Enhanced electron transport enables over 12% efficiency by interface engineering of non-fullerene organic solar cells

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ABSTRACT

Organic solar cells have attracted much attention in the recent years due to their many intrinsic advantages, such as, light weight, flexibility, low-cost, solution processing, and facile device fabrication. In this study, effective interface engineering was employed to improve all the photovoltaic parameters of an organic solar cell simultaneously by incorporating ZnO nanoparticle (ZnO-NP) interlayer in between the indium tin oxide cathode and sol-gel processed ZnO electron transport layer. The significance of incorporating a ZnO-NP/ZnO bilayer as the electron transport layer in the bulk heterojunction organic solar cells was demonstrated via systematic study, employing a high efficiency photoactive layer system (PBDB-T:ITIC). The bilayer electron transport layer demonstrated reduced work function compared to the sol-gel ZnO, which enabled effective electron transfer from the active layer to the electron transport layer. In addition, improved bilayer surface morphology, via reduction of ZnO-NP layer roughness, and better crystallinity compared to sol-gel ZnO facilitated charge separation and transmission between electron transport layer and active layer. Consequently, the devices with bilayer interlayer exhibited an enhancement of > 13% in power conversion efficiency compared to the control devices with sol-gel only ZnO as electron transport layer. The mechanisms behind the improvement in device performance were analysed using the ultraviolet and X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy. The champion bilayer device exhibited 12.24% efficiency which is much higher than the efficiency of 10.69% for the control device.

1. Introduction

Organic solar cells (OSCs) have drawn great attention of the researchers over the past two decades as a potential solution to energy crisis and environmental sustainability [1–4]. They possess the inherent merits of transparency [5–7], flexibility [8,9], light-weight [10,11], and compatibility with the roll-to-roll fabrication process which can reduce the manufacturing costs significantly [3,12–16]. Development of new organic donor and acceptor materials (including non-fullerene acceptors) and sophisticated interface engineering has enabled the OSCs to push the power conversion efficiency (PCE) beyond 11% [17–19]. For example, although fullerenes are predominant acceptor materials for OSCs, newly synthesized non-fullerene acceptors are currently gaining considerable momentum in the field of organic photovoltaics research and helping to achieve high efficiency OSCs due to their broad absorption spectrum [20,21], excellent thermal stability [17], easily tuneable energy levels and low-cost production [22–26].

Another mechanism of improving device efficiency of OSCs is using low work function (WF) electron transport layer (ETL) and cathode [27,28] in an inverted device structure, since low WF ensures injection into or collection of electrons from the lowest unoccupied molecular orbital (LUMO) of the acceptor and good ohmic contact between the ETL and the acceptor [29,30]. Low WF metal, such as Ca and Mg, were previously used in OSC as cathode, but previous literature shows that they are detrimental to device lifetime due to their heavily reactive nature and oxidation in the air [31]. Hence, Indium tin oxide (ITO), with high WF [32], is now the most commonly used cathode material for inverted OSC because of its high transparency and low resistance [2,33–36] and n-type metal-oxide-semiconductors, such as, ZnO and TiO$_x$, are inserted as ETL, in between the high WF ITO cathode and organic photoactive layer, which facilitates efficient electron extraction and transport [14,36–40]. In particular, sol-gel processed ZnO has become a well-received choice for ETL due to its low temperature processing [41], excellent electron mobility (10^{-3}–10^{-2} cm^2/V s) [42,43],

good optical transparency (bandgap ~ 3.5 eV) [42], easy fabrication technique and convenient energy alignment with fullerene acceptors [44]. Although high performance OSCs have used ZnO ETL [17,45], the efficiency of the cells can be improved further by modifying the WF of ZnO. On top of that, pristine, single layer, sol-gel ZnO has some inherent drawbacks, such as low crystallinity [46,47] and annealing induced pinholes [48,49]. It is well-known that the degree of crystallinity of ZnO has direct impact on the trap state distribution and conductivity of the transport layer [46,50]. Low temperature, sol-gel processed (for example, 160 °C) ZnO demonstrates lower degree of crystallinity, which reportedly increases the depth of trap distribution inside the ETL and negatively impacts overall device performance [46]. On the other hand, long-term, high annealing temperature processing can increase the porosity of the ZnO film and subsequently, create voids between the ZnO and active layer, which would decrease the electron collection efficiency [48,49]. Therefore, it is highly indispensable to develop a technique to modify the WF of ZnO in such a way that the active layer absorption is not compromised and the porosity of single layer ZnO can be avoided. As an alternative of single layer sol-gel ZnO ETL, double layer ZnO ETL has been reported to be more effective in perovskite solar cells due to relatively better suppression of deep trap states prevalent in very shallow ZnO thin film [48] and faster electron transport [51]. On the other hand, low-temperature sol–gel chemistries have been combined with nanoparticle based synthesis process to reduce the processing temperature of OSCs since processing temperature is considered as a key parameter alongside device efficiency for controlling interlayer deposition and device fabrication [52].

With this in mind, in this work, we have employed a ZnO nanoparticle (ZnO-NP) layer in between the ITO cathode and the sol-gel ZnO layer to compare the device performance with single layer sol-gel ZnO ETL. ZnO-NP can ensure good coverage between the thin sol-gel ETL and the active layer. Work function tunability was achieved in the modified bilayer ETL (ZnO-NP/sol-gel ZnO) that can facilitate electron transport. Devices with double layer ZnO ETL were also fabricated alongside to investigate any improvements in device performance similar to that observed in perovskite solar cells. The bilayer and double layer ZnO ETL were used between ITO cathode and a polymer:non-fullerene donor:acceptor system. The active layer includes a novel non-fullerene acceptor material, 3,9-bis(2-methylene-(3-(1,1-dicyano-methylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno [2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene (ITIC), along with a novel donor polymer, poly[[2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b′]dithiophene))-*alt*-(5,5-(1′,3′-di-2-thienyl-5′,7′-bis(2-ethylhexyl) benzo [1′, 2′-c:4′,5′-c′]dithiophene-4,8-dione))] (PBDB-T); the system has recently crossed the barrier of 11% efficiency in single junction OSCs.[17,18] By employing the bilayer ETL in this device structure, we have achieved > 12% efficiency. The average PCE of the bilayer ETL devices is 11.9%, which is 13.3% higher than that of a structurally identical control device with pristine, single layer ZnO ETL (average PCE = 10.5%). The bilayer devices have also been compared with devices with double layer, sol-gel ZnO ETL as well to observe the difference in the device performance. We have performed ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) to comprehend the electronic modification in the ITO/sol-gel ZnO cathode arising from the incorporation of a ZnO-NP layer between ITO and ZnO. In addition, we have applied electrochemical impedance spectroscopy (EIS) analysis to investigate the enhanced performance shown by ZnO-NP/sol-gel ZnO devices by extracting the active layer/ETL interface contact resistance and chemical capacitance, using the fitted data from Nyquist plots. Mott-Schottky analysis has been used to probe into the modification of built-in potential (V_{bi}) of the bilayer devices and how it has impacted the device performance.

2. Experimental section

2.1. Device fabrication

Patterned ITO-coated glass substrates (12 mm × 12 mm) from Lumtec were first washed by ultrasonication in soapy deionized (DI) water, DI water, acetone, and isopropanol. Four different ETLs were fabricated: single and double layer sol-gel ZnO, ZnO NP and ZnO NP/sol-gel ZnO bilayer, which are denoted by ZnO, DZO, ZnO-NP and bilayer ETLs, respectively. The sol-gel and nanoparticle ZnO were prepared using two different processes. For single layer sol-gel ZnO ETL, at first, sol-gel processed ZnO film was deposited on top of ITO/glass substrate in a process reported in our earlier works [40,53–55]. In brief, ZnO sol–gel solution (0.48 M) was prepared by dissolving zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, Sigma-Aldrich, > 99.0%, 0.109 g) and ethanolamine (NH$_2$CH$_2$CH$_2$OH, Sigma-Aldrich, > 99.5%, 32 μL) in 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, Sigma- Aldrich, 99.8%, anhydrous, 1 mL). The solution was spin-cast on top of the pre-cleaned ITO glass substrates at 4000 rpm for 60 s and then annealed at 170 °C for 30 min. For double coated ETL, the sol-gel ZnO spin coating and the annealing processes were repeated once. For the ZnO nanoparticle layer, 40 wt% Zinc oxide dispersion (ZnO NP) was purchased from Sigma Aldrich. A diluted ZnO NP solution (30 mg mL^{-1}, ethanol) was spin-coated at 3000 rpm for 1 min and later annealed at 145 °C for 30 min, following a process previously reported by Qian et al. [56] The bilayer ETL was prepared by depositing two consecutive layers of ZnO-NP and sol-gel ZnO (ZnO-NP/sol-gel ZnO) and annealing those layers at 145 °C for 30 min and 170 °C for 30 min, respectively. PBDB-T and ITIC (1:1 wt ratio) (Solarmer Materials Inc.) were mixed in a 20 mg mL^{-1} chlorobenzene solution with 0.5 vol% DIO in a N$_2$-filled glovebox and stirred overnight at 50 °C. The solution was spin-coated at 2500 rpm for 1 min to obtain approx. 100 nm thick active layer. The coated substrates were loaded in a vacuum chamber at a pressure of 10^{-4} Pa. 10 nm film of MoO$_3$ and 100 nm film of silver were deposited by thermal evaporation. All devices were annealed at 80 °C. At least six devices were made for each configuration.

2.2. Device characterization

The OSCs were stored in a N$_2$ glovebox and measured in air within two days of fabrication in order to reduce the effects of device degradation on the results. The current density–voltage (J–V) measurements were performed using a solar cell I–V testing system from PV Measurements, Inc. (using a Keithley 2400 source meter) under illumination power of 100 mW/cm^2 by an AM 1.5G solar simulator. A reference silicon solar cell was used for calibrating the light intensity of the solar simulator. The device area, for each type of devices with different ETLs, was fixed to be 0.12 cm^2 with the use of a metal shadow mask in order to avoid the over-estimation in short-circuit current density (J_{sc}) values, owing to lateral charge transport. All the devices were measured in room temperature. A UV–Vis–NIR spectrometer (Perkin Elmer – Lambda 950) was used for optical characterization. The film surface morphology was observed by atomic force microscopy (AFM) with a Bruker Dimension ICON SPM. Surface topology image was captured by FEI Nova NanoSEM 230 FE-SEM. X-ray diffraction (XRD) with Cu Kα radiation was done at an angle ranging from 20° to 60° by step-scanning with a step size of 0.02°. External quantum efficiency (EQE) measurements were performed using a QEX10 spectral response system from PV measurements, Inc. X-ray photoelectron spectroscopy (XPS) was carried out in ultrahigh vacuum environment (Thermo Scientific, UK; Model: ESCALAB 250Xi). Al Kα radiation source (hν = 1486.68 eV) and Thermo Scientific™ Avantage Software were used for the XPS analysis. UPS was carried out with ESCALAB