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Wrinkled substrate and Indium Tin Oxide-free transparent electrode making organic solar cells thinner in active layer

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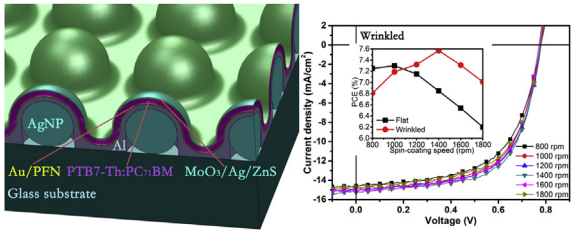
HIGHLIGHTS

- Wrinkled organic solar cells are made using silver nanoparticle arrays.
- ITO-free transparent electrode is introduced.
- Light trapping structure, thinner active layer and larger interface can be obtained.
- Exciton separation, carrier transportation and charge collection can be improved.

GRAPHICAL ABSTRACT



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ABSTRACT

To enable organic solar cells with a competent charge transport efficiency, reducing the thickness of active layer without sacrificing light absorption efficiency turns out to be of high feasibility. Herein, organic solar cells on wrinkled metal surface are designed. The purposely wrinkled Al/Au film with a smooth surface provides a unique scaffold for constructing thin organic photovoltaic devices by avoiding pinholes and defects around sharp edges in conventional nanostructures. The corresponding surface light trapping effect enables the thin active layer (PTB7-Th:$PC_{71}BM$) with a high absorption efficiency. With the innovative MoO_3/Ag/ZnS film as the top transparent electrode, the resulting Indium Tin Oxide-free wrinkled devices show a power conversion efficiency as 7.57% (50 nm active layer), higher than the planner counterparts. Thus, this paper provides a new methodology to improve the performance of organic solar cells by balancing the mutual restraint factors to a high level.

1. Introduction

Organic solar cells are good alternatives for the conventional solar cells due to the potentially low manufacturing cost, light weight, ease of processing and the realization for flexible devices [1–10]. To further improve the power conversion efficiency (PCE), however, we have to balance the mutual restraint factors like charge transport and light absorption in the device [11,12]. The charge mobilities in organic semiconductors are usually much smaller than that in the inorganic counterparts. To acquire a competent charge collection efficiency, the thickness of active layer has to be fabricated as 100–200 nm. Though organic semiconductors have a high absorption coefficient, the thin film is still insufficient for a complete solar energy absorption. For addressing

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such contradictive issue, nano-structuralizing the device architecture appears as a good choice [13–15]. The according light trapping effect increases the absorption efficiency of the active layer without making it thick. The resulting thin film and dramatically enlarged interface area are favorable for collecting the photo-generated charge carriers before recombination.

Though various semiconductor nanostructures, particularly nanowire and nanotube arrays, have been introduced as the buffer layer and antireflection layer, the resulting efficiencies are still not comparable to those of the planar devices [13,15,16]. Jeong et al. reported a solar cell by using silicon nanowire arrays, which showed an enhanced PCE because of the good antireflection effect [17]. Also, Kim et al. designed a V-shape structure to increase the light absorption of the active layer [18], and revealed that the efficiency of the devices was related to the angle of the structure. However, the sharp edges and corners in these structures are harmful to the thin film formation. To realize a complete coverage of organic semiconductors to the nanostructures, the active layer has to be thick. This causes a large amount of charges recombining in the active layer.[14] The charge recombination in the semiconductor nanostructures could not also be ignored, due to the high density of surface states [19,20]. Ascribing to the surface plasma resonance and antireflection effects, metallic nanostructures have particularly added as an important component in the active layer or the electrode, and the PCE was prominently enhanced [21,22]. Yu et al. reported an organic solar cell by using gold and silver nanoparticle [23]. The efficiency was improved obviously by the increased light absorption of the active layer, ascribing to the plasma resonance and scattering effect of metal nanoparticles. In order to improve the efficiency furthermore, it is still necessary to optimize the properties of the active layer systematically and nanostructuralizing the according thin film could be a good choice.

In the conventional devices, transparent glass/Indium Tin Oxide (ITO) substrate is usually employed as bottom electrode for light transmitting and opaque metal electrode is often deposited on the top of the solar cells [3]. In this configuration, designing nanostructures on ITO or metal electrode will unavoidably sacrifice the light absorption of the active layer or induce technical difficulty for device fabrication. In order to facilitate light control and nanostructuralizing the devices, it would be technically favorable to fabricate nanostructure on the substrate firstly and make light incident from the top electrode [24]. Thus, another transparent electrode which can be fabricated under a low temperature condition is highly required. Researchers have proposed a novel method to fabricate transparent electrode by using ultrathin dielectric/metal/dielectric films [25,26]. Although this new electrode material is not comparable to ITO, it still provides an effective method to fabricate transparent electrode on organic solar cells directly.

Herein, we propose an innovative design for organic solar cells. First, glass substrate with mono-dispersed Ag nanoparticles (AgNPs) was prepared by a convenient depositing-annealing procedure. With a subsequent Al/Au layer coated on the surface to form a wrinkled electrode, components of organic solar cells were fabricated. In particular, we develop a top transparent electrode, MoO_3/Ag/ZnS, to make sure that sufficient solar energy could be collected by the active layer. The resulting devices show an obvious improvement in photocurrent and PCE, in comparison with the planar counterpart. To be noted, the wrinkled devices present the highest PCE for the active layer spin-coated at rate of 1400 revolutions per minute (rpm), while the flat ones show the highest PCE with the active layer spin-coating rate of 1000 rpm. This indicates that we could reduce the thickness of the active layer and increase PCE synchronously, by using the wrinkled device configuration.

2. Experimental

2.1. Wrinkled surface fabrication

Plain glass substrates and ITO-coated glass substrates (15 Ω sq^{-1}) with 1.5 cm × 1.5 cm size were cleaned ultrasonically with detergent, deionized water, acetone, and isopropyl alcohol in sequence for 10 min each. Subsequently, they were treated with UV-ozone for 15 min. We deposited silver thin films on the surface of glass sheets by thermal evaporation method. Then the samples were annealed at 500 °C in the air for 30 min. In this process, the silver thin films were changed to AgNPs arrays and the thickness of the film determined the size of AgNPs. To obtain a metal wrinkled surface and cathode, we have continued to evaporate 100 nm Al and 20 nm Au on the top of the AgNPs arrays.

2.2. Device fabrication

$PC_{71}BM$ was purchased from Sigma Aldrich. Poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) and PTB7-Th were purchased from 1-Material, Inc. The additive 1, 8-diiodooctane (DIO) with 99% purity was supplied by Alfa Aesar. All the materials and solvents were used as received. The donor:acceptor blends PTB7-Th:$PC_{71}BM$ with 10:15 ratio were dissolved in chlorobenzene (CB) with 3% 1,8-diiodooctane (DIO) and stirred overnight at 50 °C in a nitrogen-filled glove box. PFN (2 mg/mL) and acetic acid (2 μL/mL) were dissolved in methanol solution and stirred overnight in a nitrogen-filled glove box.

Our wrinkled device structure was designed as Glass/AgNPs/Al/Au/PFN/PTB7-Th:$PC_{71}BM$/MoO_3/Ag/ZnS. Firstly, PFN used as the electron conducting layer was deposited onto the as-prepared wrinkled surface substrate by spin-coating at 3500 rpm for 1 min. Then, the polymer blend, PTB7-Th:$PC_{71}BM$ was deposited onto wrinkled surface by spin-coating at variable speed from 800 rpm to 1800 rpm for 1 min. Afterward, 4 nm MoO_3, 7 nm Ag and 7 nm ZnS film were evaporated onto the surface of organic active layer respectively to form a transparent anode electrode. The solar cells without wrinkled structure were also prepared as reference devices by using flat Al/Au substrates and ITO substrates. The whole process was carried out in a glove box with nitrogen and the active area of all the cells was 4 mm^2 defined by a shadow mask.

2.3. Characterization

The morphology of samples was characterized by scanning electron microscope (SEM, JSM-7401F). The reflection and absorption spectra were obtained at room temperature (RT) using ultraviolet–visible spectrophotometer (UV–vis, Persee TU-1950) equipped with an integrating sphere. The current density-voltage (*J-V*) characteristics were obtained using a Keithley 2450 source measure unit under AM 1.5G illumination with an intensity of 100 mW cm^{-2}. Incident photon-to-electron conversion efficiency (IPCE) measurements were performed at QEPVSI-b Measurement System (Newport). Impedance spectroscopy (IS) measurement was performed with a CHI electrochemical workstation under dark conditions, with an oscillating voltage of 10 mV and frequency scanning range of 10 Hz to 1 M Hz.

3. Results and discussions

3.1. Design principles for wrinkled organic solar cells

In this work, we mainly use AgNPs array to form a wrinkled Al/Au film, where the wrinkled active layer will be deposited. Fig. 1a