



Improvement of the power conversion efficiency of organic photovoltaic cells with a P3HT layer fabricated by using a sonication process and having a vertically modulated nanoscale morphology

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ABSTRACT

In organic photovoltaic (OPV) cells, the nanoscale morphology of the organic layer is an essential parameter governing their charge-transport properties. Optimization of the vertical composition gradient in the poly(3-hexylthiophene) (P3HT) active layer in an OPV cell with an enhanced efficiency was achieved by using different sonication times of 10, 15, 20, 25, and 30 min. Atomic force microscopy images confirmed that the sonication process increased the roughness of the P3HT layer in a vertically modulated nanoscale morphology. Photoluminescence spectra exhibited a strong peak corresponding to the P3HT particles. The power conversion efficiency of the OPV cells with a vertically modulated P3HT nanostructural layer sonicated at 15 min was enhanced by 1.04% due to an increase in the interfacial region between the acceptor and the donor materials.

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1. Introduction

Photovoltaic cells have attracted a great deal of interest because of their promising applications in next-generation global energy production [1]. Organic photovoltaic (OPV) cells have been spotlighted as harnessing clean energies because of their advantages of simple process, low cost, semi-transparency, high-mechanical flexibility, and light weight [2–5]. The potential applications of OPV cells with a bilayer heterojunction structure have driven extensive and successful efforts to enhance their power conversion efficiency (PCE) [6,7]. Nanoscale morphology in the active layer is essential for better transport of charge carriers in the OPV cell and for enhancing its efficiency [8,9].

High PCEs of OPV cells have been successfully achieved by selecting materials with appropriate energy levels [10], by controlling the nanoscale morphology [11], by thermal annealing of thin films [12,13], and by using suitable electrode materials [14]. Such an evolution has made organic solar cells more competitive with Si-based solar cells [15]. The two essential factors that

limit the performance of OPVs are the short exciton diffusion length of about 10 nm and the low hole mobility of approximately 10^{-6} – 10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ within the photoactive layer [16]. The short exciton diffusion lengths (~ 10 nm) in these organic materials and challenges in achieving an optimized phase separation for improved exciton-dissociation limit the thickness of the active layer [17]. Moreover, the fill-factor in these devices also suffers due to the short carrier drift length (L_d) = $\mu t E$, where μ is the carrier mobility, t is the carrier recombination time, and E is the electric field. L_d must be longer than the active layer thickness to prevent significant losses by recombination. Because the diffusion length of excitons in organic semiconductor is low, the existence in the dissociating centers close to the sites, where excitons are generated, is important. Multiple interfaces in the form of bulk heterojunction have been used for enhancing electrical characteristics of photovoltaic devices.

Several methods involving the fabrication of efficient OPV cells with a bilayer structure were developed to overcome the problem of small PCE [18–22]. For improvement of the PCE of OPV cells, a bulk heterojunction (BHJ) structure consisting of vertically graded thin films fabricated by using a spin-coating technique. Interface problems and energy losses caused by the transport of free electrons to the cathode were minimized due to the vertically graded

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morphology [23]. Ultrasonic irradiation has often been utilized to nucleate and grow molecular crystals [24]. Still the fabrication of poly(3-hexylthiophene) (P3HT)/C60 blends with suitable morphology remains a fundamental challenge in the field of conjugated polymer solar cells [25–29].

This article reports unique data for improving the PCE for OPV cells with active, vertically modulated nanostructural P3HT layers subjected to different ultrasonication processes. OPV cells with a planar P3HT layer or with a rough, active nanostructural P3HT layer were deposited using a spin-coating technique, and their device performances were investigated. Photoluminescence (PL) and atomic force microscopy (AFM) measurements were performed to characterize the optical and the surface properties, respectively, of the planar and the rough vertically modulated nanostructural P3HT layers. Current density–voltage (J - V) measurements were carried out in order to study the device characteristics of the OPV cells based on planar and rough nanostructural P3HT layers.

2. Experimental details

The OPV cells used in this study were fabricated on indium-tin-oxide (ITO)-coated glass substrates, and the measured sheet resistance of the ITO thin film was approximately $10 \Omega/\text{sq}$. The ITO substrates were cleaned in acetone and isopropanol by using an ultrasonic cleaner with a sonication amplitude of 135 W and a frequency of 42 kHz for 10 min and were rinsed in de-ionized water thoroughly. After the chemically cleaned ITO-coated glass substrates had been treated with an ultraviolet-ozone cleaner, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-coated onto the ITO-coated glass substrates at 4500 rpm for 41 s in a glove box under a high-purity N_2 atmosphere. Then, 1-wt% P3HT solution was spin-coated onto the PEDOT:PSS layer at a spin rate of 2000 rpm for 60 s and was annealed at 145°C for 15 min. The OPV cell utilizing a nanostructural P3HT film contained a mixed solution of 1 ml of 0.5-wt% P3HT and 0.1 ml of propylene glycol monomethyl ether acetate (PGMEA). The PGMEA functions to improve the solubility dielectric of P3HT solution. The mixed solution was ultrasonicated for 0, 10, 15, 20, 25, or 30 min to obtain the optimum surface morphology of the nanostructural P3HT layer. The mixed solution sonicated for 10 min was spin-coated on the PEDOT:PSS layer at a spin rate of 4500 rpm for 36 s and was annealed at 145°C for 15 min. After the annealing process, a nanostructural P3HT layer was observed to have been formed. Similarly, other mixed solutions were employed with different sonication processes to fabricate OPV cells with different rough nanostructural P3HT layers. After the nanostructural P3HT layer had been annealed, a C60 acceptor layer with a thickness of 40 nm was thermally evaporated in a vacuum chamber at a system pressure of approximately 8.5×10^{-7} Torr. Consequently, an 8-hydroxy-quinolino lithium (Liq) cathode buffer layer was deposited on the active layer by using thermal evaporation. The solar cell was completed by deposition of Al front contacts with a thickness of 100 nm; the active area of the fabricated cell was $2 \text{ mm} \times 2 \text{ mm}$. Finally, the fabricated OPV cell was annealed for 20 min at 145°C on a hot plate and subjected to characterization.

The PL spectra were obtained using an ISS PC1 System consisting of a 75-cm monochromator equipped with an RCA 31034 photomultiplier tube. The excitation source was the 440-nm line of a He-Cd laser with an excitation power density of $10 \text{ kW}/\text{cm}^2$. The sample temperature was kept at 300 K. The AFM measurements were performed by using an XE-100 atomic force microscope. The J - V curves were measured in the dark and under illumination by using a Keithley 2400 source meter. The photovoltaic characteristics

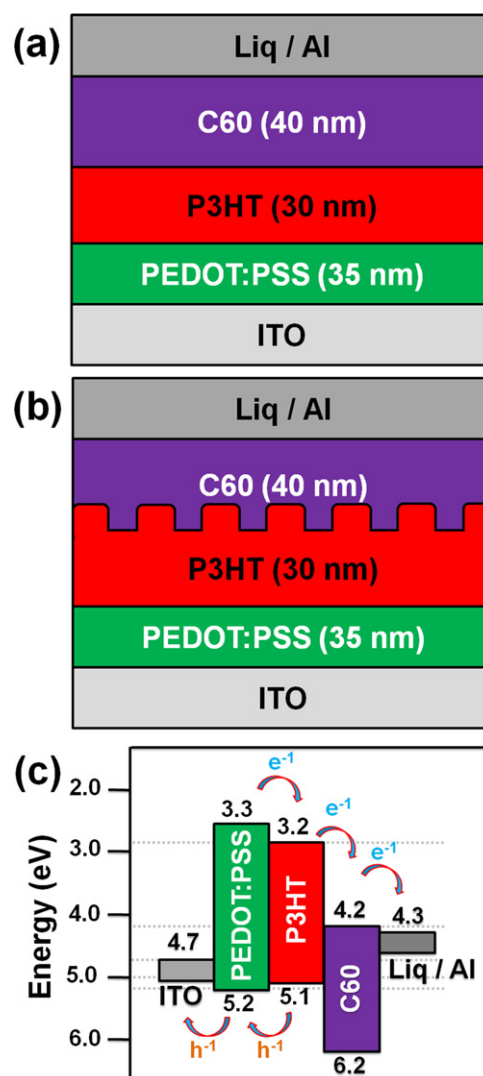


Fig. 1. Schematic diagrams of organic photovoltaic (OPV) cells with (a) a planar film and with (b) a vertically modulated P3HT nanostructural film. (c) Corresponding energy level diagram of the OPV cells.

were measured by using a xenon lamp under AM 1.5 stimulated illumination at an intensity of $100 \text{ mW}/\text{cm}^2$.

3. Results and discussion

3.1. Properties of the P3HT nanostructural layer

Fig. 1(a) and (b) shows schematic diagrams of the fabricated OPV cells consisting of an Al/Liq/C60/P3HT/PEDOT:PSS/ITO structure with either a planar or a nanostructural P3HT layer. Fig. 1(c) presents the energy level diagram of the OPV cell, where the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the materials have been taken from the literature [30]. Because the PEDOT:PSS HOMO/LUMO levels were about 5.2/3.3 eV, the excitons were dissociated at the P3HT:C60 layer. While free electrons can reach the cathode, holes can be transported through the PEDOT:PSS and accumulate at the anode. The nanostructural morphology of the P3HT layer, in turn, controls the exciton diffusion and the charge transport properties, both of which have considerable influence on the device performance, and a requirement that the nanostructural morphology of

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