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Letter

High-efficiency polymer solar cells by blade coating in chlorine-free solvents

Pei-Ting Tsai [a], Chia-Ying Tsai [b], Chun-Ming Wang [a], Yu-Fan Chang [c], Hsin-Fei Meng [a,*], Zhi-Kuan Chen [d,*], Hao-Wu Lin [e,*], Hsiao-Wen Zan [c], Sheng-Fu Horng [f], Yi-Chun Lai [c], Peichen Yu [c]

[a] Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan
[b] Institute of Photonics Technologies, National Tsing Hua University, Hsinchu 300, Taiwan
[c] Department of Photonics and the Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 300, Taiwan
[d] Institute of Advanced Materials, Nanjing University of Technology, Nanjing 210009, China
[e] Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan
[f] Department of Electrical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan

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ABSTRACT

High-performance polymer cells are typically fabricated by employing toxic solvents such as dichlorobenzene and chlorobenzene. In this study, blade coating with the chlorine-free solvents toluene and xylene is applied to polymer solar cells that contained the low band-gap polymer PBDTTT-C-T blended with [6,6]-phenyl-C71-butyric acid methyl ester ([70]PCBM). The highest efficiencies of the cells fabricated in toluene and xylene solutions were 6.09% and 6.11%, respectively. Atomic force microscopy images show that the films formed by blade coating using toluene and xylene were extremely smooth, with roughness of only 1 nm. This blade coating has a rapid-drying in a few seconds without the long-running thermal or solvent annealing. The possibility of high-volume environmentally-friendly fabrication of efficient polymer solar cells with minimal material waste is thus demonstrated using a combination of chlorine-free solvents and blade coating.

1. Introduction

Polymer solar cells based on a blend of conjugated polymers as electron donors and fullerene derivatives that serve as electron acceptors have exhibited a ever-increasing power conversion efficiency over the past decade. Recently efficiency over 8% is reported for low band-gap polymers [1–9]. However, most high-efficiency polymer solar cells have been fabricated by spin coating using chlorine-containing solvents such as dichlorobenzene, because of their high boiling point and slow evaporation. The desired donor–acceptor phase separation in the tens of nanometer scale is usually achieved by using a slow solvent evaporation method, i.e. solvent annealing, after spin coating in dichlorobenzene solvent [10]. In addition, material solubility and molecular compatibility are important considerations in designing polymer composites. The solubility of the donor polymers have a profound effect on the film morphology and solar cell performance [11–18]. Most low band-gap polymers exhibit poor solubility in commonly used chlorine-free solvents such as toluene and xylene. Therefore, uniform film with proper thickness is difficult to fabricate using chlorine-free solvents, and the solar cells by them usually exhibit unsatisfactory efficiencies [19,20]. However, solvents containing chlorine are

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* Corresponding authors. Tel.: +886 3 5731955 (H.-F. Meng), tel.: +86 25 83587982 (Z.-K Chen), tel.: +886 3 5715131x33879 (H.-W. Lin).

E-mail addresses: meng@mail.nctu.edu.tw (H.-F. Meng), iamzkchen@njut.edu.cn (Z.-K. Chen), hwlin@mx.nthu.edu.tw (H.-W. Lin).

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highly toxic and environmentally hazardous. This dilemma is a major obstacle to the potential mass production of polymer cells despite of the advantage of low-cost large-area solution fabrication. Recently, a 6.1% power conversion efficiency has been reported for polymer solar cells spin coated in a halogen-free solvent [21]. However, using spin coating alone is incompatible with high-volume production because it produces large amounts of material waste and is incompatible with the roll-to-roll process. Therefore, developing a chlorine-free polymer solar cell process involving small amounts of material waste and the compatibility to roll-to-roll fabrication is crucial.

This study focuses on the low band-gap polymer PBDTTT-C-T, [22] which exhibit an unusually high solubility in the chlorine-free non-toxic solvents toluene and xylene. Blade coating, rather than conventional spin coating, is used to deposit the active layer [23–26]. Blade coating has the advantage of exhibiting large-area uniformity, small amount of material waste, preventing of inter layer dissolution, and being compatible with the roll-to-roll process. Blade coating involves a rapid drying process that prevents the fabrication throughput from being slowed by the conventional solvent annealing process. A high efficiency of 6.1% was achieves by blade coating for solar cells comprising a combination of PBDTTT-C-T and [70]PCBM that were dissolves in toluene and xylene. In addition, the performance of these devices was insensitive to the solvent regardless of whether chlorine was included. By contrast, the archetypical polymer poly(3-hexylthiophene) (P3HT) and another low band-gap polymer poly{(benzo-2,1,3-thiadiazol-4,7-diyl)-alt-(3′,4″di(2-octyldodecyl)-2,2′;5′,2″;5″,2‴-quaterthiophen-5,5‴-diyl)}(POD2T-DTBT) were much less soluble in chlorine-free solvent than in dichlorobenzene. In sharp contrast to PBDTTT-C-T these solar cells exhibit much lower efficiency using the former solvents. The capability of using donor polymers exhibiting high solubility in chlorine-free solvents to achieve high-throughput and environmental friendly production of efficient polymer cells is demonstrated.

2. Experimental

Fig. 1 shows the energy band diagrams, detailing the work functions of the organic solar cells and the chemical structures of the active layer materials used in this study. The energy level of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) relative to the vacuum are labeled [17,22]. PBDTTT-C-T was purchased from Solarmer materials Inc. The PBDTTT-C-T and POD2T-DTBT exhibited low band-gaps of 1.58 eV and 1.59 eV, respectively, whereas P3HT exhibited a band-gap of 1.9 eV [23]. Fig. 2a illustrates the blade coating method and Fig. 2b is the picture of the auto-blade machine. The blade coater is cylindrically shaped and the gap between the cylinder and the substrate was 120 μm. The solution was delivered to the gap by using a pipette and the motion of the blade formed a wet film. The blade speed ranged from 20 to 400 mm/s. The blade coating procedure was executed on a hot plate. After coating the wet film, the hot air was applied to evaporate the remaining solvent in approximately 1–10 s. The thickness of the remaining dry film could be controlled by adjusting the blade speed. The blade coating was performed in a self-fabricated machine, which was controlled using a linear motor.

Polymer solar cells were fabricated on pre-patterned indium-tin-oxide (ITO) glass with the device structure of ITO/PEDOT:PSS (poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (CLEVIOS™ PVP AI4083, purchased from HC Starck)/PBDTTT-C-T:[70]PCBM/Ca/Al [70]PCBM was purchased from Solenne. The ITO-coated glass substrates were treated in an ultrasonic bath for 60 min in acetone, subsequently rinsed three times with deionized water and cleaned using UV ozone cleaner for 30 min. The 40 nm PEDOT:PSS layer was spin coated at 2200 rpm on the ITO substrate and baked at 200 °C in air for 15 min. To prepare the PBDTTT-C-T and [70]PCBM solutions, PBDTTT-C-T and [70]PCBM powders were mixed. The weight ratio of the PBDTTT-C-T to [70]PCBM was fixed at 1:1.5. The mixed powder was dissolved using various solvents such as toluene, chlorobenzene, and xylene.

To perform blade coating, approximately 3% (1,8-diiodooctane (DIO)/solvents (toluene, chlorobenzene, and xylene), v/v) DIO was used as an additive and was included to improve photovoltaic results. The mixed solution was heated on a hot plate at 80 °C. The active layers were coated using an auto-blade machine, as shown in Fig. 2. Rapid-drying blade coating was performed using a hot plate at 80–90 °C. The solution (70 μL) was coated using the auto-blade machine at approximately 260 mm/s to cover the 4-mm^2 active area of the device with wet film. The thickness of the active layer was 100–120 nm. Hot air produced by a hair dryer containing a diffuser was applied to enhance the drying and uniformity. Dry films formed in approximately 3 s for toluene and chlorobenzene, and 10 s for xylene. The air temperature was approximately 70 °C. To perform spin coating, approximately 3% DIO was a added to the main solvents. The mixed solution was then heated on a hot plate at 80 °C. The thickness of the active layer was 100–120 nm when spin coated at a spin rate of 1000 rpm for 40 s. The wet film was subsequently dried slowly for 2 h during the solvent annealing process. Finally, a Ca(35 nm)/Al(100 nm) electrode was formed on the top of the active layer by using thermal evaporation in a vacuum chamber with a base pressure below 3.0×10^{-6} Torr. Regarding the POD2T-DTBT devices, only Al was evaporated without Ca film. All of the devices were packaged in a glove box and measured in an ambient environment.

To determine the characteristics of the solar cell devices, the power conversion efficiency (PCE) was measured using a solar simulator (XES-301S, SAN-EI) under AM1.5G of irradiation. The incident photon conversion efficiency (IPCE) is defined as the average number of carriers per incident photon. To measure the IPCE, a 300-W Xenon lamp (Newport 66984) and a monochromator (Newprot 74112) were used as light sources. The beam spot on the sample was a square, and the spot size was 3 mm^2. A calibrated silicon photodetector with a known spectral response (Newport 818-UV). The IPCE was measure using a lock-in amplifier (Standard Research System, SR830), an optical chopper unit (SR540) operating at a 260-Hz chopping frequency, and a 1 Ω resistor in a shunt connection to convert the photocurrent to voltage. There is a sharp