



Short communication

High efficiency $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ perovskite solar cells with poly(3-hexylthiophene) hole transport layer



Francesco Di Giacomo^{a,1}, Stefano Razza^{a,1}, Fabio Matteocci^a, Alessandra D'Epifanio^b, Silvia Licocchia^b, Thomas M. Brown^a, Aldo Di Carlo^{a,*}

^a CHOSE – Center for Hybrid and Organic Solar Energy, Department of Electrical Engineering, University of Rome “Tor Vergata”, via del Politecnico 1, 00133 Rome, Italy

^b Department of Chemical Science and Technologies, University of Rome “Tor Vergata”, Via della Ricerca Scientifica 00133 Rome, Italy

H I G H L I G H T S

- Perovskite solar cells with doped P3HT hole transporter were fabricated.
- For the first time doped P3HT was used with $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ perovskite.
- Best cells showed efficiency up to 9.3%, the record for P3HT solar cells.
- Doped P3HT cells showed a high V_{OC} up to 1.01 V.
- TiO_2 dehydration step has been introduced in device fabrication process.

A R T I C L E I N F O

Article history:

Received 10 September 2013

Received in revised form

8 November 2013

Accepted 15 November 2013

Available online 1 December 2013

Keywords:

Perovskite solar cell

Doped P3HT

Thin film photovoltaics

Organometal Halide Perovskite

A B S T R A C T

We fabricate perovskite based solar cells using $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ with different hole-transporting materials. The most used 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD) has been compared to the poly(3-hexylthiophene-2,5-diyl) (P3HT). By tuning the energy level of P3HT and optimizing the device's fabrication, we reached 9.3% of power conversion efficiency, which is the highest reported efficiency for a solar cell using P3HT. This result shows that P3HT can be a suitable low cost hole transport material for efficient perovskite based solar cells.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, photovoltaic (PV) materials and associated manufacturing processes are under intensive research and development [1] to increase device efficiency, reduce cost and enable new applications for solar energy. In fact, even though silicon solar cells have reached efficiencies of up to 25% for single crystal Si [2] and 20.4% for multi-crystalline Si [3], the production of such material requires energetically demanding processes (such as Si ingot purification) and relatively expensive production lines [4]. On the other hand, thin film technologies have been proved [5] to reduce

material costs and energy payback time. Amorphous silicon, CdTe and Cu(In,Ga)Se₂ technologies have been extensively investigated [5] and have already found commercial application. More recently, new concepts for delivering solution-processed photovoltaics have been introduced to further simplify the manufacturing process to increase fabrication throughput and reliability and to reduce cost. Among solution based photovoltaics, Dye Solar Cells (DSC) represent a new class of electrochemical solar cells [6] based on sensitized mesoporous TiO_2 , a liquid electrolyte and a catalyst layer in a sandwich-like architecture. This kind of device allows achievement of efficiencies of up to 12.3% [7] whilst using simple production processes and equipment. However, the liquid electrolyte may still be problematic [8,9] for the production and stability of devices. In this class of cells, solid state DSCs (SDSCs) have been proposed to replace the liquid electrolyte with a hole transport material (HTM). The most commonly used HTM is (2,2',7,7'-tetrakis-(*N,N*-di-*p*-

* Corresponding author. Tel.: +39 (0)6 72597456.

E-mail address: aldo.dicarlo@uniroma2.it (A. Di Carlo).

¹ Both authors contributed equally to this work.

methoxyphenylamine)9,9'-spirobifluorene) (Spiro-OMeTAD) [10], which presents efficient charge transport, low recombination rates and also good pore filling of the TiO₂ layer enhancing device performance with respect to polymer HTMs. For the sake of lowering costs of the technology, poly(3-hexylthiophene-2,5-diyl) (P3HT) has been employed as a cheaper alternative for small [11] and large area [12] devices. This material shows relatively high hole mobility and can be deposited with several kinds of coating techniques [13,14], such as spin coating, spray coating, slot dye, inkjet printing, and electro-polymerization. Two main issues are commonly linked to P3HT. The size of the polymeric chain reduces the pore filling of the mesoporous TiO₂ layer [15], limiting the maximum thickness of TiO₂ layer and thus of dye absorption. Furthermore, a tight control of coating parameters and on the additives used is needed to achieve the regular morphology required to improve interchain hopping. By controlling these factors P3HT devices with Power Conversion Efficiency (PCE) of up to 4.5% have been fabricated [16].

Recently, a new class of hybrid organic halide perovskite was introduced as light harvesting material, showing strong absorption in a broad region of the visible spectrum (direct energy gap down to ~1.55 eV [17]), good electron and hole conductivity, delivering also high open circuit voltages in photovoltaic devices. A PCE of 10.2% has been reported [18] using a CH₃NH₃PbI_{3-x}Cl_x sensitized TiO₂ together with Spiro-OMeTAD as HTM. By replacing TiO₂ with Al₂O₃ a PCE of 12.3% was obtained [19]. In the latter case, the electrons are transported directly by the perovskite layer, which is anchored to a mesoporous Al₂O₃ scaffold. Remarkably, this kind of perovskite can be processed in air, which makes it a good candidate for industrial use. Another way to improve the performance of TiO₂/perovskite solar cells is to modify the TiO₂ surface using a self-assembled monolayer of C₆₀ fullerenes [18] reaching 11.7% PCE with Spiro-OMeTAD and 6.7% PCE with P3HT, while without C₆₀ the efficiency was 10.2% and 3.8%, respectively. Regarding the HTM material coupled with a CH₃NH₃PbI₃ perovskite, alternatives to Spiro-OMeTAD have been explored [20] reaching 12% efficiency with poly-triarylamine (PTAA) and 6.7% with P3HT. The high efficiency reached with PTAA already showed how polymer HTMs can lead to similar or even superior performance when systematically compared to Spiro-OMeTAD since pore filling by the HTM is not required anymore in this type of cell where the TiO₂ is capped by a layer of perovskite. However, the highest efficiency with perovskite materials was still obtained with Spiro-OMeTAD in the last works which showed efficiency equal or higher than 15% [21,22]. On the other hand, in these works the perovskite synthesis was different to the standard procedures and no comparison with polymeric HTM was performed.

In this paper, we show how P3HT can be a suitable HTM for efficient perovskite based solar cells. We propose an FTO/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/P3HT/Au architecture (scheme reported in Fig. S1) with the intention of optimizing the performance of P3HT based perovskite solar cell. For the first time doped P3HT is used in combination with CH₃NH₃PbI_{3-x}Cl_x, reaching a final device efficiency of 9.3%, which is, to the best of our knowledge, the highest reported efficiency for a solar cell using P3HT as a hole extractor and transporter. In order to assess results, we compare the P3HT cells with similar ones made with Spiro-OMeTAD. The use of P3HT, albeit showing a higher recombination rate respect to Spiro-OMeTAD [23], permits an easy, low cost scaling up of the cell promoting industrial exploitation of this technology.

2. Experimental

In order to create the desired electrode pattern, FTO/glass substrates (Pilkington, 8 Ω □⁻¹, 25 mm × 25 mm) were etched via raster scanning laser (Nd:YVO4 pulsed at 30 kHz average output

power $P = 10$ W), 4 cells were formed on each substrate. Patterned substrates were cleaned by ultrasonic bath, using detergent, acetone and isopropanol. A compact TiO₂ film was deposited onto the FTO surface by Spray Pyrolysis Deposition (SPD) technique using a previously reported procedure [16]. Onto the substrates with the TiO₂ compact a thin film of TiO₂ nanoparticles based paste (18NR-T Dyesol diluted with terpineol, ethylcellulose, isopropanol and ethanol) was screen-printed and successively sintered at 480 °C for 30 min. The final thickness of the n-TiO₂ film was measured via profilometer (Dektak Veeco 150). Profiles were smoothed using Origin 8.5 Software. To dehydrate the samples, these were heated at 120 °C for 60 min in oven. UV irradiation was performed with an estimated power density of 225 mW cm⁻² (Dymax EC 5000 UV lamp with a metal-halide bulb PN38560 Dymax that contains no UV-C).

Methylammonium iodide was synthesized following a previously reported procedure [24], while PbCl₂ (Aldrich, 98%) was used as received. The perovskite was deposited by spin coating (2000 rpm for 60 s) from a dimethylformamide (DMF) solution of methylammonium iodide and PbCl₂ (3:1 M ratio) in ambient condition which formed the perovskite after heating to 120 °C for 60 min and a second profile was measured. There was no control over the humidity during the fabrication and characterization processes. The mean humidity was equal to 60% and ambient temperature was 25 °C.

The hole-transporting material (HTM) was deposited in the first case by spin coating a solution of 2,20,7,70-tetrakis-(*N,N*-dimethoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD) at 2000 rpm for 60 s in ambient condition and left in air overnight in a closed box containing silica desiccant. In the second case, the hole-transporting layer was obtained by a spin coating in nitrogen atmosphere (glove box) a P3HT solution in chlorobenzene (Merck 15 mg mL⁻¹, MW = 94,100 g mol⁻¹), with the following parameters: 600 rpm for 12 s and finally at 2000 rpm for 40 s. LiN(CF₃SO₂)₂N (25 mM, Aldrich) and 4-tert-butylpyridine (TBP, 76 mM) were added to both HTM solutions on the spin coating solution. After HTM deposition a third profile was measured. Samples were introduced into a high vacuum chamber (10⁻⁶ mbar) in order to evaporate Au back contacts (thickness 100 nm) by thermal evaporation. An evaporation mask defined a device area of 0.1 cm² (2 × 5 mm).

Masked devices (3 × 6 mm aperture) were tested under a solar simulator (KHS Solar Contest 1200 Class B) at AM1.5 and 100 mW cm⁻² illumination conditions calibrated with a Skye SKS 1110 sensor, using a Keithley 2420 as a source-metre in ambient condition without sealing. Sun simulator spectrum was measured with a BLACK-Comet UV-VIS Spectrometer (range 190–900 nm). The sun simulator is class B in the visible and near-infrared range (class B between 700 and 800 nm and class A in the rest of the 400–1100 nm range) and has a spatial uniformity less than ±5%. Incident photon-to-current conversion efficiency (IPCE) was measured using an apparatus made of an amperometer (Keithley 2612) and a monochromator (Newport Mod. 74000). UV-vis spectra were measured with a Shimadzu UV-2550 (PC)/MPC 2200 spectrophotometer together with an integrating sphere. X-ray diffraction (XRD) analysis was performed to investigate the phases of the samples, using a Philips X-Pert Pro 500 diffractometer with Cu Kα radiation.

3. Results and discussion

The compact TiO₂ (c-TiO₂) synthesis process and thickness were previously optimized [16] on an SDSC for efficient charge collection and for avoiding recombination of electrons from the FTO back into the active layer. Adding acetylacetone (ACAC) to a conventional

Download English Version:

<https://daneshyari.com/en/article/7738325>

Download Persian Version:

<https://daneshyari.com/article/7738325>

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