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Semi-transparent small molecule organic solar cells with laminated free-standing carbon nanotube top electrodes

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ABSTRACT

We have developed semi-transparent n–i–p organic solar cells (OSC) with free-standing multi-wall carbon nanotube (f-CNT) sheets as transparent top electrodes. By a simple and damage-free room temperature orthogonal liquid solution assisted self-laminating process, f-CNT top electrodes are successfully deposited on top of ZnPc:C_{60} bulk heterojunction small molecule OSCs. The cells show high fill factors above 58% as well as efficiencies up to 1.5% and greater long-term stability compared to the device having a metal electrode. For the given cell structure with f-CNT semi-transparent electrodes, the influence of an optical spacer on light absorption is studied by a systematic variation of the hole transport layer thickness, supported by optical simulations. The results strongly indicate that OSCs with f-CNT top electrodes and optimized thin film stack are highly promising for semi-transparent OSCs, which can be used in tandem devices, in tinted smart windows, and similar applications by a simple and damage-free process in roll-to-roll configuration that can be scaled to large area manufacturing.

1. Introduction

Organic solar cells (OSC) have attracted significant attention as a promising source of renewable energy. In the recent years, much effort has been devoted to the research of OSCs architectures and processing and their efficiency has grown significantly. The efficiencies of both thermally evaporated small molecule and wet-chemically processed polymer based OSCs have been increased to 8.3% [1], with further potential for improvement. In addition to a conventional bulk heterojunction structure, investigated widely due to an efficient exciton dissociation, novel concepts such as a layer-by-layer assembly [2], block-copolymer nanowires [3], quantum dots [4], and hybrid structures [5], are also being investigated extensively. Among numerous OSCs advantages such as potentially low cost, low material consumption, flexibility, and suitability for roll-to-roll mass production, an unusual and promising property is the possible semi-transparency of OSCs devices. Semi-transparent thin film OSCs tuned for a particular visible spectrum absorption band can be used for high efficiency tandem stack solar cells, which can be both of conventional tandem type connected in series [6] and also of a parallel connection type [7], particularly enabled by carbon nanotubes (CNT), transparent sheet common electrode connecting two or more cells in multijunction OSCs. Furthermore, semi-transparent OSCs allow the installation of solar cells on windows or other architectural building elements, facilitating an efficient energy management of a building or a car by providing artistically colored and tinted light, shadow, and at the same time electricity.

The fabrication of novel efficient transparent conductive electrodes for both top and bottom contact is of great importance for semi-transparent OSCs. Especially for sensitive evaporated small molecule OSCs, the deposition process of the top electrode needs to be very gentle without damaging underlying organic layers, which can be easily shorted due to <100 nm typical thickness, giving rise to many practical difficulties. So far, metal oxides [8,9], conducting polymers [10,11], silver nanowires [12,13], and thin metal layers [14,15] have been employed as a top electrode for OSCs and organic light emitting diodes (OLED). However, avoiding damage to underlying organic layers during the deposition of inorganic materials as well as complex, expensive, slow, and small scale deposition processes of top electrodes are technological issues, which are still challenging. The development

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of vacuum evaporation free and large area technology for OSCs top electrodes remains one of major challenges in this field, particularly for large scale roll-to-roll processing on flexible substrates.

CNTs are promising as transparent conductive electrodes for optoelectronic devices because of their excellent electrical and optical performance as well as mechanical flexibility, chemical stability, and low-cost roll-to-roll compatible manufacturing process. The application of CNTs as electrodes for OSCs and OLEDs has been focused on the use of single-wall CNTs (SWCNT) via the solution based processes and as bottom electrodes for opaque devices [16–20]. The roll-to-roll compatible free-standing multi-wall CNT (f-CNT) sheets reported by Zhang et al., which are highly conductive, transparent, and show high mechanical strength, are a very promising top electrode material [21]. One of the great advantages of the dry span f-CNT sheets is the scalable fabrication of meter-long sheets with uniform electrical and optical properties. Those f-CNT sheets offer unique applications and were successfully adopted as a bottom electrode for OSCs and OLEDs, showing reasonable performances [22,23]. Moreover it has been demonstrated that f-CNT sheets, which have inherently high porosity, can provide three-dimensional (3-D) charge collection from the volume of the bulk heterojunction OSCs, with twice increased photo-current [22]. Additionally, Tanaka et al. have first reported parallel tandem architecture of OSCs with f-CNT as an intermediate electrode, showing increased total photo-current although at yet small efficiency of 0.31% [24]. Parallel tandem architectures require the bottom cell to be semi-transparent, and one of subcells to be inverted in such a way that the common intermediate CNT electrode collects charges of same sign, adding to total current, contrary to the conventional series tandem structure in which opposite charge carriers recombine at the interlayer [25,26].

In this study, we report on such inverted semi-transparent small molecule n–i–p OSCs with f-CNT top electrodes, which can be used in both types of tandem stack improving their performance. The top f-CNT electrodes are deposited on OSCs using a room temperature orthogonal liquid solution assisted self laminating process, which is simple and damage-free for organic layers. The OSCs with f-CNT top anode electrodes (f-CNT cell) show very low leakage currents, high fill factors and promising efficiencies, transparencies, and long-term stability. The OSCs parameters are systematically studied, with a variation of p-doped hole transport layer (HTL) thickness adjacent to top f-CNT anodes. The optimal optical field distribution in these OSCs is investigated by optical simulations based on the transfer-matrix formalism. These results show that f-CNT cells can serve as highly promising semi-transparent OSCs. In this report, free-standing dry drawn CNT sheets are applied as a top electrode for OSCs, providing a basis for parallel tandem OSCs or transparent applications.

2. Experimental

Small molecule OSCs are prepared by thermal evaporation in a high vacuum system (K.J. Lesker, U.K.). The base pressure of the chamber is kept around 10^{-8} mbar. The layer sequence for solar cells is inverted, as compared to usual direct OSCs with top Al cathode, since it has a bottom ITO cathode with n-doped electron transport layer (ETL) and a top f-CNT anode as follows (bottom to top): ITO as a bottom cathode/10 nm tetrakis (1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidinato)ditungsten (II) ($W_2(hpp)_4$) doped C_{60} as an ETL/30 nm C_{60} as an additional absorber layer and ETL/30 nm mixed zinc phthalocyanine (ZnPc):fullerene C_{60} (volume ratio of 1:2) as a photoactive absorber layer/X nm 10 wt.% 2,2′-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F_6TCNNQ) doped N,N′-((diphenyl-N,N′-bis)9,9,-dimethyl-fluoren-2-yl)-benzidine (BF-DPB) as a hole transport layer (HTL)/1 nm p-type dopant as a hole injection layer/a top anode. The stack is visualized in Fig. 1(a).

For the reference solar cell (Ag cell), the thickness of the HTL is 50 nm and a thin metal layer (Al 1 nm and Ag 14 nm) is evaporated as a top electrode. Subsequently, 60 nm of tris (8-hydroxy-quinolinato)-aluminum (Alq_3) is deposited on the top as a capping layer increasing the transparency of the Ag cell. The sheet resistance and transparency of this type of reference metal electrode are around 5 $\Omega\,sq^{-1}$ and 64.7% (at 550 nm, with Alq_3), respectively.

For the f-CNT cells, the HTL thicknesses are varied from 20 to 80 nm. The f-CNT sheets (sheet resistance: $\sim$250 $\Omega\,sq^{-1}$ and transparency: $\sim$38% (at 550 nm)) are prepared from a multi-walled CNT forest produced by a chemical vapor deposition (CVD) process at the Alan G. MacDiarmid NanoTech Institute as described previously [21]. The as-prepared f-CNT sheets are directly deposited by manual lamination assembly on top of organic stacks in a nitrogen filled glove box without air exposure. Afterwards, the f-CNT cells are subsequently immersed into orthogonal liquid hydrofluoroether (HFE) for several seconds to densify the f-CNT sheets (from typically 15–20 μm wide aerogel to 50–100 nm f-CNT film) on top of the solar cells. As shown before, such densification significantly improves the f-CNT electrode performance by increased transparency and improved conductivity due to dense tube to tube interconnects without any device degradation [27]. The densified f-CNT sheet used in this study turns into around 80 nm thick porous film. The solar cell active areas are 2.56–6.91 mm^2 measured using an optical microscope.

The current–voltage characteristics are examined with a source measurement unit (SMU 236, Keithley Instruments) under an AM 1.5G sun simulator (Steuernagel SC1200) in a nitrogen filled glove box. The incident light intensity is monitored by a silicon reference diode, calibrated by Fraunhofer ISE (Freiburg, Germany). The values of short circuit current density are normalized to 100 mW cm^{-2} and are not corrected for spectral mismatch. The samples were reproduced several times, showing negligible measurement deviation. External quantum efficiency measurements (details in Supplementary material) are carried out using color filters in the same setup. The transparency of the electrodes and solar cells is measured using a spectrophotometer (Perkin-Elmer Lambda 900), which includes the optical loss of the glass substrate ($\sim$8%). Optical simulations are done with a transfer-matrix formalism based simulation program [28,29]. Optical constants of ITO, f-CNT, and organic layers are obtained by transmission and reflection measurements, calculated from several samples with different thicknesses on glass. The atomic force microscopy (AFM) images of f-CNT are recorded in tapping mode (AIST-NT Combiscope).

3. Results and discussion

ZnPc:C_{60} bulk heterojunction based small molecule OSCs with n–i–p configuration are fabricated with top f-CNT electrodes. A schematic drawing of the fabrication process for f-CNT cells, a photograph of the semi-transparent cell, atomic force microscopy (AFM), and scanning electron microscope (SEM) image of an f-CNT sheet on top of the device after densification are shown in Fig. 1. It is known that f-CNTs have predominant orientation with respect to the direction of drawing. Laminated nanotubes on the device keep their orientation, as visible in microscope images [21]. The averaged transparency of the f-CNT cell (HTL of 50 nm)