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SciVerse ScienceDirect

Solar Energy 91 (2013) 204–211

SOLAR ENERGY

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Functionalized nanodiamond as a charge transporter in organic solar cells

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Received 25 September 2012; received in revised form 22 January 2013; accepted 25 January 2013
Available online 22 March 2013

Communicated by: Associate Editor Frank Nuesch

Abstract

We demonstrate for the first time the efficiency improvement of poly(3-hexylthiophene) (P3HT)–fullerene (C_{60}) bulk heterojunction photovoltaic cells by the introduction of functionalized nanodiamonds (NDs) into the photoactive layer. A novel covalently bonded C_{60}—ND composite was synthesized via a microwave induced functionalization approach. As compared to control devices with only C_{60}, the addition of carboxylated ND resulted in 53% improvement in short circuit current density J_{sc}. Such a device design takes advantages of both C_{60} for electron accepting and ND for efficient electron transport. The results indicate that C_{60} decorated NDs are promising additives for the performance enhancement of polymer photovoltaic cells.

Keywords: Nanodiamonds; Fullerenes; C_{60}; Electron transport; Photovoltaic

1. Introduction

The organic photovoltaics (OPVs) are excellent alternatives to conventional silicon and thin film solar cells because they attempt to achieve moderate power conversion efficiencies (PCEs) at significantly lower cost. Typical OPVs are based on the creation of bulk heterojunctions consisting of blends of an electron-donating semiconducting polymer and an electron-accepting molecule such as fullerene (C_{60}) or its derivative (Yuen et al., 2012; Pivrikas et al., 2011; Oelhafen and Schuler, 2005; Wong et al., 2012; Yap et al., 2011; Karagiannidis et al., 2011; Dennler et al., 2009; Ray et al., 2011; Blom et al., 2007; Hoppe and Sariciftci, 2006; Ruderer and Muller-Buschbaum, 2011; Yamanari et al., 2009; Boland et al., 2010; Zhu et al., 2009). Improvement in OPVs can be brought about by addressing some of its limitations, namely, improving absorption of a wide range of the solar radiation spectrum (Bundgaard and Krebs, 2007; Wang et al., 2011), and enhancing the electron and hole mobilities. Moreover, components like PCBM that require multistep synthesis are quite expensive, underscoring a key economic advantage of OPVs (Li et al., 2007).

In spite of relatively high open circuit voltages (V_{OC}) and high external quantum efficiencies (EQEs), bulk heterojunction OPVs suffer from low PCE because they tend to have low short circuit current density (J_{sc}). Achievement of a better charge carrier transport without sacrificing EQE and V_{OC} could be the solution for higher PCE. Moreover, in a heterojucntion structure, the free carriers generated from exciton dissociation encounter their opposite carriers during transport, leading to charge recombination(Deibel and Dyakonov, 2010). Considering all these, efficient charge carrier transport and optimization of conditions for their facilitation is of great importance for the future development of OPVs.

Carbon nanotubes (CNTs) have been used to demonstrate that nanomaterials with a higher conductivity can

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0038-092X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.solener.2013.01.024

be added to the OPV composite to act as a charge carrier transporters (Li et al., 2007, 2010; Li and Mitra, 2007). This has been accomplished by compositing CNTs with fullerenes. While the CNTs are highly conductive, they themselves are not appropriate for efficient charge separation, and their high charge mobility has been found to enhance PCE. However, the gains in PCE have been modest due to the large size of the CNTs (micron scale length) and the fact that CNTs tend to be heterogeneous and show a wide range of band gap from 0.3 to 2.0 eV, work function between 4.5 and 5.1, but electron and hole mobilities of the order of 10^8 cm^2/V s and 10^3 cm^2/V s respectively (Spitalsky et al., 2010; Coleman et al., 2006; Song et al., 2010; Kim et al., 2007; Zhu et al., 2009).

The relatively inexpensive large scale production of nanodiamonds (NDs) by a detonation synthesis process has made them commercially viable for a broad range of applications. NDs have tetrahedral network structures, large grain boundary density and low negative electron affinity which makes them attractive for electronic applications such as field emission (Shen et al., 2011). The wide band gap ($Eg \approx 5.4$–5.6 eV) makes ND a semiconductor material with a wide range of applications. The combination of high mechanical strength, stiffness, light weight, and low coefficient of friction make ND attractive for the fabrication of structural composites (Raty and Galli, 2005; Subramanian et al. 2011). NDs comprise a diamond core (sp^3), a middle core (sp^{2+x}) and a graphitic outer core (sp^2). The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy of NDs are −5.5 eV and −3.0 eV respectively, are quite uniform (Nagata, 2010) and NDs have modest charge mobility (Stoneham, 2004). Based on these considerations, it is conceivable that NDs can serve as charge carriers in OPVs, and with typical size distribution of 2–10 nm, they may be appropriate for OPV fabrication (Shenderova et al., 2002). The objective of this letter is to study the implementation of NDs in OPV structures especially as electron carrier in the acceptor phase. The other objective is to functionalize the NDs to a high degree to synthesize a composite suitable for OPV applications.

2. Experimental

2.1. Preparation and characterization of carboxylated NDs

Pristine ND (Purity 95%) and all other chemicals were purchased from Sigma Aldrich Inc. with purity higher than 95%. NDs were functionalized in a Microwave Accelerated Reaction System (Mode: CEM Mars) fitted with internal temperature and pressure controls. The as-received pristine NDs were treated with 1:1 70% nitric acid and 97% sulfuric acid in microwave reaction vessels. The microwave power was set to 95% of a total of 1600 W and the temperature at 75 °C. Reaction was carried out for 1 h. This oxidizing procedure generated carboxylic group on the pristine NDs referred to as ND—COOH. The resulting solid was filtered through a 10 μm membrane filter, washed with water to a neutral pH and dried under vacuum at 80 °C to a constant weight. The carboxylated NDs were characterized by scanning electron microscopy (SEM) and Fourier transformed infrared (FTIR). SEM data was collected on a LEO 1530 VP scanning electron microscope equipped with an energy-dispersive X-ray (EDX) analyzer. FTIR measurements were carried out in purified KBr pellets using a Perkin–Elmer (Spectrum One) instrument.

2.2. Preparation and characterization of fullerene–NDs complexes

Fullerene powder with a purity of 99.98% was obtained from MER Corporation, and orthodichlorobenzene (ODCB) was obtained from Fisher Scientific. The C_{60}—ND and C_{60}—ND—COOH complexes were prepared as follows. First, C_{60} solution was prepared at a concentration of 10 mg/ml. ND—COOH powder was sonicated in ODCB for 10 min at a concentration of 0.1 mg/ml. Then, 0.05 ml of ND—COOH solution was mixed with 2 ml of C_{60} solution by sonication for 10 min. The mixture was reacted by microwave irradiation at 300 W for 10 min. C_{60}—ND—COOH complex and C_{60}—ND complex were deposited on a cleaned Si wafer to take SEM images. FTIR spectra of C_{60} and C_{60}—ND—COOH composite were collected in KBr pellets.

2.3. Fabrication and characterization of OPV

The bulk heterojunction OPVs were formed as follows. Regioregular P3HT was obtained from Reike Metals Inc. P3HT was added to the mixtures of the C_{60}—ND complex and C_{60}—ND—COOH at a 50 wt.%, and the mixtures were stirred overnight at room temperature. A similar solution of P3HT and C_{60} at 1:1 weight ratio was also prepared by dissolving directly in ODCB and stirring overnight. OPVs were fabricated onto indium-tin-oxide (ITO) coated glasses. These were patterned prior to being cleaned with detergent, rinsed with deionized (DI) water and followed by acetone and isopropanol wash. They were dried with compressed nitrogen and put inside the oven for 5 min at 110 °C. Poly(ethylenedioxy)-thiophene:poly(styrene)sulfonate (PEDOT:PSS) aqueous dispersion was filtered and spin coated onto the cleaned glass substrates at 2600 rpm for 50 s. Then the samples were dried inside the oven under one atmosphere at 110 °C for 30 min. The composite solution was spin coated on top of the PEDOT:PSS buffer layer at 400 rpm for 15 s, and then for 5 s at 730 rpm. Finally, a 75 nm thickness of Aluminum (Al) cathode layer was deposited by thermal evaporation at 7×10^{-7} torr. The fabricated samples were annealed on hot plates at 120 °C for 10 min in a glove box filled with nitrogen. The active cell area was around 0.293 cm^{-2} and was defined by the intersection of Al and ITO layers. Morphology of the active layer was measured with tapping-mode atomic force microscopy (AFM) (Digital Instrument, NanoscopeII).