



An easily prepared carbon quantum dots and employment for inverted organic photovoltaic devices



Xinyuan Zhang^a, Chunyu Liu^a, Zhiqi Li^a, Jiabin Guo^a, Liang Shen^a, Wenbin Guo^{a,*}, Liu Zhang^{b,*}, Shengping Ruan^a, Yongbing Long^c

^aState Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China

^bCollege of Instrumentation & Electrical Engineering, Jilin University, 938 Ximinzhu Street, Changchun 130061, China

^cState Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Eastern South Lake Road, Changchun 130033, China

HIGHLIGHTS

- Dual electron transporting layer is used in organic solar cells.
- The energy barrier for electron transport is decreased.
- The balanced charge transfer of electron and hole is achieved.
- Well contact of active layer and cathode is realized.
- Electron extraction improvement by a good energy levels tailorment.

ARTICLE INFO

Article history:

Received 2 November 2016

Received in revised form 16 January 2017

Accepted 17 January 2017

Available online 19 January 2017

Keywords:

Electron transport and extraction

Self-assembled monolayer

Power conversion efficiency

Work function

ABSTRACT

In this paper, the performance enhancement of organic solar cells based on PCDTBT:PC₇₁BM and P3HT:PC₆₀BM are demonstrated via employing carbon quantum dots (CQD) to modify the metal oxide electron transport layer. The incorporated CQD with carboxylic acid (–COOH) groups could induce self-assembled monolayer (SAM) with TiO₂ buffer layer, which lowered the energy barrier for electron transfer and reduced the inherent incompatibility between the metal oxide and organic active layers. Further investigation shows that SAM of TiO₂ with CQD can improve the photo-induced exciton dissociation and charge transfer, leading to a low electron accumulation in charge transport layer and a reduced interface recombination loss.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

High efficiency organic bulk-heterojunction (BHJ) photovoltaics (OPVs) have been intensive studied because of low cost fabrication, facile processing methods, and portable energy source compared with Si-based inorganic solar cells [1,2]. Upon using new designed low bandgap polymers, controlling the active layer microstructure, and optimizing the device structure, the power conversion efficiency (PCE) of OPVs has been increased to more than 10% [3–7]. For practical applications, the inverted structure OPV (I-OPV), usually owns a metal oxide (such as TiO_x, ZnO) electron buffer layer (EBL) on ITO glass and high work function metal (Ag) as anode, which can improve air stability and manufacturing compatibility

[8–14]. However, I-OPVs are still suffering from relatively lower PCE to meet the commercialization, possibly because the electrons are trapped on the interface between the active layer and the metallic oxide buffer layer, which are caused by the EBL surface defects as well as electron loss from slow charge injection due to the mismatch of work functions (WF) [15–18].

Several semiconductor materials have been used as the cathode interlayer for I-OPVs to lower the barrier of electron transfer from active layer to the ITO electrode. Among which titanium oxide (TiO₂) is one of the most extensively investigated to enhance the electron collection at the cathode for high efficiency and air-stable solar cells [19,20]. TiO₂ prepared by a simple sol–gel method is provided to be a multifunctional buffer layer including oxygen barrier, an optical spacer, and a hole blocking layer due to its merits of high electron affinity, high transparency, and excellent electrical/optical properties [21,22]. Nevertheless, the sol–gel EBLs still

* Corresponding authors.

E-mail address: guowb@jlu.edu.cn (W. Guo).

suffer from some inadequacies, such as sensitive to moisture and the pin-holes introduced by thermal treatment lessen the blocking process, which are responsible for the loss of electron collection. The oxygen vacancies exist in TiO_2 film, which are energetically deep trap levels, inducing a severe recombination loss [23–26]. Moreover, a key limitation for high efficiency cells is that the electrical properties of the TiO_2 films are strongly related to the processing conditions. Therefore, the electron transport and collection may be less effective in TiO_2 buffer layer, and the highest reported electron mobility is $1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is still lower than that of polymer photo-layer and results in electron accumulation [27–30]. For these reasons, many efforts have been made to facilitate efficient electron transport, enhancing electro-conductibility and suppressing trap-assisted recombination. For example, noble metal nanoparticles and quantum dots (QDs) materials have been used to dope into metal oxide and modify EBL surface with self-assembled monolayer (SAM) [31–36]. The SAM method provides a unique shortcut to regulate the physical and chemical properties of underlying substrate surfaces. On one hand, the SAM can adjust the surface energies and properties of underlying materials, which could promote the interfacial adhesion between the metal oxide EBL and the adjoining polymer photo-layer [37–40]. On the other hand, the SAM can not only affect the electrical property but also tailor band alignment of the underlying film, and thus enhance charge transfer [41].

In this study, we prepared carbon quantum dots (CQD) by a facile way and capped it on the sol–gel TiO_2 as the combined electron transport layer (ETL) for I-OPVs. Compared with conventional semiconductor QDs, CQD with the virtues of similar fluorescence properties, excellent electrical conductivity, low cost, ease of synthesis, and low toxicity in addition to photochemical and chemical stability are employed to effectively modify EBL [42,43]. As the most popular materials, Poly [*N*-9'-hepta-decanyl-2,7-carbazole-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]:[6,6]-phenyl *C*₇₁-butyric acid methyl ester (PCDTBT:PC₇₁BM) and poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-*C*₆₀-butyric acid methyl ester (P3HT:PC₆₀BM) are used as the BHJ active layer in I-OPVs system. Herein, we demonstrated a possible mechanism to explain the relation between EBL components, surface morphology, charge carrier transport properties, and electrical contact with photo-to-electrical energy conversion process. By applying a SAM TiO_2 /CQD as EBL, the short-circuit current (J_{sc}) and fill factor (FF) are both increased and achieved a higher PCE, and thus proposes an attractive strategy for realizing roll-to-roll, high efficiency, and commercially available solar cell production.

2. Experimental

2.1. CQD Preparation and property

The microwave synthesis of CQD follows procedures given in our previous work [44,45]. A sample of the CQD was diluted in aqueous solution, which was purified in a centrifuge (10,000 r/min, 20 min) to remove large or agglomerated particles, and the sizes of left CQD are in the range from 1 to 5 nm. The schematic molecule structure of CQD is exhibited in Fig. 1a, and the substituent group of SAM that has great affinity to the surface –OH of TiO_2 . CQD can be bound on the surface with –COOH group anchored surface with Ti–OH groups to form a carboxylate bond and the other one oriented towards vacuum.

2.2. Device fabrication and characterization

The devices were made with the structure of indium tin oxide (ITO)/titanium dioxide (TiO_2)/active layer/molybdenum oxide

(MoO_3)/silver (Ag), and the energy levels of all used materials are also shown in Fig. 1b. The patterned ITO-coated glass substrates were washed by acetone, anhydrous alcohol, and deionized water in sequence and subsequently dried with nitrogen. Anatase- TiO_2 layer (thickness of 40 nm) was prepared on the cleaned substrates using sol–gel method. For the control devices, the active layers (100 nm) of PCDTBT:PC₇₁BM and P3HT:PC₆₀BM were spin-coated on top of pristine TiO_2 films and annealed for 20 min in glove box and named Device I and Device II, respectively. While for the optimal devices, in order to form a SAM layer, the substrates with TiO_2 films were first immersed into the low concentration aqueous alkaline solution for 6 h. Then, the prepared CQD solutions with different concentrations of 1.2, 2.8, and 4.0 mg/mL were spin-coated on the top of hydroxylation processed TiO_2 with 5 min thermal treatment at 100 °C. The detailed process of SAM is demonstrated in Fig. 3. The active films were forming on different concentrations of CQD modified EBLs under the same condition with control devices. These cells with structure of ITO/ TiO_2 /CQD/active layer/ MoO_3 /Ag are named as Device A, B, and C for PCDTBT system, and Device D, E, and F for P3HT system, respectively. Furthermore, in order to facilitate comparison, the devices with structure of ITO/ TiO_2 /CQD/active layer/ MoO_3 /Ag were made with CQD directly spin-coating on TiO_2 film without SAM process and the corresponding cells are named as Device a, b, c, d, e, and f accordingly. Finally, the OPVs were finished by thermal evaporation of 4 nm MoO_3 and 100 nm Ag as a hole transport layer (HTL) and electrode without encapsulation. All the other experimental parameters were based on previous experience. The active area of the device was about 0.064 cm².

Atomic Force Microscope (AFM) images in tapping mode were carried out using a Veeco multimode with a nanoscope III controller. Current density–voltage (J–V) characteristics of the finished devices were measured using a computer-programmed Keithley 2400 source/meter under AM 1.5G solar illuminations with an Oriel 300 W solar simulator intensity of ~100 mW cm⁻² (about one sun) in air. The light intensity was measured with a photometer (International light, IL1400) corrected by a standard silicon solar cell. The incident photon-to-current efficiency (IPCE) was measured with Crowntech QTest Station 1000 AD. The absorption and transmittance spectra were measured by means of ultraviolet/visible spectrometer (UV 1700, Shimadzu).

3. Results and discussion

As shown in Fig. 2, the SAM processes including three steps in our experiment (I) The hydroxylate of TiO_2 , in which the –OH or O (oxygen atom) will facilitate adsorbed onto the film surface, and Ti (Titanium atom) will has a positive charge (M^+). (II) The neutralization reaction of strong Lewis acidic and alkali. Carboxyl groups with a negative charge caused by ionization will ionic bond with the M^+ firmly and the ionized H^+ will integrate the –OH or O resulted into –OH or H_2O . (III) Electrostatic interaction leads to an immediate and uniform formation of strong dipoles matrix pointing toward the surface of TiO_2 induced by electron-withdrawing terminal functional group of SAM [46–48]. Employing a thin SAM CQD interlayer can induce an interfacial dipole and thereby reduce the work function (WF) of ETL in theory. More importantly, Carboxylic-acid linkages tend to be more stable than –NH₂ (ammonium groups) and –OH bonds under wet conditions. Even under dry condition, the pressure of 10–12 atmosphere are required to reduce a full monolayer to half coverage, which was investigated by Moreira [49].

The interaction between the oxide and organic materials is immensely vital in dominating the surface property and interfacial

Download English Version:

<https://daneshyari.com/en/article/6466424>

Download Persian Version:

<https://daneshyari.com/article/6466424>

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