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Continuous dripping method as a deposition route for high-performance mesoporous perovskite solar cells

Guo Chen[a], Lingling Zheng[ab] , Fengyan Zhang[a*]

[a]*School of Energy Research, Xiang'an Campus, Xiamen University, Xiamen 361100, Fujian, China*

[b]*Renewable Energy Research Group (RERG), Department of Building Services Engineering, The Hong Kong Polytechnic University, Hong Kong*

Abstract

The past five years have witnessed the uniquely rapid emergence of the mixed organic-inorganic halide perovskite solar cells. Here, a modified deposition process, continuous dripping method, is reported for fabricating high-performance and reproducible perovskite solar cells. The best power conversion efficiency (PCE) of 17.76 % and an average PCE of 16.74 % were obtained via this process. Moreover, the conventional solution two steps method was also carried out as a comparison to this process. This work provides a new simple solution approach to obtain high quality of perovskite thin films for high-performance and reproducible PSCs.

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Keywords: Perovskite solar cells; Two-step process; Continuous dripping method.

* Corresponding author. Tel :+86-18750266918

E-mail address: fengyanzhang5454@gmail.com

1. Introduction

Over the past 5 years, solar cells based on organic-inorganic hybrid perovskite materials, have emerged as a novel and very promising solar cells due to its excellent performance [1-4]. Metal-halide perovskite materials are born with a lot of fascinating properties [5, 6], high absorption coefficient, high carrier mobility and tunable band position and bandgap [5, 7, 8]. Recently, the PCE of perovskite solar cells (PSCs) with a certificated 22.1 % are reported [9].

Recently, $CH_3NH_3PbI_3$ ($MAPbI_3$) has been most frequently employed as light harvester in the PSCs device fabrication. Two steps solution deposition process has been widely adopted to fabricate $MAPbI_3$ perovskite solar cell [10, 11]. Nevertheless, this deposition method always suffers from some unwanted

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consequences such as perovskite films peeled off from the substrate [12, 13] and PbI_2 residual in the perovskite [14]. Here, we present a modified deposition process, continuous dripping method (Figure 1), to manufacture high crystallinity, large-grained and crack-free perovskite films. The impact of different deposition method on the growth, morphology and crystallinity of $MAPbI_3$ films has been systematically investigated. In particular, the best performance device with a PCE exceeding 17 % was successfully achieved in this work.

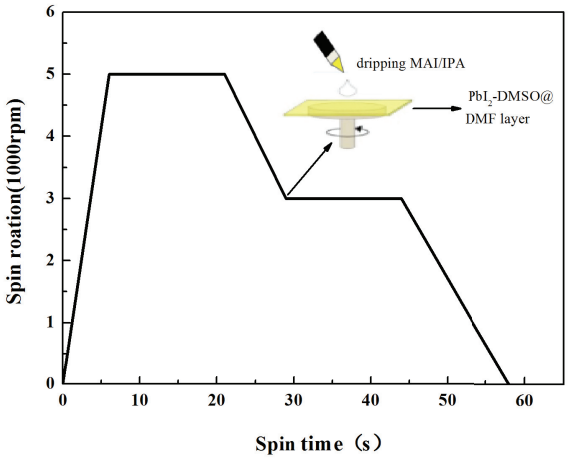

Figure 1. The detailed spin coating process of the continuous dripping method procedures. The inset shows schematic of an ultrahigh concentration MAI/IPA solution dripping on a first PbI_2-DMSO@DMF precursor layer.

2.Experimental section

Patterned F-doped tin oxide (FTO) coated glasses were sequentially washed with liquid detergent, deionized water and cleaned by ultrasonic cleaning with acetone, and alcohol and finally treated under oxygen plasma for 15 min. Compact TiO_2 (C-TiO_2) was deposited by spin coating 0.15 M titanium diisopropoxide bis (acetylacetonate) solution at 2000 rpm for 20 s, then repeated twice, followed by sintering at 500°C for 30min. Then the substrate was immersed into 70 ℃ 40 mM $TiCl_4$ solution for 30 min followed by washing with alcohol. Mesoporous TiO_2 (mp-TiO_2) layer were deposited by a spin coating TiO_2 paste (diluted in alcohol at a 1:10 mass ratio) at 5000 rpm for 20 s then annealed at 500 ^oC for 30 min.

To prepare the perovskite layers, the 1.3M PbI_2-1.5DMSO@DMF first precursor solution (0.5993g, (1 Mmol) PbI_2, 0.1521g DMSO (1.5 Mmol) were dissolved in 1ml DMF) was spread on the mesoporous TiO_2 layer and spun at 5000 rpm for 15 s; For the continuous dripping method (deposition spinning

details in Figure 1), 0.377 M MAI/IPA solution was dripped on the spinning substrates at the first second when the speed was slowed to 3000 rpm. The spinning lasted 15 s after dripping MAI solution. The samples were then heated on a hot plate to 150 °C for 20 min. For comparison, the conventional two steps process was also performed. In detail, after spinning the first precursor layer at 5000 rpm, the substrates was loaded 0.377 M MAI/IPA solution for 5 s then spun at 3000rpm for 15 s. Ultimately, the film was also treated for 150 °C for 20 min. Spiro-OMeTAD solutions (Spiro-OMeTAD solution was employed with 72.3 mg Spiro-OMeTAD, 28.8 μL of 4-tert-butyl pyridine and 17.5 μL of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TSFI in 1 mL acetonitrile) in 1 mL of chlorobenzene) were then deposited on the perovskite film by spinning at 3000 rpm for 30s. Finally, 80 nm thick Au were deposited by electron beam evaporation under pressure of $<10^{-7}$ torr.

The current density–voltage (J-V) characteristics of PSCs were measured by Keithley 2400 source meter under simulated AM 1.5 G solar light condition. Incident photon-to-electron conversion efficiency (IPCE) was determined by an IPCE system (Newport). And both the systems were calibrated by the certified silicon solar cell. The devices were measured using a mask with a metal aperture to define the active area of 0.09 cm^2.

3. Results and discussion

Figure 2a and 2b show the SEM top-view of the $MAPbI_3$ films obtained via continues dripping method and conventional solution two steps separately. As shown in figure 2a, the $MAPbI_3$ film prepared via continues dripping method, forms a homogeneous, highly-crystallized and crack-free film. However, it can be clearly seen in figure 2b that gaps between the $MAPbI_3$ crystals seem to be larger indicating a poor crystal quality via conventional two steps process. It has been reported that the cracks between crystals will reduce the shunt resistance of devices and lead to leakage [1]. As a result, it will decrease the fill factor and photocurrent density which are detrimental for devices performance.

All the devices were measured under simulated air mass at AM1.5G solar irradiation by applying a reverse bias scan with a fixed delay time 40ms. The photovoltaic parameters of these devices fabricated with two different manufacturing process were shown in Fig2a-d and listed in Table 1. As expected, devices fabricated via continues dripping method exhibits better performance: open-circuit voltage (V_{oc}) of 1.01 V, short-circuit density (J_{sc}) of 22.98 mA/cm^2, fill factor (*FF*) of 71.78 %, and PCE of 16.74 %. However, an average PCE of 11.48% can be only achieved via conventional two steps process and all the photovoltaic parameters decreased for devices. It can be also clearly observed that devices fabricated via continuous dripping method show higher Jsc, which may be due to a higher light absorption, as well as a better injection of carriers. From Figure 3, one can see that the champion device can reach the highest

PCE of 17.76%. Integral short-circuit current 20.80 mA.cm^{-2} was calculated from the IPCE (do not show in the paper), which generated around 12% mismatch as compared to the value as shown in Figure5b. This mismatch may be due to the lack of a few seconds light soaking which stabilizes the current density of the cell [15, 16]

This result confirms the correctness of the discussion in the SEM analysis. The cracks between crystals will reduce the shunt resistance of devices, leading to leakage, and will decrease the fill factor and photocurrent density which are detrimental for devices performance [1].

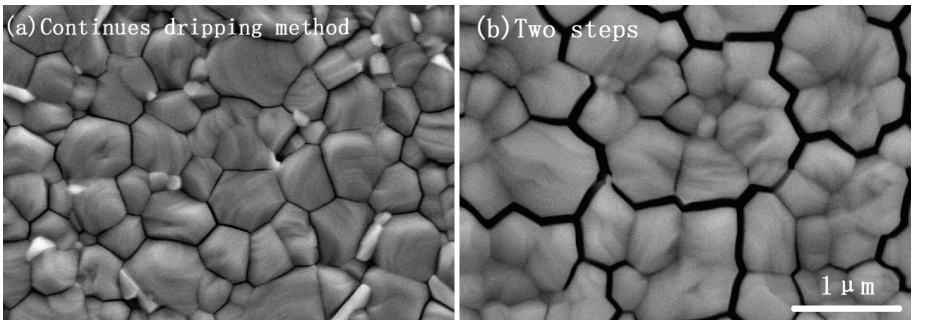

Figure 2. SEM top-view of a perovskite film deposited on mesoporous TiO_2 layer via continuous dripping method (a) and conventional solution two steps (b).

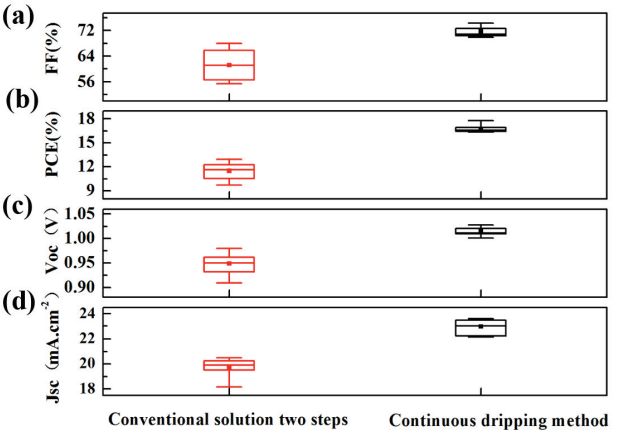

Figure 3. Photovoltaic parameters depending on the manufacturing process. Data calculated from for a batch of 10 devices.

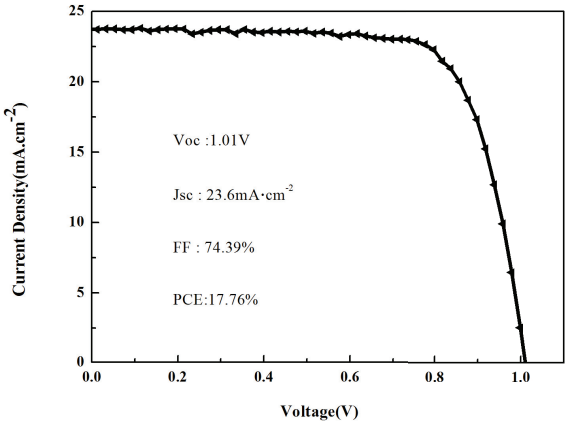

Figure 4. The J–V curve of the best performing perovskite device.

Table 1. The average and best performance of perovskite solar cells fabricated with two different manufacturing processes. Data calculated from for a batch of 10 devices.

Device		PCE (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)
Continuous dripping method	Average	16.74	1.015	22.98	71.78
	Best	17.76	1.010	23.62	74.39
Two steps	Average	11.48	0.95	19.75	61.25
	Best	12.94	0.98	20.06	65.86

4. Conclusions

We have presented a modified process, continuous dripping method and the best PCE with 17.76 % of $MAPbI_3$ perovskite solar cells. We have found that the crystallinity and morphology of $MAPbI_3$ perovskite were very strongly dependent on manufacturing processes. Conventional two-step solution method was also performed compared with continuous dripping method, which conforms that the advantages via using continuous dripping method to obtained the high-performance PSCs. We expect that this study can provides a new approach towards the goal of high quality of perovskite thin films for high-performance and reproducible PSCs with simple solution processes.

5. Copyright

6.Acknowledgements

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References

[1] W. Qiu, T. Merckx, M. Jaysankar, C.M. de la Huerta, L. Rakocevic, W. Zhang, U.W. Paetzold, R. Gehlhaar, L. Froyen, J. Poortmans, D. Cheyns, H.J. Snaith, P. Heremans, Pinhole-free perovskite films for efficient solar modules, Energy Environ. Sci, 9 (2016) 484-489.
[2] M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, H.J. Snaith, Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites, Science 338 (2012) 643-647.
[3] M. Grätze, Perovskite photovoltaics with outstanding performance produced by chemical conversion of bilayer mesostructured lead halide/TiO2 films, Adv. Mater. 28 (2016) 2964–2970.
[4] N. Ahn, D.Y. Son, I.H. Jang, S.M. Kang, M. Choi, N.G. Park, Highly Reproducible Perovskite Solar Cells with Average Efficiency of 18.3% and Best Efficiency of 19.7% Fabricated via lewis base adduct of lead(II) iodide, J. Am. Chem. Soc. 137 (2015) 8696-8699.
[5] H.S. Jung, N.G. Park, Perovskite solar cells: from materials to devices, Small, 11 (2015) 10-25.
[6] C.C. Stoumpos, M.G. Kanatzidis, The renaissance of halide perovskites and their evolution as emerging semiconductors, Acc. Chem. Res. 48 (2015) 2791-2802.
[7] W. Geng, L. Zhang, Y.N. Zhang, W.M. Lau, L.M. Liu, First-principles study of lead Iodide perovskite tetragonal and orthorhombic phases for photovoltaics, J. Phys. Chem. C 118 (2014) 19565-19571.
[8] C.C. Stoumpos, C.D. Malliakas, M.G. Kanatzidis, Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties, Inorg. Chem. 52 (2013) 9019-9038.
[9] National Renewable Energy Laborary, http://www.nrel.gov/ncpv/images/efficiency_chart.jpg.
[10] W. Li, J. Fan, J. Li, Y. Mai, L. Wang, Controllable grain morphology of perovskite absorber film by molecular self-assembly toward efficient solar cell exceeding 17%, J. Am. Chem. Soc. 137 (2015) 10399-10405.
[11] J. Burschka, N. Pellet, S.J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin, M. Gratzel, Sequential deposition as a route to high-performance perovskite-sensitized solar cells, Nature 499 (2013) 316-319.
[12] N. Li, H.P. Dong, H. Dong, J.L. Li, W.Z. Li, G.D. Niu, X.D. Guo, Z.X. Wu, L.D. Wang, Multifunctional perovskite capping layers in hybrid solar cells, J. Mater. Chem. A 2 (2014) 14973-14978.
[13] K.N. Liang, D.B. Mitzi, M.T. Prikas, Synthesis and characterization of organic-inorganic perovskite thin films prepared using a versatile two-step dipping technique, Chem. Mater. 10 (1998) 403-411.
[14] D.Y. Liu, M.K. Gangishetty, T.L. Kelly, Effect of CH3NH3PbI3 thickness on device efficiency in planar heterojunction perovskite solar cells, J. Mater. Chem. A 2 (2014) 19873-19881.
[15] J. Kim, J.S. Yun, X. Wen, A.M. Soufiani, C.F.J. Lau, B. Wilkinson, J. Seidel, M.A. Green, S. Huang, A.W.Y. Ho-Baillie, Nucleation and growth control of HC(NH2)2PbI3 for planar perovskite solar Cell, J. Phys. Chem. C 120 (2016) 11262-11267.
[16] M.R. Leyden, M.V. Lee, S.R. Raga, Y. Qi, Large formamidinium lead trihalide perovskite solar cells using chemical vapor deposition with high reproducibility and tunable chlorine concentrations, J. Mater. Chem. A, 3 (2015) 16097-16103.