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Rod-coil block copolymer as nanostructuring compatibilizer for efficient CdSe NCs/PCPDTBT hybrid solar cells

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ABSTRACT

In this work the performance improvement of hybrid solar cells (HSCs), constituted by polycyclopentadithiophene-benzothiadiazole (PCPDTBT) and CdSe nanocrystals (NCs), achieved thanks to the use as additive of an on-purpose designed rod-coil block copolymer (BCP), is evaluated. The rod-coil BCP, namely polycyclopentadithiophene-benzothiadiazole-*block*-poly(4-vinylpyridine) (PCPDTBT-*b*-P4VP), is synthesized with a chain growth-like procedure starting from a PCPDTBT macroinitiator suitably tailored in order to achieve molecular similarity with the commercial PCPDTBT homopolymer here used in the HSCs, in order to optimize the interactions between the two materials in the device. Nitroxide-mediated radical polymerization (NMRP) of 4-vinylpyridine generates the rod-coil flexible chain which is maintained short to limit the insertion of insulating moieties in the additive structure. The employment of the rod-coil BCP as additive is demonstrated to be an effective alternative to the standard post-deposition thermal treatment. The device with 1% of additive performs better than the thermal annealed one and shows an improvement of 60% in power conversion efficiency (PCE) if compared to the pristine CdSe NCs/PCPDTBT cell. The optical and morphological analysis of the CdSe NCs/PCPDTBT films with and without additive elucidates the relation between the device performance and the active layer microstructure and clearly highlights how the improvement of the miscibility between the polymer and the inorganic NC species can be associated to the increased efficiency in HSCs. A future development of this room-temperature processing approach of the active layer, not requiring any additional post-fabrication annealing steps, could implement HSCs fabrication by common printing technologies for a cost-effective fabrication of devices onto large-area and flexible substrates.

1. Introduction

Colloidal nanocystals (NCs) based hybrid solar cells (HSCs) have attracted significant interest due to the possibility of combining the easy and cost effective processing of organic materials with the environmental stability and intrinsic higher

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electron mobility of inorganic semiconductors [1]. Additionally, HSCs exploit the undeniable advantage of mixing together two efficient light harvesting species: conjugated polymers with high extinction coefficients (such as polythiophenes) and semiconductor NCs with tunable absorption spectra as a result of the quantum confinement effect (such as PbS, CdS, CdSe, and CdTe) [2–5]. Despite the recent developments and the potential advantages, the photovoltaic performance of the HSCs is still low compared to all-NC [6] or polymer/fullerene derivative based solar cells [7,8]. One of the limits stays in the poor chemical interaction between the organic and inorganic materials that leads to an inevitable macroscopic phase separation between the donor (polymer) and the acceptor (NCs) at high NCs concentration and requires the use of complex mixture of solvents to allow for the differing solubility of the donor and the acceptor materials [9]. Hence, the control of the active layer morphology is a key factor to improve photovoltaic performance as, ideally, an interpenetrating network of the polymer and the NCs domains is crucial to maximize charge separation, transfer and transport [10].

In HSCs sunlight can be absorbed *via* polymer or NC species and fast exciton dissociation should occur either at the interface between the two materials or through percolation channels between NCs and both electrodes [11]. Indeed, due to the high loading of NCs in the nanocomposite, percolation channels among NCs towards electrodes can be thought as suspended in the polymer [12]. Considering both the hypotheses, the nanomorphology control has a paramount importance in determining the device performance since it can maximize charge transfer processes and charge collection to the electrodes. In order to prevent recombinations of free electron-holes, large interpenetrating domains of polymer and NCs are preferred. However, small domains are needed to increase the number of excitons able to reach along the polymer an interface to dissociate within their short diffusion length prior to recombination. Thus, the ideal morphology required for designing high efficiency devices can be obtained when exciton dissociation and charge transport and collection are balanced. Aiming at optimizing the nanostructure of the active layer to promote the electron transfer from the donor to the acceptor, as well as to minimize the charge recombination, different post-fabrication strategies are reported in literature. For instance, in organic solar cells (OSCs) either thermal or solvent-activated annealing process is required to obtain performing devices. However, both the approaches have intrinsic disadvantages that make them unsuitable for the industrial implementation [13]. Another possible and promising approach to promote the organization of the desired co-continuous network relies on the insertion of chemical additives into the binary blend. Such a method is particularly amenable, due to its prompt and ready applicability to polymeric materials, without requiring any additional step in the device fabrication process.

In this perspective, BCPs have been explored as additives to improve the miscibility of the materials blended in OSCs [14]. Commonly, each block forming the copolymer has a specific chemical affinity to one of the components in the blend, thus ensuring the miscibility of the BCP and the materials forming the active layer of OSC. Consequently, due to their ability to thermodynamically self-assemble leading to a nanophase separation, BCPs can reduce the interfacial energy between the immiscible components of the active layer, thus decreasing the segregation of donor and acceptor domains in the active layer and creating pathways for an efficient charge collection to the electrodes. In polymer-fullerene solar cells, rod-coil BCPs compatibilizers have been employed taking advantage of flexible blocks with either pendant fullerene derivatives [15–17] or fullerene compatible moieties through non-covalent interactions, as polystyrene (PS) [18], poly(2-vinylpyridine) (P2VP) or poly(4-vinylpyridine) (P4VP) [19,20], poly(ethyleneoxide) (PEO) [21], and polyisoprene (PI) [22]. More recently, the rod-coil BCPs have been exploited into organic-inorganic blends prepared using differently shaped nanoparticles (NPs) and various polymer/NCs ratios. BCPs, containing regioregular poly(3-hexylthiophene) (P3HT) in the rigid block and P2VP or P4VP in the flexible one, have been used as additive in blend of P3HT homopolymer with TiO_2 or ZnO NPs respectively [23,24]. In all cases, the enhancement of device performance, in particular photocurrent and fill factor (FF), has been attributed to an increase of charge separation, due to an improved interface interaction between the hydrophobic homopolymer and the NPs. Kim *et al.* have reported on the crystallization behavior of CdSe quantum dots (QDs) driven by a rod-coil BCP poly(3-hexylthiophene)-*block*-poly(2-vinylpyridine) with different regioregularity in P3HT and coil block lengths [25]. The photovoltaic applications of rod-coil BCPs, poly(3-hexylthiophene)-*block*-polystyrene, with coil blocks displaying different phosphorus-containing pendant groups able to coordinate CdSe NCs, have been also investigated. Unfortunately, the low loading of the as-prepared NCs in the active layer has resulted in a poor device performance when compared with other approaches [26].

Previously poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) has been used in HSCs with CdSe tetrapods [27] or a mixture of CdSe QDs and nanorods [28] obtaining good performances. The use of the low band gap copolymer PCPDTBT as the electron donor material ensures an extended absorption spectrum into the NIR region [27–30]. In previous papers where PCPDTBT is used as donor material with CdSe NPs, exciton dissociation and charge carrier transport have been implemented by NPs surface modification because the presence of insulating ligands is detrimental for both. The result has been obtained by post-synthetic treatments with *tert*-butylthiol [31] and hexanoic acid [32] or by post deposition treatments with ethanedithiol [33] and benzenedithiol in acetonitrile [34].

Herein, we report the performance of HSCs based on PCPDTBT (sketched in Fig. 1) and CdSe NCs incorporating in the active layer the properly tailored rod-coil BCP poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)]-*block*-poly(4-vinylpyridine) (PCPDTBT-*b*-P4VP, hereafter referred as BC) as additive. The BC is constituted by a rigid block of the same conjugated polymer PCPDTBT covalently linked to a short flexible moiety of P4VP. The direct interaction and the occurrence of an efficient cooperative effect of the P4VP coil moiety with CdSe NCs surface have been recently demonstrated [35]. Indeed, although the weak affinity of each single pyridine, such an interaction is based on the general cooperative effect resulting in an overall amplification of NCs coordination. Spherical NPs are used in