Organic Electronics 26 (2015) 487–494

Contents lists available at ScienceDirect

Organic Electronics

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

Interfacial engineering of ZnO nanoarrays as electron transport layer for polymer solar cells

Haiyan Fu [a], Bing Li [a], Xiangchuan Meng [a], Licheng Tan [a,b,*], Xingxing Shen [c], Yiwang Chen [a,b]

[a] *School of Materials Science and Engineering/Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China*
[b] *Jiangxi Provincial Key Laboratory of New Energy Chemistry, College of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China*
[c] *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

ARTICLE INFO

Article history:
Received 21 March 2015
Received in revised form 13 August 2015
Accepted 17 August 2015

Keywords:
Nanoarrays
Zinc oxide
Core/shells
π–π interactions
Polymer solar cells

ABSTRACT

Highly uniform one-dimensional ZnO nanoarrays (ZnO NAs) fabricated by hydrothermal process were successfully explored as electron transport layer (ETL) for offering a direct and efficient path for electron transport in inverted polymer solar cells (PSCs). The inorganic CdS shell layer by *in situ* growth on the ZnO NAs surface was used to passivate and repair the surface defects of ZnO NAs. To further engineer the ZnO surface and improve the compatibility between ETL of inorganic ZnO/CdS core/shell and polymer blend contact junction, those organic molecules of 3,6,7,10,11-pentakis-(hexyloxy)-2-hydroxytriphenylene (TP-OH), 1-pyrenol (Py-OH) and 4′-(7-hydroxy-heptanoyl)-biphenyl-4-carbonitrile (BP-OH) were respectively spin-coated on the ZnO NAs/CdS surface to fabricate ETL based on ZnO/CdS/TP-OH NAs, ZnO/CdS/Py-OH NAs, ZnO/CdS/BP-OH NAs. The π–π interactions between the organic molecules and fullerene acceptors could lead to the well-organized distribution of active layer materials, which is in favor of the enhancement of electron selectivity and the reduction of recombination probability of electrons and holes. The incorporation of ZnO/CdS/Py-OH NAs as ETL into the inverted PSCs based on P3HT:PC$_{61}$BM resulted in a superior power conversion efficiency (PCE) of 4.2% with enhanced short circuit current (J_{sc}) and fill factor (FF), compared to 3.1% for bare ZnO NAs, due to the intermolecular close-stacking and relative stronger π–π interaction energy between Py-OH and fullerenes. In addition, the sensitized ZnO surface led to intimate interface between ETL and active layer, which would be in favor of increasing the stability of the device.

1. Introduction

Renewable solar energy research has aroused various approaches and attention as solar energy is the largest reproducible source and a key to meet future energy needs. In particular, solar photovoltaic (PV) technology is regarded as the most promising sustainable and clean way of converting solar energy to electricity. At present, the PV market is mainly dominated by inorganic thick polycrystalline silicon devices. But significant obstacles exist for the wide spread usage of this PV technology, such as the high manufacturing cost of polycrystalline silicon. To overcome this difficulty, organic polymer solar cells (PSCs) with an active layer composed of a conjugated polymer as the donor and a fullerene derivative as the acceptor have attracted extensive focuses as its synthetic variability, clean, lightweight, semitransparency, flexibility and low cost for roll to roll fabrication process [1–4], and which make it possible to compete with its inorganic counterparts such as amorphous silicon.

There are two types device structure of PSCs: conventional PSCs and inverted PSCs. For a conventional PSCs, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) used as hole transport layer is coated on the anode of transparent indium tin oxide (ITO), and Al metal electrode with low work function is used as the cathode. However, previous reports have revealed that conventional bulk heterojunction PSCs cause stability issues since the PEDOT:PSS layer is acidic and hygroscopic [5,6], which is corrosive to ITO electrode and obviously affecting the stability of the device, and also, the Al electrode of the device is oxidized easily [7], resulting in degradation of the PSCs. In order to alleviate these problems, inverted PSCs have been employed, in which the positions of the anode is reversed with air-stable high work function metals (Au, Ag) to collect holes, and ITO is used as the cathode to collect electrons. In the inverted architecture, n-type metal oxides such as

---

* Corresponding author at: Jiangxi Provincial Key Laboratory of New Energy Chemistry, College of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China.

E-mail address: tanlicheng@ncu.edu.cn (L. Tan).

http://dx.doi.org/10.1016/j.orgel.2015.08.014
1566-1199/

titanium oxide (TiO_x) [8,9], cesium carbonate (Cs_2CO_3) [10], and zinc oxide (ZnO) [11,12] used as electron transport layer (ETL) are deposited between the ITO electrode and the active layer. Among them, the air-stable ZnO is one of the promising candidates for the hole blocking layer and electron selective layer due to its relatively high electron mobility, conduction band edge and optical transparency, as well as ease of synthesis [13–15].

ZnO nanoarrays (NAs) with one-dimensional nanostructure have been reported to enhance the performance of PSCs because of providing direct electron conduction pathway for electron transport and minimizing the probability of carrier recombination [16–18]. However, the major challenge in using ZnO as ETL is the presence of surface defects with interstitial Zn and adsorbed oxygen [19,20], which would hinder the transport of electron and increase the carrier recombination. All that would decrease the efficiency of exciton separation and charge collection, and further reduce the performance of the devices. Accordingly, there is a need to develop low-defect and uniform ZnO films so as to realize high efficiency for inverted PSCs.

The inorganic semiconductor quantum dots (QDs) as its good stability, good optical property and high electron affinity have been regarded as a superb candidate to sensitize the surface of ZnO NAs. Several research groups have tried to engineer the surface of ZnO NAs. Yang and Greene [21] have used titanium dioxide (TiO_2) film as shell layer to modify ZnO NAs, resulting in ZnO/TiO_2 core/shell nanorod arrays (ZnO-TiO_2 NAs). Recently, QDs including cadmium sulfide (CdS) [22], lead sulfide (PbS) [23] and lead selenide (PbSe) [24] etc. have been used to sensitize ZnO NAs to boost the performance of devices. Yang reported on using a quasi-quantum well structure (ZnSe/CdSe/ZnSe) as the sensitizer for the first time, which is deposited on ZnO tetrapods, attaining PCE of 6.20% [25]. The engineered ZnO with QDs enable an intimate interface with fewer defects for efficient exciton dissociation and charge transfer, meanwhile, the loading of QDs further increase the interfacial area between ETL and active layer, which could make more electron transporting to the corresponding electrodes and optimize carrier transfer and collection capability.

It is known that the active layer based on polymer blends and electron transport layer with metal-oxides possess very different properties. For example, polymer blends tend to be hydrophobic while metal-oxides are hydrophilic, which lead to poor interfacial contact between organic active layer and inorganic ETL, and thus resulting in poor electron extraction [26]. So, it is crucial to engineer the interfacial characteristics between ETL and active layer. To this end, the organic materials (for example, organic dyes [27], fullerene derivative (PCBE-OH) [28], poly(vinylpyrrolidone) (PVP)) [11] have been reported to passivate the surface defects of ZnO NAs and eliminate the poor interfacial contact, which could be important approaches for enhancing interfacial charge transfer and minimizing contact recombination. Although organic interfacial modification could improve the compatibility between the active layers and the ZnO NAs layer, several primary issues should be considered such as the relative low electrical conductivity (even insulating nature), which could result in a limited transportation of photogenerated electrons to the electrode. Moreover, the molecular weight of the polymer sensitizers is too high, which is not good for infiltrating into the nanoarrays. In addition, to promote the permeation of active layer components into ZnO NAs, and meanwhile, to drive the self-assembly of active layer materials without additional treatments, the small molecules with its structure similar to fullerene are considered to decorate ZnO NAs further. And the mutual π–π interactions [29] between the organic molecules and acceptor molecules could induce the acceptor molecules gathering at the ETL, which could pave the path for electrons direct transport to ETL and electrode, consequently improving the photovoltaic performances of devices.

In view of decreasing the surface defects and promoting the permeation of active layer components into ZnO NAs, herein, we reported a simple method to fabricate ZnO/CdS NAs with core–shell structure as ETL, in which ZnO NAs were synthesized via hydrothermal method according to the previous reported work [30]. Then CdS precursor was spin-coated on the surface of ZnO NAs, followed by thermal decomposition. The CdS between ZnO and the organic small molecules is used to sensitize the ZnO NAs surface and enhance the interface compatibility, and which could also tune the band structure of the ZnO. The organic molecules of 3,6,7,10,11-pentakis-(hexyloxy)-2-hydroxytriphenylene (TP-OH), 1-pyrenol (Py-OH) and 4′-(7-hydroxy-heptanoyl)-biphenyl-4-carbonitrile (BP-OH) were firstly respectively spin-coated on the ZnO/CdS NAs surface to form interfacial layer. Such an ETL with core–shells could passivate the surface defects of ZnO NAs to hinder carrier recombination, offer a direct electron pathway to boost the electron transport and collection, as well as protect device against oxygen and moisture. Furthermore, the organic molecules of TP-OH, BP-OH and Py-OH owning π–π interaction energy with fullerene acceptor could enhance the compatibility between the organic active layer and inorganic buffer layer for more efficient interfacial charge transfer, consequently further optimizing the device performance.

2. Results and discussion

The performance of the solution-processed PSCs could be optimized significantly by inserting the nanoarrays as ETL between the active layer and ITO electrode. Scheme 1 schematically summarizes the synthesis process of ETL in this work, and the detailed experiment and characterization sections are shown in Supporting Information. The ZnO NAs were prepared via low temperature hydrothermal method reported previously [30]. Prior to modifying by organic molecules, a metal xanthate precursor $Cd(S_2COEt)_2(C_5H_4N)_2$ solution was spin-coated onto ZnO NAs for *in situ* growth of CdS shell layer. The organic molecules of TP-OH, Py-OH and BP-OH were respectively spin-coated on the ZnO/CdS NAs surface to form interfacial layer. And then, the active layer of poly(3-hexyl thiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) were spin coated on the ETL layer. Furthermore, the organic molecules of TP-OH, Py-OH and BP-OH possess the intermolecular interactions with fullerene acceptors which were calculated by quantum chemical method. The initial and optimized configurations of these complexes including three organic molecules and C_{60} are shown in Figs. S1 and S2, respectively, in which organic molecular models with shorter side chains are used for TP-OH and BP-OH in the calculations for the optimized configurations of fullerene and the organic modifiers. As shown in Fig. S3, the shortest intermolecular distances for complex TP-OH/C_{60}, Py-OH/C_{60}, and BP-OH/C_{60} are 3.921, 3.975, and 4.008 Å, respectively. In order to compute the interaction energy between the three organic molecules and C_{60}, the single point energies of these optimized complexes were computed considering Basis Set Superposition Error (BSSE), and the calculated results are listed in Table S1. The calculated interaction energy of the optimized complexes including TP-OH/C_{60}, Py-OH/C_{60} and BP-OH/C_{60} are −6.83, −6.55, and −3.97 kcal/mol, respectively. Compared to BP-OH/C_{60}, TP-OH/C_{60} and Py-OH/C_{60} display smaller intermolecular spacing, larger intermolecular interaction, and better π–π stacking. In addition, because TP-OH has larger steric hindrance due to its long side chains, Py-OH/C_{60} forms better π–π stacking than TP-OH/C_{60} in devices. Based on the above theoretical basis, it can be achievable that upon annealing, the π–π interactions between the organic sensitizers and $PC_{61}BM$ acceptors could drive $PC_{61}BM$ to rich-aggregate nearby ETL based on sensitized ZnO NAs, which