



# Solution processed pristine PDPP3T polymer as hole transport layer for efficient perovskite solar cells with slower degradation

Ashish Dubey<sup>a,1</sup>, Nirmal Adhikari<sup>a,1</sup>, Swaminathan Venkatesan<sup>a</sup>, Shaopeng Gu<sup>a</sup>, Devendra Khatiwada<sup>a</sup>, Qi Wang<sup>a</sup>, Lal Mohammad<sup>a</sup>, Mukesh Kumar<sup>b</sup>, Qiquan Qiao<sup>a,\*</sup>

<sup>a</sup> Center for Advanced Photovoltaics, Department of Electrical Engineering and Computer Science, South Dakota State University, Brookings, SD 57007, USA

<sup>b</sup> Functional and Renewable Energy Materials Laboratory, Department of Physics, Indian Institute of Technology Ropar, Punjab 140001, India

## ARTICLE INFO

### Article history:

Received 7 August 2015

Received in revised form

9 October 2015

Accepted 11 October 2015

Available online 6 November 2015

### Keywords:

Pristine polymer

Hole transport layer

Perovskite

PDPP3T

Slower degradation

## ABSTRACT

We report solution processed pristine diketopyrrolopyrrole (DPP) based polymer (PDPP3T) as hole transport layer (HTL) for perovskite ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) solar cells. The pristine PDPP3T based perovskite solar cells achieved comparable photovoltaic performance (12.32%) as that (12.34%) of doped spiro-OMeTAD based cells. After exposing to air having 40% relative humidity at room temperature, PDPP3T based perovskite solar cells showed much slower degradation than spiro-OMeTAD cells. The PDPP3T based devices showed an efficiency decrease by 26.6% after being in air for 73 h and 60.6% for 172 h, while the spiro-OMeTAD cells exhibited a much larger efficiency decrease of 41.4% for 73 h and 82.9% for 172 h. The use of pristine PDPP3T does not require processing HTL in air and adding any additives such as lithium salt dissolved in acetonitrile, 4-tert-butylpyridine (TBP), which are needed for the spiro-OMeTAD HTL preparation. This prevents exposure of the perovskite layer to ambient air and avoids corrosion of perovskite layer by acetonitrile solvent and formation of  $\text{PbI}_2 \cdot x\text{TBP}$  complex which leads to slow down the cell degradation and improves device stability.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Perovskite solar cell is a new entry in the line of next generation solar cells, with rapidly increasing performance getting close to those of silicon solar cells. Perovskite solar cells were first reported by Miyasaka et al. in 2009 with power conversion efficiency (PCE) of 4% [1]. With further progress in device design and fabrication methods, lead halide based perovskite solar cells have yielded a PCE exceeding 15% [2–5]. Perovskite material exhibits broad light absorption and high carrier diffusion length, thus making it a suitable material for fabricating efficient solar cells [6–8]. Different from dye-sensitized solar cells, perovskite solar cells use 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirofluorene (spiro-OMeTAD) as solid state hole transporter [9–12]. The solid state hole transport material (HTM) was doped with lithium salt or cobalt-complex [13], for higher hole mobility [14,15]. In addition to lithium salt, 4-tert-butylpyridine (TBP) was also added in spiro-OMeTAD HTM to reduce charge recombination in the film [16]. Multiple doping elements in spiro-OMeTAD make it costly and complex in preparing a HTM solution. To simplify the

complexity of multiple additives (e.g., lithium salt and TBP), another additive with dual function namely, N-butyl-N'-(4-pyr-idylheptyl) imidazolium bis(trifluoromethane) sulfonimide (BuPyIm-TFSI) was introduced to enhance electrical properties and reduce charge recombination [17]. Polymers [18,19], small molecules [20–23], composites [24], and inorganic hole conductors [25] have been used as hole transport layer (HTL) in perovskite solar cells. Doped polymers such as poly(3-hexylthiophene) (P3HT) and poly[2,5-bis(2-decyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-(E)-1,2-di(2,20-bithiophen-5-yl)ethene (PDPPDBTE) were reported as HTL in perovskite solar cells [26,27].

Conjugated polymers have been widely used to fabricate polymer solar cells [28]. Several polymers such as P3HT [29,30], MEH-PPV [31], PDPP3T [32,33], PBT-T1 [34,35], have shown excellent photovoltaic properties. As an efficient HTL for perovskite solar cells, polymer should have good band alignment, compatibility with perovskite layer, low temperature film formation and no post deposition annealing requirement. So far there have been very few reports of using pristine polymers as hole transport layer for efficient perovskite solar cells.

Herein we report the use of a pristine polymer, poly(diketopyrrolopyrrole-terthiophene) (PDPP3T) as HTL in lead-halide perovskite solar cells. Polymer PDPP3T has a high hole mobility ( $\mu_h \sim 0.04 \text{ cm}^2/\text{V s}$ ) [33], compared to other p-type polymers including P3HT ( $\mu_h \sim 10^{-3} \text{ cm}^2/\text{V s}$ ). It possesses balanced electron

\* Corresponding author

E-mail address: [Qiquan.Qiao@sdstate.edu](mailto:Qiquan.Qiao@sdstate.edu) (Q. Qiao).

<sup>1</sup> Ashish Dubey and Nirmal Adhikari contributed equally.

and hole mobility. Because terthiophene unit is attached to the conjugated DPP unit, it has high planarity that helps induce packing across the chains and enhance charge carrier mobility [33]. PDPP3T is solution processable, does not require post annealing treatment and has perfect energy level alignment with bottom perovskite layer for efficient hole extraction. Previously, a pristine DPP based polymer namely, PCBDPP has been reported with a very low device performance ( $\sim 5.55\%$ ) [36]. Another DPP based polymer namely PDPPDBTE was reported with a PCE of 9.2%, where lithium salt and TBP were added as additives [26].

Another important aspect of solar cells is its stability in ambient air. Device stability has been an important issue which has been studied in several photovoltaic devices such as dye sensitized solar cell (DSSC) [37–39], polymer solar cell [40], and even in perovskite solar cell [26]. Perovskite films are prone to decomposition from moisture in air [41,42], which is a major challenge for the development and commercialization of stable perovskite solar cells. Numerous research on sealing and encapsulation of perovskite solar cell [10,43], has been reported to show long term stability. Stability studies of these perovskite solar cells have concluded degradation mechanism arising from moisture, electrode material [43], and chemical vapors [44]. Improved device stability by use of DPP based polymer was reported where enhanced device stability was observed due to hydrophobic nature of DPP based polymer, which prevents penetration of water into perovskite layer [26]. Other important advantage of using DPP based polymer PDPP3T was its solution processing in inert atmosphere without any need of corrosive dopants, which will further lead to reduction in degradation of perovskite layer.

To the best of our knowledge, till yet there have been no reports on use of pristine DPP based polymer as HTL in perovskite solar cells with efficiency higher than 10%. In this work, we have demonstrated that using pristine polymer PDPP3T as HTL exhibited comparable device performance with improved air stability to devices made using doped spiro-OMeTAD as HTL. Our study suggests that polymer PDPP3T can act as a replacement for widely used doped spiro-OMeTAD HTL and also significantly improve the stability of perovskite solar cells in ambient air by avoiding the processing of HTL in ambient air and addition of any corrosive dopants (acetonitrile, TBP, etc.).

## 2. Experimental procedures

### 2.1. Preparation of methylammonium iodide

Lead halide based perovskite ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) was used for making solar cells via a two-step dip coating procedure.  $\text{CH}_3\text{NH}_3\text{PbI}_3$  was formed by two precursors  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbI}_2$ . Methylammonium iodide ( $\text{CH}_3\text{NH}_3\text{I}$ ) was synthesized via a simple inorganic synthetic route in the lab. Hydroiodic acid (10 ml, 0.227 mol) and methylamine (9.266 ml, 0.273 mol) were prepared by stirring in an ice bath for 2 h. The  $\text{CH}_3\text{NH}_3\text{I}$  precipitate was obtained by drying the solution in a rotary evaporator at 50 °C. Yellowish precipitate of  $\text{CH}_3\text{NH}_3\text{I}$  was then washed with diethyl ether and recrystallized from a mixed solvent of diethyl ether and ethanol.  $\text{CH}_3\text{NH}_3\text{I}$  was then filtered and the solid precipitate was taken and dried at 60 °C for 24 h in vacuum oven. All the above steps were prepared outside glovebox.

### 2.2. Device fabrication

Fluorine doped tin oxide (FTO) coated glass substrates were cleaned by ultrasonication in soap water, distilled water, acetone and isopropanol for 20 min each. The cleaned substrates were dried and plasma treated for 20 min in presence of oxygen. 75 wt%

titanium diisopropoxide bis(acetylacetonate) solution in 2-propanol was diluted into 0.15 M and 0.3 M, respectively, by adding anhydrous ethanol. After spin coating 0.15 M compact  $\text{TiO}_2$  layer solution, the films were annealed at 160 °C for 5 min. Then 0.3 M compact  $\text{TiO}_2$  solution was spin coated, followed by annealing the film at 450 °C for 30 min. Then a 500 nm thick mesoporous  $\text{TiO}_2$  (Dyesol 18NRT, 20 nm particle size paste was diluted with ethanol in 2:7 wt. ratio) was spin coated at 3000 rpm for 60 s, followed by annealing at 450 °C for 30 min.  $\text{TiCl}_4$  treatment was then performed on  $\text{TiO}_2$  films by immersing in a 25 mM  $\text{TiCl}_4$  aqueous solution at 70 °C for 30 min followed by rinsing with DI  $\text{H}_2\text{O}$  and ethanol, which was then annealed at 450 °C for 30 min to improve interfacial contact with nanocrystalline  $\text{TiO}_2$ . Films were then transferred into a nitrogen filled glovebox for perovskite absorber and HTL deposition. Perovskite films were deposited using a two-step process involving spin coating lead iodide ( $\text{PbI}_2$ ) and dipping  $\text{PbI}_2$  film in  $\text{CH}_3\text{NH}_3\text{I}$  solution inside glove box.

$\text{PbI}_2$  layer was spin coated at 4000 rpm, 40 s using 0.1 ml solution of  $\text{PbI}_2$  at a concentration of 462 mg/ml in dimethylformamide (DMF), followed by annealing at 70 °C for 30 min.  $\text{PbI}_2$  films were pre-wetted by quickly dipping the  $\text{PbI}_2$  film in 2-propanol for 1 s followed by dipping in  $\text{CH}_3\text{NH}_3\text{I}$ -2-propanol solution (10 mg/ml) for 50 s, leading to formation of dark brown color perovskite film. The films were then annealed at 100 °C for 15 min on a hot plate inside  $\text{N}_2$  filled glovebox. PDPP3T polymer solution (7 mg/ml) was prepared in chlorobenzene, which was spin coated at 1000 rpm for 60 s inside  $\text{N}_2$  filled glovebox. Spiro-OMeTAD solution was prepared by mixing 72.3 mg of spiro-OMeTAD, 17.5  $\mu\text{L}$  of 520 mg/ml lithium bis-(trifluoromethylsulfonyl)imide salt in acetonitrile, and 28.8  $\mu\text{L}$  of 4-tert-butylpyridine in 1 ml chlorobenzene, which was then spin coated at 2000 rpm for 40 s in ambient atmosphere.  $\text{PbI}_2$  solution concentration and its annealing temperature [10], perovskite film annealing temperature [45], spiro-OMeTAD concentration [10] were used following all related references. Silver (150 nm) electrode was then deposited using high vacuum thermal evaporation. The active area of device was 0.16  $\text{cm}^2$ , which was defined by a mask.

### 2.3. Characterization

Light absorption of films was carried out using Agilent 8453 UV-vis spectrophotometer G1103A. Scanning electron microscopy (SEM) images were obtained using Hitachi S-3400N. X-ray diffraction (XRD) spectra were recorded from the Rigaku Smartlab system. The fabricated solar cells were characterized for their current density-voltage ( $J$ - $V$ ) characteristics, incident photon current efficiency (IPCE) and transient photovoltage/photocurrent measurements. The  $J$ - $V$  curves were measured using Agilent 4155C under illumination of a solar simulator (Xenon lamp, Newport) with a light intensity of  $\sim 100 \text{ mW}/\text{cm}^2$  (AM 1.5). IPCE measurements were carried out using a Xenon lamp (Newport) attached to a monochromator (Newport). Two focusing lenses were used to focus the monochromatic light to the active area of solar cell. National Renewable Energy Laboratory (NREL) calibrated photodiodes were used as reference for IPCE measurements. Transient measurements were performed using OBB's Model OL-4300 nitrogen laser (crisp pulse at 337 nm) to pump the model 1011 dye laser to generate short pulse, which acted as an excitation source with a pulse duration  $< 1 \text{ ns}$  and a repetition rate  $\sim 4 \text{ Hz}$ .

## 3. Results and analysis

Fig. 1 shows (a) polymer PDPP3T chemical structure, (b) device structure and (c) energy level band diagram of perovskite solar cells. The pristine diketopyrrolopyrrole (DPP) based polymer (PDPP3T) (Fig. 1a) was used as hole transport layer (HTL). The solar

Download English Version:

<https://daneshyari.com/en/article/77673>

Download Persian Version:

<https://daneshyari.com/article/77673>

[Daneshyari.com](https://daneshyari.com)