



Poly(9-vinylcarbazole) as a hole transport material for efficient and stable inverted planar heterojunction perovskite solar cells



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ABSTRACT

Conjugated polymer poly(9-vinylcarbazole) (PVK) has been explored as an efficient hole transport material (HTM) to replace poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) for the preparation of p-i-n type, inverted planar heterojunction perovskite solar cells. The PVK film can be facilely deposited by room-temperature solution-casting without any doping or post treatments. Using MAPbI₃ as the photoactive layer, a 15.8% stabilized power conversion efficiency was achieved in ITO/PVK/MAPbI₃/PCBM/Ag devices, which is a significant improvement compared with 12.1% from devices using PEDOT:PSS as the HTM. The perovskite photoactive layer cast on PVK HTM has higher crystallinity and less PbI₂ residues, leading to a higher charge recombination resistance of the device. After a storage of 1000 h, the PCE of PVK- and PEDOT:PSS-based devices dropped to 82.5% and 56% respectively, and demonstrated that the PVK-based perovskite devices is more stable compared with the PEDOT:PSS-based devices.

1. Introduction

The world's increasing consumption of energy, together with the decreasing supply of fossil fuels has driven the development of energy from renewable sources, especially solar cells. The past few years evidence a rapid progress of perovskite solar cells, with the state-of-the-art power conversion efficiency (PCE) climbs from 3.8% [1] to over 22% as stated in the efficiency chart issued by the National Renewable Energy Laboratory (NREL) [2]. This achievement benefits from the superior optoelectronic properties of perovskite materials, including tunable band gap, strong light absorption, long carrier diffusion length and facile solution processing properties [3–6].

Great attention has been paid to planar heterojunction perovskite solar cells which can simplify the device fabrication by omitting the mesoporous layer that was usually processed at a high temperature (ca. 500 °C) [7,8]. Here, the direct planar heterojunction perovskite solar cells are referred to the n-i-p structure and the inverted planar heterojunction perovskite solar cells are referred to the p-i-n structure. Besides the componential design and morphological optimization of the perovskite semiconductors to improve device efficiency and stability [9,10], the charge transport materials have also been found to be critical as they can influence device performance significantly [11–15]. For n-i-p perovskite solar cells, the most widely used hole transport material (HTM) is 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-

9,9'-spirobifluorene (spiroOMeTAD) which needs to be doped with Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI) and *tert*-butylpyrriidine (*t*-BP) to increase the conductivity and consequently photovoltaic performance [16], however, the hydroscopicity of Li-TFSI and light induced photolysis of *t*-BP result in bad air stability of perovskite solar cells [17]. For p-i-n perovskite solar cells, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) is the most widely used HTM as it can be solution-processed using green solvent with scaling-up processibility [18]. However, PEDOT:PSS is acidic and hydrophilic that result in water absorption and accumulation at the PEDOT:PSS/perovskite interface and consequently leads to the degradation of perovskite with poor air stability [19].

Some p-type inorganic HTMs with better air stability and high work function, *e.g.* Cu₂O, CuSCN, and NiO_x, have been developed [20,21]. Nonetheless, these inorganic HTMs either need to be prepared to be a few nanometers thick only, *e.g.* Cu₂O and CuSCN, to avoid high series resistance (R_s) which leads to poor photovoltaic performance [22,23], or need to be deposited using the costly method such as pulsed laser [24] or processed under high temperatures, *e.g.* NiO_x need to be baked at a high temperature of 500 °C [25]. P-type polymers, *e.g.* poly[bis(4-phenyl)-(2,4,6-trimethylphenyl)amine] (PTAA) [26,27], poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl) benzidine] (poly-TPD) [28], poly-[[9-(1-octylnonyl)-9*H*-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) [27],

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cross-linked N4,N4'-bis(4-(6-((3-ethyloxetan-3-yl) methoxy)hexyl)phenyl)-N4,N4'-diphenylbiphenyl-4,4'-diamine (c-OTPD) [27] and copolymer of 1,4-bis(4-sulfonatobutoxy)benzene and thiophene moieties (PhNa-1T) [29], have been employed as the HTM for perovskite solar cells attributing to their favorable properties, such as hydrophobicity, solution processability, tunable energy level, moderate hole conductivity and flexibility. Some of these HTMs demonstrate poor charge transport properties compared with PEDOT:PSS, for example, PCDTBT [27], while other HTMs demonstrate better charge transport property and device PCE. For example, Huang's group obtained perovskite solar cells with a prominent PCE of 18.1% by adopting 2,3,5,6-Tetrafluoro-7,7,8,8-Tetracyanoquinodimethane (F4-TCNQ) doped PTAA as the HTM [27], and later achieved better PCE of 19.4% using bare PTAA layer without any doping treatments [30]. Initially dopant like 4,4',4''-Tris[phenyl(m-tolyl)amino] triphenylamine (m-MTDATA) was found necessary to improve the wettability of perovskite on PTAA [26], this process was later omitted and high quality perovskite layers were cast on top of the PTAA layer [31]. Replacing PEDOT:PSS with c-OTPD yields a PCE improvement from 12.3% to 17.8% but c-OTPD needs to be crosslinked with the addition of a photoinitiator and then cured by an ultraviolet treatment [27]. Perovskite devices adopting PhNa-1T as the HTM enhanced the PCE to 16.3% from 11.4% of the PEDOT:PSS counterpart, yet PhNa-1T is highly soluble in water and potential stability issues during the long-term operation of perovskite devices is still possible [29].

Herein, we introduce a conjugated polymer poly(9-vinylcarbazole) (PVK) to replace PEDOT:PSS for the preparation of inverted planar heterojunction (p-i-n type) perovskite solar cells ITO/HTM/MAPbI₃/PCBM/Ag. The PVK film is hydrophobic, thermally stable with a relatively high glass transition temperature (T_g) of ca. 200 °C [32], and can be easily deposited through low-temperature solution casting without any doping and post treatments. The perovskite film (MAPbI₃) deposited by sequential spin-coating is smooth, uniform, compact and of high quality. After optimization, our champion device reached a high PCE of 15.8% with no obvious hysteresis using PVK as the HTM, much higher than that of 12.1% using PEDOT:PSS as the HTM. The light-soaking problems in these PVK-based perovskite solar cells can be eliminated within a short light exposure of 2 mins. After a storage of 1000 h, the PCE of PVK- and PEDOT:PSS- based devices dropped to 82.5% and 56% respectively and demonstrated that the PVK-based perovskite devices is more stable compared with the PEDOT:PSS-based devices.

2. Experimental

2.1. Materials

The Methylammonium iodide (CH₃NH₃I or MAI) was synthesized by mixing 30 ml methylamine (33 wt% in methanol, Aladdin) and 27.5 ml hydroiodic acid (45 wt% in water, Macklin) at 0 °C for 2 h. More details can be found in our previous work [33]. Lead(II) iodide (PbI₂, 99.9%) was purchased from You Xuan Ltd. Phenyl-C60-butyric acid methyl ester (PC₆₁BM) was purchased from Luminescence Technology. PEDOT:PSS (Clevios Al4083, Heraeus, Germany) were purchased from Nichem. PVK was purchased from Sigma-Aldrich with an average molecular weight ca. 1100 kDa.

2.2. Device fabrication and characterizations

The perovskite devices was fabricated on ITO glass substrate (20×15 mm²). The ITO glass substrate was sequentially cleaned with ethanol, acetone, ethanol and isopropanol under ultrasonication, then dried with N₂ flow and followed with UV/Ozone cleaning for 10 mins. PVK films with the thickness of 3, 4, 5, 6.5, 10 and 15 nm were cast by spin coating its chlorobenzene (CB) solution for 30 s from 1.5 mg/ml solution at 7000 rpm, 2 mg/ml solution at 6000 rpm, 2.5 mg/ml

solution at 7000 rpm, 2.5 mg/ml solution at 4500 rpm, 5 mg/ml solution at 7000 rpm and 5 mg/ml solution at 3500 rpm, respectively. The PEDOT:PSS solution was filtered through a 0.45 μm PVDF filter prior to spin coating onto the ITO substrate at 5000 rpm for 30 s and then immediately baked at 140 °C for 15 mins in air to form a ca. 35 nm thickness film. After that the substrates were transferred into the glovebox for further processing. The perovskite precursor solution was deposited as described below. 50 μl of the mixed precursor containing PbI₂ (605 mg/ml) and MAI (50 mg/ml) in dimethyl sulfoxide (DMSO) and N,N-Dimethylformamide (DMF) (1:9) was first dropped onto the PEDOT:PSS or PVK film substrate spinning at 6000 rpm for 15 s, then 75 μl of MAI in its IPA solution (35 mg/ml) was cast on top at 4000 rpm for 45 s. The substrate was then annealed at 100 °C for 30 min to form a MAPbI₃ film of ca. 250 nm thick. Then the perovskite film was cooled down to room temperature, and a ca. 35 nm thick PC₆₁BM layer was spun onto it at 2000 rpm for 30 s using 40 μl of CB (15 mg/ml) solution. Finally, a 100 nm Ag layer was deposited by thermal evaporation under a base pressure of at least 2×10⁻⁶ Torr through a shadow mask to form the cathode. The active layer of the device defined by the size of the cathode layer is 4 mm².

All the measurement was carried out in ambient conditions. Device characterization was performed under AM 1.5 G by using a Newport 3 A solar simulator. The light intensity was calibrated by a standard Si reference cell certified by NREL. *J-V* characteristics were collected by *J-V* sweep software developed by Ossila Ltd. (Sheffield, UK) and a Keithley 2612B source meter unit. An aperture mask with well-defined light-exposing area of 2.12 mm² was put on top of the device for each cells' measurement to eliminate the influence of stray and wave guided light. All *J-V* measurements were carried out at a scanning step of 50 mV. The forward scan range is from -0.1 to 1.1 V, whilst the reverse scan is from 1.1 to -0.1 V under one Sun. The external quantum efficiency (EQE) measurements were performed using a Zolix IPCE measurement system (Zolix SCS10-X150-DSSC) at a scanning step of 5 nm.

Photoluminescence (PL) spectroscopy and mapping were obtained using a PL microscopic spectrometer (Flex One, Zolix, China). The excitation source of PL utilizes a 532 nm CW laser and the mapping was performed on an area of 2.5×2.5 mm² with a step size of 0.01 mm. The absorption spectra of the PEDOT:PSS and PVK film were obtained by spectroscopic ellipsometry measurements (J.A. Woollam, USA). The XRD patterns were obtained by an X-ray diffractometer (RU-200B/D/MAX-RB RU-200B, Japan). The optical images of perovskite were taken by an Olympus BX51 microscope. The surface morphologies of the PEDOT:PSS, PVK and perovskite films were characterized by scanning probe microscope (SPM) (NT-MDT, Russian) and scanning electron microscope (SEM) (Hitachi S4800, Japan). The digital photographs of devices were taken by Digital Single Lens Reflex (Nikon D7000). The film thicknesses were double checked by Dektak XT surface profiler (Bruker, USA) and ellipsometry. The work function measurements were performed on Kelvin probe system (KP020, KP Technology, UK). The contact angle of PEDOT:PSS and PVK films were measured using a microscopic contact angle meter (JC2000C, Powereach). The impedance measurements were carried out on the CHI660E electrochemical workstation (CH instruments, Inc.) under dark with a bias of 0.9 V, a AC voltage signal amplitude of 5 mA, and a frequency range from 1 MHz to 1 Hz. Equivalent circuit simulations were conducted using the software ZView 3.1 (Scribner Associate, Inc).

3. Results and discussion

We fabricated two groups of perovskite solar cells with the structure of ITO/PEDOT:PSS or PVK/MAPbI₃/PCBM/Ag (shown in Fig. 1). During the preparation of PEDOT:PSS films, the glass/ITO substrates need UV/Ozone treatment in order to form smooth and uniform films with full surface coverage, and the as-cast films need to be baked at a temperature over 100 °C for several minutes to remove residual water.

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