

Photophysical and photovoltaic properties of a polymer–fullerene system containing CdSe nanoparticles

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ARTICLE INFO

Article history:

Received 2 July 2012

Received in revised form 5 November 2012

Accepted 15 December 2012

Available online 31 January 2013

Keywords:

Conducting polymers

CdSe nanoparticles

Hybrid solar cells

Photophysical studies

ABSTRACT

In this report, the photophysical studies and the photovoltaic performance of the P3HT:PCBM system containing CdSe nanoparticles were investigated. The addition of CdSe into P3HT:PCBM system promoted a decrease in the photocurrent and in the efficiency of the solar cells. The reduction in photocurrent and efficiency observed after addition of even small portions of CdSe can be associated to a strong interaction between polymer and CdSe nanoparticles, as evidenced by absorption and emission measurements. To investigate the possible contribution of a morphological effect induced by CdSe in P3HT:PCBM film, atomic force microscopy images were also obtained. To get a better understanding of how this ternary system works, comparison was made with another system: PCBM:CdSe and poly(9,9-*n*-dihexyl-2,7-fluorenylenevinylene-*alt*-2,5-thienylenevinylene (PFT), as reported by de Freitas et al. [Journal of Material Chemistry 20 (2010) 4845]. Our results indicate that the chemical structure of the chosen polymer is an important issue in ternary systems and, and that P3HT, a polymer whose chain contains a large concentration of thiophene units, favors polymer–nanoparticle aggregation.

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1. Introduction

Organic solar cells are a promising alternative for renewable energy resources [1–3]. To our best knowledge, the highest efficiency achieved for an organic solar cells is 10.1% by Mitsubishi Chemical [4,5]. Several of these devices are assembled by mixing conducting polymers and fullerene derivatives. The conducting polymer acts as light absorber, electron donor and hole transporter while the fullerene acts as an electron acceptor and transporter [6,7].

The mechanical flexibility, large area and low-cost production of devices based on conducting polymers can enable large-scale implementation [8,9]. However, organic solar cells have lower charge mobility and narrower spectral range absorption of solar energy compared to inorganic-based photovoltaic devices [10].

In this scenario, hybrid solar cells based on the combination of conducting polymers and inorganic nanoparticles have been studied as promising alternatives. Among the conjugated polymers, poly(3-hexylthiophene) (P3HT) is one of the most studied materials and the incorporation of several types of inorganic particles has been tested. For example, Sun et al. [11] reported devices based on mixtures of P3HT with CdSe tetrapods with 2.8% efficiency. Zhou et al. [12] removed the capping ligand treating the HDA–CdSe

QD with hexanoic acid. This treatment was beneficial resulting in devices with power conversion efficiencies of up to 2%. More recently, Dowland et al. [13] reported a successful alternative to eliminate the passivation layer by *in situ* formation of CdS network in P3HT films. The authors have obtained devices with an efficiency of 2.17%. The best results were reported by Dayal et al. in a hybrid devices made of a bulk heterojunction containing CdSe tetrapods and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) with an efficiency of 3.2% [14].

Despite the partially successful application of inorganic nanoparticles in polymer solar cells, there are only a few papers investigating the incorporation of inorganic nanoparticles into polymer–fullerene systems. Kim and Carrol [15] observed an increase of 50–70% in efficiency in poly(3-octylthiophene) (P3OT):buckminsterfullerene C₆₀ bulk heterojunction photovoltaic devices after addition of Ag and Au nanoparticles. Topp et al. [16] reported that addition of Au nanoparticles into the active layer of P3HT:[6,6]-phenyl-C61 butyric acid methyl ester (PCBM) solar cells promoted a decrease in the efficiency of these devices assigned to poor hole mobility because of the disordered polymer phase. Wang et al. [17] reported an increase in the photocurrent (J_{sc}) and incident photon-to-current efficiency (IPCE) when large Au nanoparticles (70 nm) are introduced in P3HT:PCBM heterojunction. The improvement was attributed to enhanced light absorption due to light scattering of the large Au nanoparticles in the active layer. The introduction of metallic nanoparticles in ternary system,

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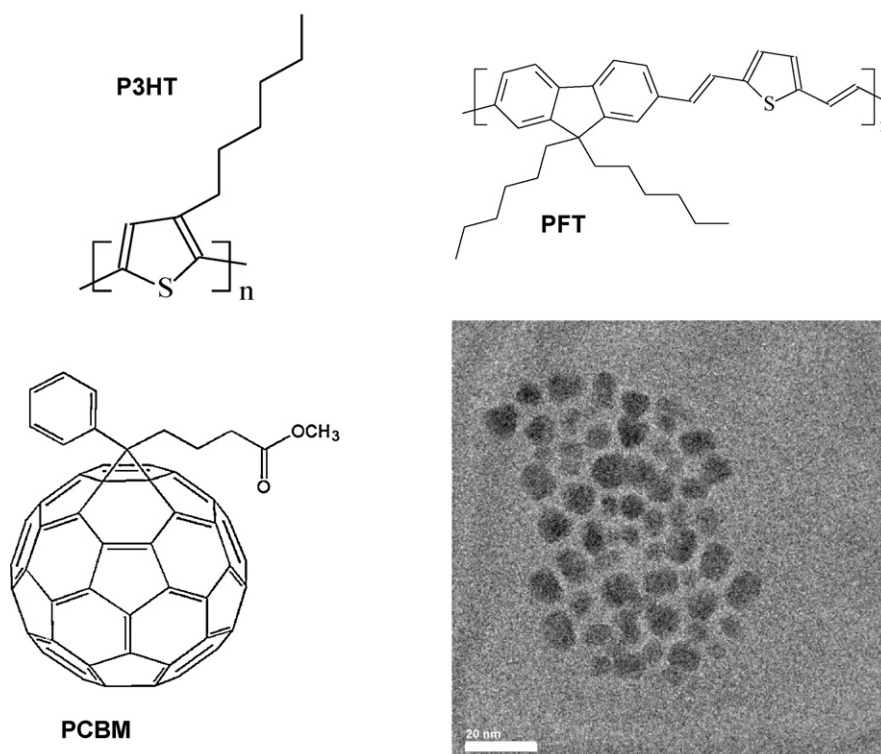


Fig. 1. Structures of P3HT, PFT and PCBM and HRTEM images of CdSe nanoparticles (4 nm of preferential diameter) used in this work.

especially Au nanoparticles, is followed by contradictory results. Wang's report raised the important observation that nanoparticle size is a crucial parameter in such complex systems. Fu et al. investigated hybrid solar cells based on P3HT:PCBM:CdSe system in an inverted cell configuration. The incorporation of 10 wt.% pyridine-capped CdSe nanodots (ratio to P3HT or PCBM) into P3HT:PCBM system increased the power conversion efficiency from 2.06 to 3.05% in devices with high stability [18].

The work reported here is an extension of that carried out by de Freitas et al. [19] which investigated hybrid solar cells based on a ternary system composed of poly(9,9-*n*-dihexyl-2,7-fluorenylenevinylene-alt-2,5-thienylenevinylene) (PFT), PCBM and CdSe nanoparticles. They observed that the best results of photocurrent and efficiency were obtained for the system in which the amount of polymer was kept at 20 wt.% with 1:1 wt.% PCBM:CdSe ratio. The improved device performance was associated with increased absorption of light after the addition of nanoparticles and with the formation of a more suitable nanomorphology of the active layer, as demonstrated by AFM images. In the previous work no comparison with other studies could be made because of the particular properties of the conjugated polymer PFT. In this work, the effects of the addition of CdSe nanoparticles into the well-known and well-established P3HT:PCBM system are more systematically investigated. Fig. 1 shows the structure of the materials detailed in this manuscript: P3HT, PFT, PCBM and CdSe nanoparticles. The results are discussed and compared to those obtained for the previously reported PFT:PCBM:CdSe system [19].

2. Experimental

2.1. Materials

Regioregular P3HT and PCBM were purchased from Rieke Metals and Nano-C Inc., respectively. These materials were used without any further purification. The synthesis and characterization of CdSe

nanoparticles [19] with 4 nm of preferential diameter capped with trioctylphosphine oxide (TOPO) and the characterization of PFT [6] were published elsewhere.

2.2. Sample preparation

For the photophysical studies, solutions of P3HT and PFT (0.025 mg mL⁻¹) were prepared by dissolving these polymers in chlorobenzene under stirring for 24 h. PCBM was dissolved in chlorobenzene to form 1 mg mL⁻¹ solution and CdSe was dispersed in chlorobenzene in the concentration of 1 mg mL⁻¹.

For morphological studies, nanocomposites of P3HT:PCBM, P3HT:CdSe and P3HT:PCBM:CdSe were obtained by preparing chlorobenzene solutions containing a fixed amount of P3HT (8 mg mL⁻¹) and 50 wt.% of PCBM and/or CdSe, where the PCBM:CdSe ratio was varied. Films of these nanocomposites were deposited by spin-coating (1500 rpm, 60 s) onto indium tin oxide (ITO) coated glass substrate.

2.3. Fabrication of photovoltaic devices

Bulk-heterojunction solar cells were assembled in the following configuration: ITO/PEDOT:PSS/Active Layer/Ca/Al. Indium tin oxide (ITO) coated glass substrate was first cleaned with water and detergent, ultrasonicated in acetone and isopropanol for 15 min each and dried under a nitrogen flow. Poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, in aqueous solution, Aldrich) layer (40 nm) was spin-coated onto the ITO-glass and dried at 120 °C for 20 min. In a glovebox, the active layer (250 nm), consisting of P3HT:PCBM mixture (2.2% in dichlorobenzene, Aldrich) before or after the addition of CdSe nanoparticles (10, 20 and 30 wt.%). The percentage relates to the amount of CdSe, considering as the total amount all the three components (P3HT + PCBM + CdSe). Finally, it was then deposited on top by spin-coating (700 rpm, 60 s) and subjected to annealing of 140 °C for 10 min, followed by deposition of the Ca (20 nm) and Al electrodes

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