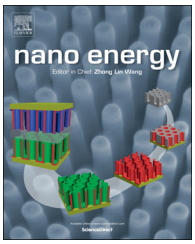

RAPID COMMUNICATION

Gas-assisted preparation of lead iodide perovskite films consisting of a monolayer of single crystalline grains for high efficiency planar solar cells

Fuzhi Huang[a], Yasmina Dkhissi[b], Wenchao Huang[a], Manda Xiao[c], Iacopo Benesperi[c], Sergey Rubanov[d], Ye Zhu[a], Xiongfeng Lin[a], Liangcong Jiang[a], Yecheng Zhou[b], Angus Gray-Weale[b], Joanne Etheridge[a,e], Christopher R. McNeill[a], Rachel A. Caruso[b,f], Udo Bach[a,f,g], Leone Spiccia[c,*], Yi-Bing Cheng[a,]**

[a]*Department of Materials Engineering, Monash University, Victoria 3800, Australia*
[b]*School of Chemistry, The University of Melbourne, Victoria 3010, Australia*
[c]*School of Chemistry, Monash University, Victoria 3800, Australia*
[d]*Bio21 Institute, The University of Melbourne, Victoria 3010, Australia*
[e]*Monash Centre for Electron Microscopy, Monash University, Victoria 3800, Australia*
[f]*Commonwealth Scientific and Industrial Research Organization, Manufacturing Flagship, Clayton, Victoria 3168, Australia*
[g]*Melbourne Centre for Nanofabrication, 151 Wellington Road, Clayton, VIC 3168, Australia*

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Abstract
The simple planar configuration of organic–inorganic hybrid perovskite solar cells produced by a solution coating process has great potential to be a low-cost and high efficiency photovoltaic technology. However planar perovskite films produced by "normal" spin coating usually show a dendritic grain morphology giving many gaps in the film, resulting in poor coverage of the substrate and thus a low power conversion efficiency. Here a facile gas-assisted solution processing technique is reported that has changed the kinetics of nucleation and crystal growth of the perovskite during the spin coating, producing very uniform perovskite thin films consisting of densely packed single crystalline grains. This microstructure is an ideal candidate

*Corresponding author. Tel.: +61 3 9905 4526; fax: +61 3 9905 4597.
**Corresponding author. Tel.: +61 3 9905 6264; fax: +61 3 9905 4940.
E-mail addresses: leone.spiccia@monash.edu (L. Spiccia), yibing.cheng@monash.edu (Y.-B. Cheng).

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for the *p-i-n* solar cell device. Planar perovskite solar cells constructed from these films produced a highly reproducible average power conversion efficiency of 15.7±0.7%. The highest efficiency achieved was 17.0% with a slightly lower steady-state value of 16.5% at the maximum power output of the solar cell.

Introduction

Perovskite solar cells (PSCs) have attracted intense attention in recent years due to the rapid rise in their power conversion efficiency [1-5]. In a PSC, organic-inorganic hybrid perovskite materials, such as $CH_3NH_3PbI_3$ or $CH_3NH_3PbCl_xI_{3-x}$, act as a light absorber as well as a charge conductor [5,6]. Two general PSC device architectures have been reported: (a) a mesoporous structure, formed by a thin layer of an inorganic scaffold material, such as either TiO_2 [2,7], Al_2O_3 [5,8] or ZrO_2 [9,10]; and (b) a planar structure [1,11], where a *p-i-n* junction is formed. Compared to the mesostructured devices, the planar structure has the advantage of being a simpler arrangement that is easier to fabricate [12-15]. In a planar structure, each layer should be pinhole free and provide good contact with the adjacent layers to minimize the series resistance and maximize the shunt resistance. Thus, a dense perovskite layer is crucial to achieve a high efficiency device. Snaith et al. employed a dual-source vapor deposition method to fabricate a planar device achieving a homogenous deposition of the perovskite layer and an efficiency above 15% [1]. However, to reduce the manufacturing cost, a solution-based process that is compatible with printing technologies would be desirable.

In previous studies, a spin-coating method (a solution process) has been used for making mesostructured PSCs [3,8]. This method was, however, shown to produce perovskite films with poor coverage of the substrate [2]. Islands of micrometer-sized perovskite grains were formed on the top of the mesoporous TiO_2 film, leaving a significant fraction of the underlying TiO_2 film uncovered [7,16]. This results in a reduction in light harvesting and significant charge recombination losses across the TiO_2/spiro-OMeTAD interface under forward bias conditions [3]. A two-step sequential deposition method has recently been developed, where PbI_2 was first coated on a mesoporous TiO_2 film on the conductive glass substrate, which was then dipped in a CH_3NH_3I solution [2]. The pre-formed PbI_2 particles react quickly with CH_3NH_3I to form a full coverage of $CH_3NH_3PbI_3$ [11]. But the surface of the perovskite film fabricated by the two-step method is relatively rough and this method is more suitable for the mesostructured PSC [11]. Alternatively, a PbI_2 film was annealed in CH_3NH_3I vapor for several hours to form the perovskite film with good substrate coverage [17]. A dense perovskite film was also obtained by the introduction of a second solvent to promote fast crystallization [18,19] or by the additive of 1,8-diiodooctane in the perovskite solution to control the crystallization of the perovskite [20]. In this work, we report a facile gas-assisted method that results in fast-solvent evaporation, promoting rapid supersaturation and precipitation, and the formation of a smooth thin film comprised of densely packed single grains of the alkylammonium lead iodide perovskite material. By controlling the subsequent annealing conditions, an average power conversion efficiency (PCE) of 15.7±0.7% was achieved.

Experimental section

Materials

Unless specified otherwise, all materials were purchased from either Alfa Aesar or Sigma-Aldrich and used as received. Spiro-OMeTAD (2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene) was purchased from Luminescence Technology Corp. CH_3NH_3I was synthesized by mixing 24 mL CH_3NH_3 (33% in ethanol) and 10 mL HI (57% in water) in 100 mL ethanol. After stirring for 2 h, the solvent was removed on a rotary evaporator. The white crystals were washed by diethyl ether and then recrystallized from ethanol. The final product was dried in a vacuum oven at 60 °C for 5 h.

Device fabrication

A TiO_2 dense blocking layer was first deposited on the clean FTO glass by pyrolysis spray of a bis(isopropoxide)-bis(acetylacetonate)titanium(IV) solution at 450 °C [21]. After cooled to room temperature, the substrate was cut into around 1 cm^2. A 25 μL 45 wt% $CH_3NH_3PbI_3$ DMF solution, prepared from PbI_2 and CH_3NH_3 in a molar ratio of 1:1, was spread on it, on a spin-coater. For the conventional spin-coating method, the solution was spun at 6500 rpm for 30 s, while for the gas-assisted method, a 40 psi dry Argon gas stream was blown over the film during spinning at 6500 rpm in 2 s after the spin-coating commenced. The films were then annealed at different temperatures (35-100 °C) on a hotplate for 10 min, and then cooled to room temperature on a steel substrate. A 25 μL spiro-OMeTAD solution (prepared by dissolving 41.6 mg spiro-OMeTAD, 7.5 μL of a stock solution of 520 mg mL^{-1} lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 16.9 μL 4-tert-butylpyridine in 0.5 mL chlorobenzene) was coated on the perovskite film by spin-coating at 3000 rpm for 30 s. A 70 nm silver layer was deposited by thermal evaporation to form the complete device.

Characterization

The surface and sub-surface of the prepared perovskite films were examined using an FEI Nova NanoSEM 450 microscope. To obtain the cross-section image, the device was milled using a FEI Nova Dual Beam by a focused ion beam (FIB). The milling of the cross sections used a gallium