Nano Energy (2016) 20, 126–133

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy

RAPID COMMUNICATION

Perovskite as an effective V_{oc} switcher for high efficiency polymer solar cells

Yuliang Zhang[a,b,1], Wei Yu[a,c,1], Wei Qin[a,c], Zhou Yang[a,d], Dong Yang[d], Yedi Xing[a,c], Shengzhong (Frank) Liu[a,d,*], Can Li[a,b,*]

[a]State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[b]Collaborative Innovation Center of Chemistry for Energy Materials, Xiamen University, Xiamen 361005, China
[c]Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[d]Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education; Institute for Advanced Energy Materials, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China

Received 10 June 2015; received in revised form 2 August 2015; accepted 25 August 2015
Available online 2 September 2015

KEYWORDS
V_{oc} switcher;
Phase-dependent photocurrent generation;
Phase-dependent charge transport;
Thermalization loss;
Shockley-Queisser limit

Abstract
In the perovskite/polymer based parallel-like tandem solar cell, the distinctive absorption spectra between the organic-inorganic halide perovskite absorber ($CH_3NH_3PbI_3$ (MAPI)) and poly-(diketopyrrolopyrrole-terthiophene) (PDPP3T) polymer absorber make it possible to investigate the electronic properties of charge carriers generated in either the perovskite or PDPP3T layer separately. The current density-voltage (*J-V*) curves of the device are measured under the monochromatic LED irradiation at significantly different wavelengths to confirm the charge carrier generated in MAPI offer higher V_{oc}. The voltage biased external quantum efficiency (EQE) measurement is employed to understand the charge transport mechanism in the system. The *J-V* curves and EQE data confirm that charge carriers generated by the photons absorbed in the perovskite layer or in PDPP3T behave independently. Compared with the bulk heterojunction structure, this parallel-like tandem structure increases V_{oc} while reducing thermalization loss, providing a possibility to break the traditional Shockley-Queisser (S-Q) limit set for single junction devices.

*Corresponding authors at: State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, Liaoning Province 116023, China.
E-mail addresses: szliu@dicp.ac.cn (S.(Liu), canli@dicp.ac.cn (C. Li).
[1]Contribute equally to this work.

http://dx.doi.org/10.1016/j.nanoen.2015.08.016
2211-2855/

Introduction

Polymer solar cells (PSCs), for its potential high efficiency and low fabrication cost, are widely viewed as the third generation photovoltaic technology. The champion power conversion efficiency (PCE) of the PSCs has been improved to over 10% [1,2]. A great deal of research have been devoted to optimize absorption to harvest full spectrum of sunlight. In this regard, dedicated efforts includes synthesizing narrow bandgap polymers [3-5], optimizing optical electronic cavity [6-9], exploring electron acceptor with high absorption [10,11], exploring processing method [12-14] and solvent treatment [15], and also designing device structures [16-18]. There have been intensive work conducted to improve the open circuit voltage (V_{oc}) of the PSCs, e.g. by using buffer layers. The most common buffer layers studied include p-type materials like poly(3,4-ethylenedioxylenethiophene)-polystyrene sulfonic acid (PEDOT:PSS) [19,20], MoO_3 [21,22], graphite oxide (GO) [23], and n-type materials, such as ZnO [6,7,24,25], TiO_2 [26], etc. These buffer layers play important roles in device performance. For example, they modify energy levels and optical distribution; they can function as hole transport layer (HTL) or electron transport layer (ETL) for improved V_{oc}, J_{sc}, and fill factor (FF). Unfortunately, the low dielectric constants of the common polymers often lead to the Frenkel Exciton [27,28], which are strong coulomb bound electron-hole pairs, resulting in low V_{oc} and unnecessary energy loss. The intrinsic drawback of polymers hinders the further efficiency improvement. In this work, we strike the design of buffer layer in PSCs to boost V_{oc} and therefore PCE to a new regime.

Organolead trihalide perovskite (PVK) materials, such as $CH_3NH_3PbI_3$ (MAPI), $CH_3NH_3PbCl_xI_{3-x}$ are among the most promising photon absorbers in photovoltaic technology due to their excellent optical and electronic properties, such as high extinction coefficient, broad absorption spectra, long balanced electron-hole transport, low defect density, recombination properties, and small exciton binding energy [29-36]. Extensive research has been conducted to develop crystallization control [37-39], additive solvent [40], morphology optimization [41-43], stability study [44-46], hole transport materials (HTM)-free cells [47,48] and interface engineering [49].

It is interesting to see that very recently, MAPI was used as an effective hole transport layer in the PSC [50,51]. However, the fundamental physics and the role of the MAPI in the PSC device is not clear. In this work, we employed the typical MAPI layer in poly(diketopyrrolopyrrole-terthiophene): phenyl-C61-butyric acid methyl ester (PDPP3T:PCBM) bulk heterojunction (BHJ) PSCs, and designed a parallel-like tandem solar cell. The materials in this system are properly chosen with suitable energy levels, distinct and complementary absorption spectra. We find that by incorporating the MAPI in the PSCs, this system reduces thermalization loss and increases V_{oc}, providing a new possibility to boost the PCE of PSCs to a higher regime than the Shockley-Queisser (S-Q) limit of single junction devices. The voltage biased EQE spectra and monochromatic light irradiating *J-V* curves are effective techniques to provide straightforward evidences to understand the charge transport mechanism in solar cells. To our knowledge, this represents the first time observation of phase dependent photocurrent generation and charge transport in this system. The charge carriers generated in MAPI and BHJ photon absorbers transport independently.

Experimental

Materials

CH_3NH_3I was synthesized using a recipe as reported in the reference.[42] PbI_2 was purchased from Sigma-Aldrich. Poly (diketopyrrolopyrrole-terthiophene) (PDPP3T), poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b;4,5-b′]dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl] (PBDTTT-C) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) were bought from Solarmer Materials Inc. Polymers of polythieno [3,4-b] thiophene/benzodithiophene (PTB7), and poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th) were purchased from 1-Material Inc.

Device fabrication

MAPI cell

The FTO/glass substrates were ultrasonicated in deionized water, isopropanol and ethanol for 15 min respectively. After the clean FTO/glass substrates were treated with UV-ozone for 15 min, PEDOT:PSS (Clevios 4083, purchased from H. C. Starck) was spin coated on clean substrate with a thickness of ca. 45 nm. The samples were then annealed on a hot plate at 120 °C for 15 min in air. The $CH_3NH_3PbI_3$ layer was processed by a two-step method.[52] PbI_2 (400 mg mL^{-1} in N,N-dimethylformamide (DMF)) was spin coated on top of PEDOT:PSS/FTO/glass, then dry at 70 °Cfor 30 min. Then MAI (45 mg mL^{-1} in isopropanol) was spin coated at the speed of 6000 rpm for 35 s. Perovskite crystals were formed after anneal at 100 °Cfor two hours. Then PCBM layer was spin coated from PCBM solution (20 mg mL^{-1} in Chlorobenzene), followed by C_{60}/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP)/Al thermal deposition.

BHJ cell

After spin coated $a\sim$40 nm thick PEDOT: PSS layer onto the clean ITO/glass, the samples were dried on a hot plate at 150 °Cfor 15 min in air. Then, the photoactive layers of PDPP3T:PCBM (1:2, weight ratio, in dichlorobenzene, total concentration of 15.0 mg mL^{-1}) with a thickness of 90-110 nm were spin-coated onto the PEDOT:PSS layer. PTB7:PCBM (1:1.5 weight ratio), PTB7-Th:PCBM (1:1.5 weight ratio) and PBDTTT-C:PCBM (1:1.5 weight ratio) were dissolved in mixed solvents of dichlorobenzene: 1,8-diiodoctane (ODCB:DIO, 97:3 v%) respectively with total concentration of 30 mg mL^{-1}. Finally, metallic layers, Ca (10 nm) and Al electrode (100 nm) were deposited onto active layers by thermal evaporation at 2×10^{-4} Pa with a metal mask to form an active area of 0.064 cm^2.

MAPI/BHJ cell

The ca. 40 nm PEDOT:PSS (Clevios Al 4083) were spin coated on cleaned glass/FTO substrates, then the samples were annealed on a hot plate at 120 °Cfor 15 min in ambient. $CH_3NH_3PbI_3$ layer with ca. 200 nm was processed by a two-