Morphological consequences of ligand exchange in quantum dot - Polymer solar cells

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ABSTRACT

Mixtures of conjugated polymers and quantum dot nanocrystals present an interesting solution-processable materials system for active layers in optoelectronic devices, including solar cells. We use scanning transmission electron microscopy to investigate the effects of exchanging the capping ligand of quantum dots on the three-dimensional morphology of the film. We created 3D reconstructions for blends of poly((4,8-bis(octyloxy)benzo (1,2-b:4,5-b')-dithiophene-2,6-diyl)(2-((dodecyloxy)carbonyl)thieno (3,4-b)-thiophenediyl)) (PTB1) and PbS quantum dots capped with oleic acid (OA), butylamine (BA), OA to 3-mercaptopropionic acid (MPA), and BA to MPA. We use these reconstructed volumes to evaluate differences in exciton dissociation and charge transport as a function of ligand processing. We show that the MPA exchange without an intermediate BA treatment results in severe changes to the film structure and a non-ideal morphology for an effective device. We also show that with a BA exchange, the morphology remains largely unchanged with the additional MPA treatment. This quantitative characterization elucidates previously reported device performance changes caused by ligand exchange and should inform future device fabrication protocols.

1. Introduction

Solution-processed photovoltaic (PV) devices have been extensively studied due to their potential for fabrication using large scale roll-to-roll manufacturing methods that would result in low cost–per–watt emission–free electricity production. Conjugated polymer-fullerene blends called bulk-heterojunctions (BHJs) have been exhaustively studied with the result that several validated efficiency records exceeding 10% power conversion efficiency (PCE) have been published [1–4]. Quantum dots (QDs) present an alternative to fullerenes as electron acceptors in polymer-based PV devices and pose several advantages including tunable band gap [5], increased thermal stability [6,7], reduced carrier recombination [8,9], and the potential for multiple exciton generation [10,11]. Recent work with polymer-QD films has yielded devices with PCE of up to 5.5% [12] and pure QD devices have been fabricated exceeding 10% efficiency [13].

Improvements in PCE of these devices can be achieved through a better understanding of the morphology resulting from processing conditions. It is widely accepted in organic photovoltaic (OPV) device

modeling that the performance of a device could be more completely understood if an accurate three-dimensional map of material location could be measured. High angle annular dark field electron tomography (HAADF-ET) provides a means of acquiring this information. HAADF scanning electron microscopy provides image intensity proportional to the atomic number squared of the species being measured, which creates considerable contrast in the case of PbS particles with a conjugated polymer [14]. A series of projection images of a film in a range of ±65–70° with respect to the beam is acquired and used to create 3D reconstructions of the volume via the discrete algebraic reconstruction technique (DART) [15]. The angular range is limited compared to the ideal ±90° case due to the sample geometry being a film; at angles larger than 70° the film absorbs most of the electrons due to increased effective thickness. The limited angle range results in missing information and the so-called "missing wedge artifacts" in the reconstructions, leading to difficulty in quantifying data especially in the direction of the film thickness [16]. DART is an iterative technique that segments the reconstruction volume into distinct phases with known gray values (exploiting knowledge of density) with each iteration, as

opposed to conventional reconstruction techniques which require a manual segmentation after a complete volume has been reconstructed. DART computes more accurate reconstructions from a small angular range or with noisy projection data than alternative methods [15]. Recently, the DART algorithm has been used to quantify the 3D morphology of P3HT: fullerene blends [17,18]. Although domain size information can be obtained from measuring the photoluminescence quenching of donor/acceptor films using photo-induced absorption, this data is a statistical average assuming spherical domains over the entire volume [9]. Tomographic data is of particular use in that it provides a quantitative three dimensional direct space map of the film morphology, providing details of horizontal and vertical material segregation, as well as domain connectivity and detailed charge-transport pathways.

It is necessary to control the relative solubilities of polymers and QDs to generate a solution processed BHJ mixture. Mutual solubility allows for a well-mixed morphology to develop in one deposition step as opposed to lengthy layer by layer processes. For polymer/fullerene BHJs, the device efficiency depends on several processes that occur at different length scales. Efficient charge separation is governed by diffusion of excitons to a donor acceptor interface with exciton diffusion lengths of 5–10 nm [19,20]. After charge separation occurs, the hole and electron must hop to contiguous adjacent sites with a pathway to the anode and cathode [21]. Finally, the total process efficiency is highest when the hole and electron are prevented from recombining, which is best achieved in a bilayer with minimized interface area between donor and acceptor domains [22]. An ideal BHJ layer would have nanoscale phase separation for optimized exciton separation and also straight pathways for charge transport to both electrodes. Since the materials are mixed in solution this optimized BHJ needs to self-–assemble during the drying process.

For polymer/QD BHJ devices, the solubility of the QDs is controlled using a capping ligand [5]. In early devices, little attention was placed on the capping ligand with the effect that in some devices the phase separation was too high due to low solubility of the QDs. In other devices, the QD was highly miscible with the polymer, but the capping ligand was a long chain that prevented charge transport between adjacent QDs [23]. For record holding all-QD (no polymer) PV devices, PbS QDs are deposited and undergo ligand exchanges monolayer by monolayer, resulting in a highly uniform film at the cost of labor-intensive fabrication [8,24–26]. In contrast, the single-step film deposition of polymer–QD blend films is more aligned with the requirements of large scale fabrication.

More recently, blends of polymer/QD BHJs were fabricated in two steps. First films with long chain ligands (typically oleic acid (OA)) on the QD are coated to create a well mixed film. Then in a post deposition processing step, the long chain ligand is replaced with a shorter chain ligand to improve the charge hopping between QDs and to maintain high efficiency photogeneration [23,27–30]. This processing step, known as ligand exchange, is depicted in Fig. 1 along with the ligands studied here. Several different short chain ligands have been investigated including butylamine (BA), which is simply shorter [29], ethanedithiol (EDT), which could bind two different QDs [31], and mercaptopropionic acid (MPA) that is shorter and improves inter-particle electronic coupling [32]. These three short chain ligands have notably different polarities with MPA > EDT > BA which could strongly affect miscibility with the non-polar polymer. It has also been reported that ligand exchange in two steps first with BA followed by MPA yields a higher efficiency PV device than a single exchange step using only MPA [31]. In this case, the BA exchange is performed in solution prior to film deposition. It was recently shown that blends of poly((4,8-bis(octyloxy)benzo(1,2-b:4,5-b')-dithiophene-2,6-diyl)(2-((dodecyloxy)carbonyl)thieno (3,4-b)-thiophenediyl)) (PTB1) and PbS QDs show drastically different external quantum efficiencies depending on the ligand exchange processing [31].

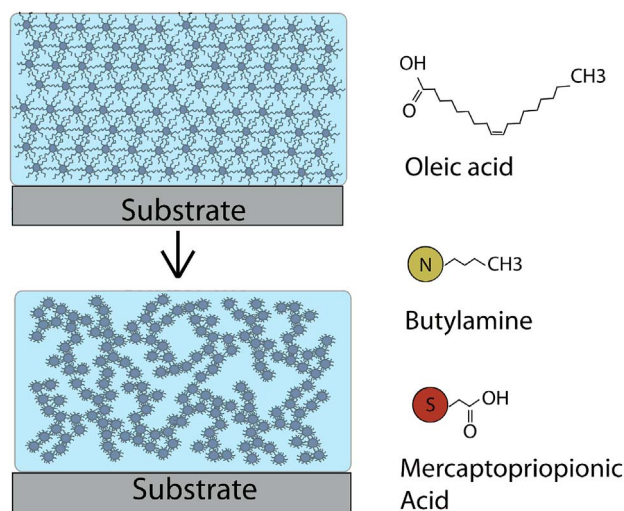The purpose of this article is to quantitatively study the 3D

Fig. 1. Schematic of ligand exchange process. As-cast films starting with long OA ligands or shorter BA ligands undergo an in-situ ligand exchange to MPA.

morphology of PTB1/PbS layers with different capping ligands before and after ligand exchange with MPA to determine whether and how much the ligand exchange steps change the BHJ morphology. We focus here on lead sulfide QD's because PbS is a low-band gap material that is composed of earth abundant materials and has been demonstrated to function in solution cast hybrid polymer/QD photovoltaic devices with >5% power conversion efficiency [12]. Furthermore, the high atomic number contrast provided by the QDs provides good imaging conditions for HAADF TEM and tomographic reconstructions [33]. We further validate these electron microscopy methods for blend characterization with a focus on differentiating the morphology of the PTB1:PbS system as a function of processing conditions.

2. Results and discussion

Fig. 2 shows 2D HAADF STEM images comparing 1:9 wt ratio PTB1:PbS films with various capping ligands. HAADF yields Z-contrast
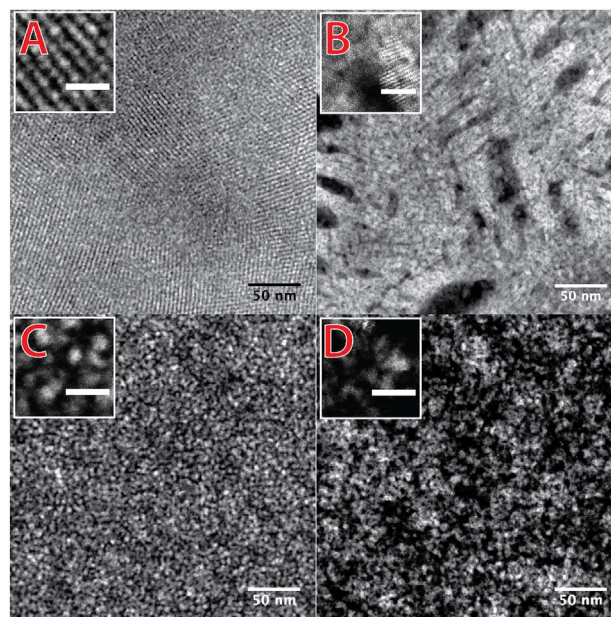

Fig. 2. 2D STEM micrographs showing different morphologies. A - OA as cast. B - OA-MPA treated. C - BA as cast. D - BA-MPA treated. Insets show additional magnification, inset scale bars are 10 nm.