Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 105 (2017) 188 – 193

Energy Procedia

The 8th International Conference on Applied Energy – ICAE2016

Hole Blocking Layer-Free Perovskite Solar Cells with over 15% Efficiency

Lingling Zheng[a,b], Yingzhuang Ma[c], Yuanhao Wang[b,d]*, Lixin Xiao[c]†, Fengyan Zhang[a] and Hongxing Yang[b]

[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*
[c] *State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing 100871, China*
[d] *Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, New Territories, Hong Kong*

Abstract

The past five years have witnessed the significant breakthrough of perovskite solar cells (PSCs). High certificated power conversion efficiency (PCE) of 22.1% was achieved in a short time after the inorganic-organic perovskite was firstly used as the light absorber in the solar cells. It is believed that PSCs now become one of the most promising photovoltaic in the new-generation solar cells, which may rival silicon based solar cells. In this article, simplified planar perovskite solar cells without a hole-blocking layer were fabricated by a two-step spin-coating method, and the highest PCE of 15.1% was achieved with an average PCE of 13.6%. Moreover, it is found that the hysteresis effect is reduced in this kind of devices. The research on improved performance for the PSCs with simplified device architecture is very important both for understanding the working mechanism of cells, and for fabricating low-cost and high-performance PSCs to approach commercial applications.

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.

Keywords: Perovskite solar cells; Hole-blocking layer free; Morphology control.

* Corresponding author. Tel.:+852-9340-6258.
E-mail address: yuanhaowang@yahoo.com.

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.
doi:10.1016/j.egypro.2017.03.300

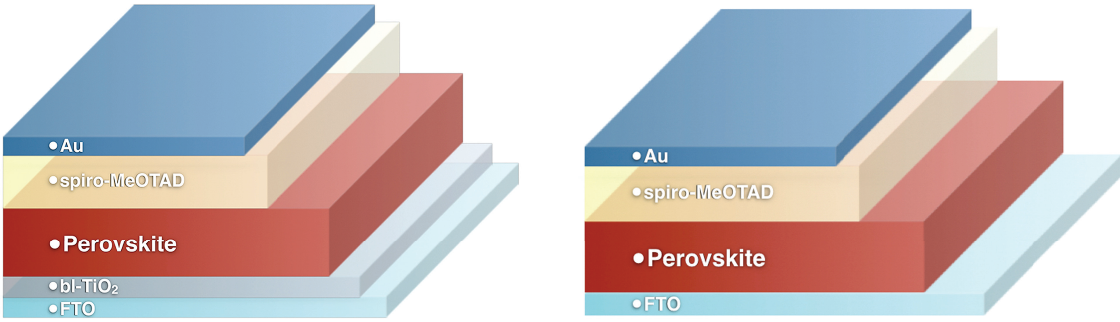

Fig. 1. The schemes of device architecture with (left) or without (right) TiO_2 based hole-blocking layer.

1. Introduction

Perovskite solar cells (PSCs) became one of the most attractive topic in new-generation solar cells over the past 5 years. The power conversion efficiency (PCE) of PSCs has dramatically increased to the certificated 22.1% at warp speed after firstly used as the light absorbers in solar cells [1,2]. It's attributed to the excellent optoelectronic properties of inorganic-organic perovskite, such as the intensive light absorption in the whole visible spectrum, very long carrier diffusion length and suitable band structure [3-5]. Generally, two different kinds of architectures are adopted for PSCs, the mesoporous device and the planar device. The electron transport layer (hole-blocking layer) and hole transport layer are usually employed in the device to achieve efficient charge transport, fast charge extraction and less recombination, between which the perovskite was sandwiched [6]. The metal oxide materials are commonly used as the electron transport layer and hole-blocking layer, among which TiO_2 is the most wide-used and always chosen in the most high-efficiency devices [7,8]. However, it requires a very high temperature sintering process (> 450 ^{o}C), which will severely increase the cost of the device and be unfavorable for the flexible application [9]. For manufacturing purposes, the device with a simplified architecture is a good choice.

Liu et al. firstly demonstrated an efficient planar perovskite solar cell without using any hole-blocking layer by sequential deposition method, and the PCE of 13.5% was achieved, indicating that the hole-blocking layer can be unnecessary for an efficient PSC [10]. Recently, more literatures proved this, in which PSCs by different film-forming methods with such simplified architecture exhibit quite excellent performance [9,11-15]. In this article, planar perovskite solar cells were fabricated without a hole-blocking layer by two-step spin-coating method. (**Fig. 1**) By this method, a full-covered perovskite film composed of interconnected crystals was obtained, resulting in the highest PCE of 15.1% and an average PCE of 13.6%, which should be one of the most efficient for $CH_3NH_3PbI_3$ based PSCs with simplified architecture. Moreover, weak hysteresis effect was found in these devices. The research on improved performance for the PSCs with simplified device structure is very important both for understanding the working mechanism of cells, and for fabricating low-cost, high-performance PSCs to approach the commercial applications.

2. Experimental section

Fluorine doped tin oxide (FTO) glass was cleaned via detergent, water, acetone, and ethanol under ultrasonication for 10 min sequentially, and then treated with O_2 plasma for 20 min. For devices with hole-blocking layer, a compact TiO_2 layer on the FTO glass was prepared by spin-coating at 4,000 r.p.m. for 30 s using 0.15 M of titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol, Aldrich) in 1-butanol. After dried at 125 ^{o}C for 5 min, repeated with 0.3 M of titanium diisopropoxide bis(acetylacetonate) solution, and baked at 500 ^{o}C for 15 min finally. PbI_2 films were deposited on TiO_2 or FTO directly (the simplified device) by spin-coating of 1M PbI_2 (99.999%, Alfa Aesar) solution in DMF at 6000 r.p.m. After drying at 70 ^{o}C, 100 μL of a 10mg/mL solution of CH_3NH_3I in 2-propanol (99%, Fisher) was load on PbI_2 films for 30s, then spin coated at 4000 r.p.m for 30s. The resultant films were annealed at 100 ^{o}C for 45 min. A solution of 2,2',7,7'-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD)/chlorobenzene (72.3 mg/mL) with 28.8 μL 4-*tert*-butylpyridine, and 17.5 μL Li-TFSI/ acetonitrile (520 mg/mL) was spin-coated at 3000 r.p.m. for 60 s as the hole transport materials. Finally, 80 nm Au was thermally evaporated under vacuum to act as the electrode.

Photovoltaic performances were recorded by Keithley 2611 source meter under simulated sunlight from Oriel 300 solar simulator. The absorption spectrum was measured with UV–visible spectrophotometer (Agilent 8453). The morphology was obtained by scanning electron microscope (SEM) (HITACHI 4300). The incident photon to current conversion efficiency (IPCE) was measured by using a lock-in amplifier coupled with a monochromator and 500 W xenon lamp (Crowntech, Qtest Station 2000). Both the systems were calibrated against a certified reference solar cell. All the measurements of the solar cells were performed at room temperature under ambient atmosphere without encapsulation.

3. Results and discussion

The scanning electron microscope (SEM) images were used to observe the morphology of the $CH_3NH_3PbI_3$ crystals. As shown in **Fig. 2**, perovskite crystals on different substrates exhibit uniform grain size of round 300 nm simultaneously. They form a textured and dense film with full coverage in the absence of pinholes. No exposure of the FTO substrate is found, which will shrink the carrier recombination caused by the direct contact of the FTO and the hole transport material spiro-MeOTAD [16,17]. Furthermore, it can be observed that the crystals are interconnecting without clear boundaries rather than stacking individually. The X-ray diffraction results confirm the complete conversion from PbI_2 to $CH_3NH_3PbI_3$, and its tetragonal (I4/mcm) symmetry.

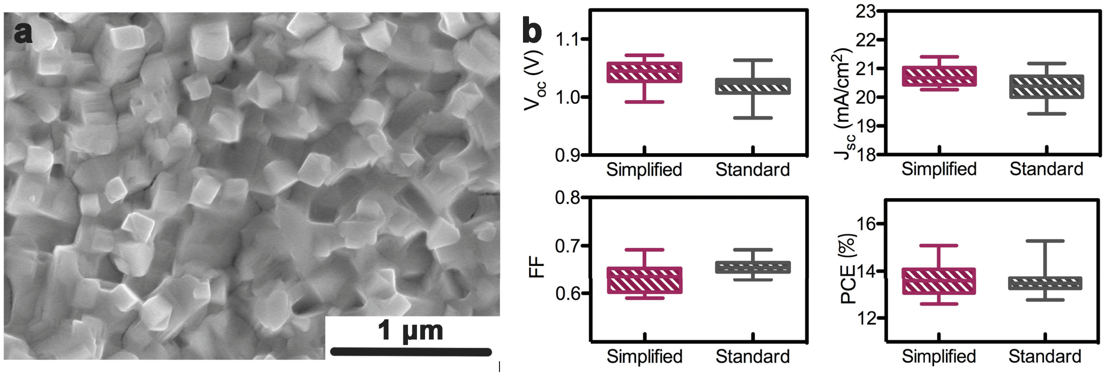

Fig. 2. (a) The top-view SEM image of perovskite crystals on FTO substrate; (b) The photovoltaic parameters of perovskite solar cells with and without a hole-blocking layer. Each parameter comes from the average of a set of at least 15 individual devices.

Table 1. The average and best performance of perovskite solar cells with and without a hole-blocking layer. Each data point represents the average of a set of at least 15 individual devices.

Device		V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
$FTO/TiO_2/PVK/HTL/Au$	Average	1.02	20.4	0.66	13.5
	Best	1.06	21.2	0.68	15.3
FTO/PVK/HTL/Au	Average	1.04	20.7	0.63	13.6
	Best	1.07	20.4	0.69	15.1

Spiro-MeOTAD and Au were deposited on the perovskite film to fabricate the full planar devices sequentially. As a comparison, standard devices containing widely used compact TiO_2 as the hole blocking layer were also fabricated. *J-V* curves was measured at reverse scan under air mass AM 1.5G one sun illumination at 100 mW cm^2. The photovoltaic parameters of these two kinds of devices were shown in **Fig. 2b** and listed in **Table 1**. The average PCE of the devices with standard architecture reached 13.5%, with an average short-circuit current (J_{sc}) of 20.4 mA cm^{-2}, an average open circuit voltage (V_{oc}) of 1.02 V and an average fill factor (*FF*) of 0.66. By adopting the simplified architecture, an average PCE of 13.6% with an average J_{sc} of 20.7 mA cm^{-2}, an average V_{oc} of 1.04 V and an average *FF* of 0.63 is achieved. Above these photovoltaic parameters, the average J_{sc} and V_{oc} of simplified devices are slightly higher than those of standard devices, indicating more photocurrent generation and less carrier recombination [18]. It can be attributed to the high-quality polycrystalline perovskite layer fabricated by two-step spin-coating method. But the standard devices show a higher *FF* than simplified device, demonstrating a smaller serious resistance [18,19]. It might be ascribed to the slightly enhanced interface resistance for simplified devices lacking of an interface layer. Therefore, both kinds of devices exhibit comparable PCE. Moreover, the highest PCE of hole-blocking layer-free PSCs exceeds 15%, with a high V_{oc} of 1.07 V for $CH_3NH_3PbI_3$ based devices. These results verify the feasibility that a planar PSC can work efficiently without a hole-blocking layer if the high-quality perovskite layer can be deposited.

It should be mentioned that unfavorable hysteresis effect is quite weak for the hole-blocking layer-free devices compared to TiO_2 based standard planar devices according to the literatures [20,21]. The deviations of the resultant photovoltaic parameters measured at forward scan and reverse scan are less than 8% for simplified planar PSCs. The integrated J_{sc} calculated from the incident photon to current conversion efficiency (IPCE) are well matched with the J_{sc} from *J-V* curves. The reasons and mechanisms of reduced hysteresis effect should be further investigated by different characterization methods.

4. Conclusions

An efficient planar perovskite solar cell with simplified architecture was fabricated without hole-blocking layer. Very dense films composed of interconnected perovskite crystals were successfully deposited on the FTO by two-step spin-coating method. The corresponding photovoltaic devices reached a highest power conversion efficiency of 15.1%, which is one of the most efficient $CH_3NH_3PbI_3$ based simplified devices to our knowledge. Hole-blocking layer-free planar perovskite solar cells with improved performance is very essential for low-temperature manufactures and plastic applications of perovskite solar cells.

5. Copyright

Acknowledgements

The work described in this paper was supported by a grant from the CII-HK/PolyU Innovation Fund and Hong Kong Scholars Program. And the great help from Department of Electronic and Information Engineering of The Hong Kong Polytechnic University and The Hong Kong Polytechnic University Research Institute for Sustainable Urban Development (RISUD) is appreciated.

References

[1] Kojima A, Teshima K, Shirai Y, et al. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells, *J Am Chem Soc* 2009;**131**: 6050.

[2] National Renewable Energy Laborary, http://www.nrel.gov/ncpv/images/efficiency_chart.jpg.

[3] Stranks SD, Eperon GE, Grancini G, et al. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* 2013;**342**:341.

[4] Baikie T, Fang Y, Kadro JM, et al. Synthesis and crystal chemistry of the hybrid perovskite $(CH_3NH_3)PbI_3$ for solid-state sensitised solar cell applications. *J. Mater. Chem. A* 2015;**1**:5628.

[5] Xing G, Mathews N, Sun S, et al. Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic $CH_3NH_3PbI_3$. *Science* 2013;**342**:344−347.

[6] Yang G, Tao H, Qin P, et al. Recent progress in electron transport layers for efficient perovskite solar cells. *J Mater Chem A* 2016;**4**: 3970.

[7] Li X, Bi D, Yi C, et al. A vacuum flash–assisted solution process for high-efficiency large-area perovskite solar cells. *Science* 2016; 10.1126/science.aaf8060.

[8] Yi C, Li X, Luo J, et al. Perovskite Photovoltaics with Outstanding Performance Produced by Chemical Conversion of Bilayer Mesostructured Lead Halide/TiO_2 Films. *Adv Mater* 2016;**28**:2964-2970.

[9] Xu X, Chen Q, Hong Z, et al. Working Mechanism for Flexible Perovskite Solar Cells with Simplified Architecture. *Nano Letters* 2015;**15**:6514-6520.

[10] Liu D, Yang J, Kelly L. Compact Layer Free Perovskite Solar Cells with 13.5% Efficiency. *J Am Chem Soc* 2014;**136**:17116-17122.

[11] Ke W, Fang G, Wan J, et al. Efficient hole-blocking layer-free planar halide perovskite thin-film solar cells. *Nature Communications* 2015;**6**:6700.

[12] Huang L, Hu Z, Xu J, et al. Efficient planar perovskite solar cells without a high temperature processed titanium dioxide electron transport layer. *Solar Energy Materials & Solar Cell*s 2016;**149**:1-8.

[13] Zhu Q, Bao X, Yu J, et al. Compact Layer Free Perovskite Solar Cells with a High-Mobility Hole- Transporting Layer. *ACS Appl Mater Interfaces* 2016;**8**:2652-2657.

[14] Zheng E, Wang X, Song J, et al. PbI_2-Based Dipping-Controlled Material Conversion for Compact Layer Free Perovskite Solar Cells. *ACS Appl Mater Interfaces* 2015;**7**:18156-18162.

[15] Huang L, Xu J, Sun X, et al. Toward Revealing the Critical Role of Perovskite Coverage in Highly Efficient Electron-Transport Layer-Free Perovskite Solar Cells: An Energy Band and Equivalent Circuit Model Perspective. *ACS Appl Mater Interfaces* 2016;**8**:9811-9820.

[16] Eperon GE, Burlakov VM, Docampo P, et al. Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells. *Adv Funct Mater* 2014;**24**: 151.

[17] Zheng L, Ma Y, Chu S, et al. Improved Light Absorption and Charge Transport for Perovskite Solar Cells with Rough Interfaces by Sequential Deposition. *Nanoscale* 2014;**6**:8171-8176.

[18] Zheng L, Chung YH, Ma Y, et al. A Hydrophobic Hole Transporting Oligothiophene for Planar Perovskite Solar Cells with Improved Stability. *Chem. Commun* 2014;**50**:11196-11199.

[19] Dualeh A, Moehl T, Tétreault N, et al. Impedance Spectroscopic Analysis of Lead Iodide Perovskite-Sensitized Solid-State Solar Cells. *ACS Nano* 2014;**8**:362-373.

[20] Kim HS, Park NG. Parameters Affecting I−V Hysteresis of $CH_3NH_3PbI_3$ Perovskite Solar Cells: Effects of Perovskite Crystal Size and Mesoporous TiO_2 Layer. *J Phys Chem Lett* 2014;**5**:2927-2934.

[21] Unger EL, Hoke ET, Bailie CD, Hysteresis and transient behavior in current– voltage measurements of hybrid-perovskite absorber solar cells. *Energy Environ Sci* 2014;**7**:3690-3698.

Biography

Lingling Zheng is currently a postdoctoral fellow at Renewable Energy Research Group (RERG), Department of Building Services Engineering, The Hong Kong Polytechnic University, Hong Kong. She received her PhD degree at the Department of Physics, Peking University (China) in 2015. Her current research interests are on perovskite solar cells.