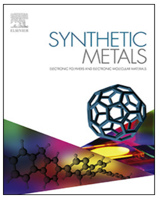
Synthetic Metals 243 (2018) 17–24

Contents lists available at ScienceDirect

Synthetic Metals

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



Understanding the mechanism of PEDOT: PSS modification via solvent on the morphology of perovskite films for efficient solar cells

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ARTICLE INFO

Keywords:
PEDOT: PSS
Modification
DMSO
Smooth surface
Coordination ability

ABSTRACT

The properties of hole transport layers (HTL) greatly affect the performance of inverted planar heterojunction perovskite solar cells (PSC). To understand the mechanisms involved, solvent treatments to HTL poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) by DMSO, ethanol, ethanol:10 vol% DMSO, DMF and acetonitrile were performed when fabricating the PSC devices. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) results show that the crystal size of $CH_3NH_3PbI_3$ ($MAPbI_3$) increased after solvent treatment to PEDOT: PSS. $MAPbI_3$ film with a uniform crystal size and smooth surface was obtained when being deposited on top of PEDOT: PSS that has been modified with solvent with a strong coordination ability. In the other cases, crystal size homogeneity and surface roughness of the $MAPbI_3$ film was worse. The improved surface roughness and crystal size homogeneity of the $MAPbI_3$ film enhanced the short circuit current (J_{SC}), and therefore the power conversion efficiency (PCE) of PSC. It was found that both the stability of the intermediate phase MAI-DMSO-PbI_2, which is related to the coordination ability of the solvent molecules, and the morphology of PEDOT: PSS film, influenced the morphology of the $CH_3NH_3PbI_3$ ($MAPbI_3$) film. Our findings provide the basis for better controlling the morphology of $MAPbI_3$ films in inverted planar heterojunction PSC.

1. Introduction

Perovskite solar cells (PSCs) are a promising photovoltaic technology because of their high power conversion efficiency (PCE) and solution processing technique, which is compatible to future flexible techniques, such as roll-to-roll [1–3]. The PCE has now exceeded 20% [4] narrowing the gap to the PCE of commercialized Si based solar cells [5]. Even though PSCs still suffer from instability and lack of reliable manufacturing techniques [6], they have good prospects for application.

Planar heterojunction PSCs evolved from dye-sensitized solar cells, and have become a new direction for PSCs [7]. Compared with the n-i-p structure device, which commonly use TiO_2 and spiro-OMeTAD as electron and hole transport layers (ETL and HTL), the device with p-i-n structure (also called inverted planar structure) has a lower fabricating temperature and a much weaker voltage-current density hysteresis [8,9]. Due to the sandwich device structure with perovskite film layered between the ETL and HTL, the device performance is influenced greatly by the properties of the ETL and HTL [10,11]. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) is the most commonly used HTL because of its simple solution processing technique, relatively high electrical conductivity, and smooth surface morphology. However, the properties of PEDOT: PSS are far from perfect [12–14]. According to the previous reports, the performance of PSCs could be significantly improved by optimizing the properties of PEDOT: PSS [15–23]. For example, the electrical conductivity of PEDOT: PSS increased after surface modification by methylammonium iodide (MAI) solution, resulting in an increase in short circuit current (J_{SC}) of the PSC [18]. The incorporation of PSSNa with PEDOT: PSS increased its work function, leading to an increase in open circuit voltage (V_{OC}) of the PSC [19–21]. By modifying the pH value of PEDOT: PSS with a mild base, the surface texture and electronic properties of PEDOT: PSS were tuned, which promoted quality and crystallization of the perovskite film deposited on top of it [22]. Huang et al. found that after doping dimethyl sulfoxide (DMSO) into PEDOT: PSS, the aggregation of PEDOT-rich on the surface could induce the crystalline of perovskite on top of it, leading to an increase of perovskite crystal size [23]. Hence, PEDOT: PSS plays an important role in achieving high

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https://doi.org/10.1016/j.synthmet.2018.05.012
Received 18 December 2017; Received in revised form 25 May 2018; Accepted 27 May 2018

performance PSCs.

As is well-known, PEDOT: PSS has also been widely used in organic photovoltaic and organic light-emitting diodes (OLEDs) [24,25]. Various approaches have been tried to improve the properties of PEDOT: PSS. Solvent treatment on the surface of PEDOT: PSS was a simple and effective method. After being treated by methanol, ethanol, H_2O, DMF, DMSO or ethylene glycol, the electrical conductivity of PEDOT: PSS can be increased [20,21,26,27]. However, the PCE of PSC decreased after treating PEDOT: PSS by H_2O or H_2O: ethanol [21]. Recently, we also noted that the performance of PSC based on solvent treated PEDOT: PSS by ethanol, DMF, DMSO and acetonitrile were very different from each other despite the similar properties of the treated PEDOT: PSS layers. That is to say, apart from the electrical conductivity of PEDOT: PSS, there must exist other factors that influence the performance of PSCs after solvent treatment. However, the precise mechanism was not well understood because the previous reports were mainly focused on the properties of PEDOT: PSS, without considering the interaction between solvent molecules and perovskite precursor solution. Hence, it is necessary to understand the influence of solvent treatment to PEDOT: PSS on the performance of PSCs in detail.

In this work, we designed a series of experiments to investigate the effect of solvent treatment to PEDOT: PSS on the morphology of $CH_3NH_3PbI_3$ ($MAPbI_3$) and the performance of PSCs. Polar solvents such as DMSO, ethanol, ethanol/10 vol% DMSO, DMF and acetonitrile were used to perform solvent treatment. After being treated by different solvents, PEDOT: PSS films exhibited similar properties including surface morphology, optical absorption and electrical conductivity. However, the morphology of $MAPbI_3$ films deposited on top of the solvent treated PEDOT: PSS were different, resulting in significant differences in solar cell performance. It was found that $MAPbI_3$ film with a smooth surface and homogeneous crystals can be obtained if deposited on PEDOT: PSS treated by solvent with a strong coordination ability, leading to an improved PCE of the PSC. In other cases, PEDOT: PSS modified by a solvent with a weak coordination ability increased the surface roughness and grain inhomogeneity of $MAPbI_3$ film, which deteriorated the performance of the PSC. Detailed study suggested that both of the stability of the intermediate phase, which depends on the coordination ability of solvent molecules used for PEDOT: PSS treatment, and the morphology of PEDOT: PSS were important in controlling the morphology of $MAPbI_3$ film and the performance of the PSC.

2. Experimental methods

2.1. Materials and solvents

PbI_2 (99.99%), $PC_{61}BM$ (99.5%), MAI, γ-Butyrolactone (GBL), DMSO and toluene (98%) were all purchased from Sigma Aldrich and used as received. PEDOT: PSS (P4083) was purchased from Bayer. The $MAPbI_3$ precursor solution was composed of 1.4 M PbI_2 and CH_3NH_3I (1:1/n:n) in DMSO and GBL (7:3/v:v). Before spin-coating, the $MAPbI_3$ precursor solution was stirred at 66 °C for 24 h in N_2 atmosphere glove box.

2.2. Solar cell fabrication

Perovskite solar cells with device configurations of ITO/PEDOT: PSS (20 nm)/ $MAPbI_3$ (380 nm)/PCBM (65 nm)/ bathocuproine (BCP) (10 nm)/Ag (150 nm) were fabricated. Before using, the ITO substrates underwent a succession of ultrasonic cleaning in deionized water, acetone and ethanol, for 20 min. for each. After being dried by the N_2 flow, 5 min. of ozone plasma was applied to remove any organic residues. Immediately after, 20 nm of PEDOT: PSS film was spin-coated onto the pre-cleaned ITO-coated glass at 3000 rpm for 50 s and baked at 150 °C for 20 min. The thickness was determined by profilometry (Bruker DektakXT). After that, the ITO substrates were quickly transferred into a N_2 protected glovebox with water and oxygen content less than 1 ppm. Following this, the solvent treatment was carried out by spin-coating polar solvents of DMSO, ethanol, ethanol/ 10 vol% DMSO, DMF or acetonitrile at 2000 rpm for 1 min, respectively. Then, $MAPbI_3$ precursor solution was spin-coated. Specifically, the spin-coating process was composed of two stages: 1000 rpm for 15 s and then 4000 rpm for 25 s. For toluene washing during the spin-coating of $MAPbI_3$ precursor solution, at delay time of 16 s from the beginning of the second stage, 600 μL of toluene was dripped. After being thermally annealed at 100 °C for 10 min., PCBM solution in chlorobenzene (40 mg/mL) was spin-coated at 3000 rpm for 20 s and then 6000 rpm for 20 s. After that, the substrates were annealed at 70 °C for 40 min. Finally, 10 nm-thick BCP and 150 nm-thick Ag were sequentially thermally evaporated at a basic pressure of 3×10^{-4} Pa. The active area defined by a shadow mask was 0.096 cm^2.

2.3. Device characterizations

The current density-voltage (J–V) curves were collected by a Keithley 2602 source meter under illumination of 1 sun (100 mW/cm^2 AM 1.5 G) provided by a solar simulator (Oriel/Newport, model 94,043 A, USA), which was calibrated with a Si photodiode. The scan voltage step size was 0.01715 V. The scan directions from 0 to 1.2 V and from 1.2 to 0 V were referred to as forward scan and reverse scan, respectively. The surface morphology of $MAPbI_3$ films was investigated using a Hitachi S4800 microscope (SEM). The microscopic surface morphology measurements were conducted by Bruker icon Dimension with scan Asyst atomic force microscopy (AFM). X-ray diffraction (XRD) experiments were conducted by a Bruker D8 ADVANCE X-ray diffractometer. The absorption spectra were measured by a UV–vis spectrophotometer (UV3600). Incident photon-to-current efficiency (IPCE) data were collected by using a QTest Station1000. The steady-state PL spectra were collected by a steady-state spectrometer (Edinburgh Instruments F900) under excitation by a Xenon lamp (Xe900, 520 nm). The contact angles were examined by a contact angle measurement (KRUSS DSA20). All the above measurements were carried out in atmosphere, and the devices were not encapsulated.

3. Results

PSC with configuration of ITO/PEDOT: PSS (20 nm)/$MAPbI_3$ (380 nm)/PCBM (65 nm)/BCP (10 nm)/Ag (150 nm) was fabricated. Polar solvents of DMSO, ethanol, ethanol/ 10 vol% DMSO, DMF and acetonitrile were spin-coated on the thermal annealed PEDOT: PSS, respectively, to perform solvent treatment.

The photovoltaic characteristics of PSCs with or without solvent treatment to PEDOT: PSS were compared. Fig. 1a showed the J–V plots of PSCs as a function of the solvent used for PEDOT: PSS treatment. The champion control device exhibited a PCE of 11.6%, with a V_{OC} of 0.98 V, a J_{SC} of 16.73 mA/cm^2 and a fill factor (FF) of 70.6%. The PCE value of the control cell is comparable to the reported results from similar device structures [23,28–30]. After PEDOT: PSS was treated by using DMSO, ethanol or ethanol/10 vol% DMSO, the J_{SC} values of the corresponding champion devices increased to 17.9, 17.59 and 19.61 mA/cm^2, respectively. Meanwhile, the FF increased slightly to 73.6, 73.1 and 73.2%, while, the V_{OC} values slightly reduced to 0.896, 0.937 and 0.90 V, respectively. As a result, the PCE increased to 11.77, 12.04 and 12.97%, respectively. That is to say, the highest PCE value was achieved by treating PEDOT: PSS using ethanol/10 vol% DMSO. The performance values (with both forward scan and reverse scan) of the device based on ethanol/10 vol% DMSO treated PEDOT: PSS were also shown in Table 1 and Fig. S1a. The very small deviation between forward scan and reverse scan demonstrated a negligible voltage-current density hysteresis. The significant J_{SC} enhancement was further demonstrated by the IPCE data shown in Fig. 1b. The calculated J_{SC} values of control device and devices based on solvent treated PEDOT: PSS by DMSO, ethanol and ethanol/10 vol% DMSO were 14.79, 17.34,