

Polymer Based Nanostructured Donor–Acceptor Heterojunction Photovoltaic Devices

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ABSTRACT

Bulk heterojunction photovoltaic devices based on blends of conjugated polymers and fullerenes have achieved efficiencies of 3.5% under AM1.5 illumination. This is a result of efficient exciton dissociation at donor–acceptor interfaces. However, the intimate blending of the electron and hole transporting species leads to detrimental charge carrier recombination in the bulk of these devices. We are investigating a solution to this problem by fabricating nanostructured oxide–conjugated polymer composite structures. Porous SnO₂ films with pore diameters of ~100 nm have been fabricated. Intercalation of polymers into the pores by adsorption from solution yielded structures with approximately 75% of the free volume filled with polymer. The resulting composite structures are promising candidates for developing polymer-based solar cells with short carrier-to-electrode path lengths while retaining high optical absorption, thus leading to increased efficiencies. Additionally, a carboxylic acid fullerene derivative was shown to bind to the SnO₂ surface, a necessary step in creating a nanostructured electron-accepting surface.

1. Introduction

Organic molecular and polymeric semiconductors have undergone a dramatic evolution over the last several decades into a mature field with products such as organic light emitting diodes [1] now available commercially [2]. The essentially infinite variety of organic molecules that can be designed and synthesized provide a framework in which a wide range of optical and electronic properties can be obtained. Solution-based fabrication techniques used for polymeric materials lend themselves to very low cost, high throughput manufacturing techniques such as inkjet printing and screen printing [3]. This aspect of polymer-based devices is particularly interesting to the field of photovoltaics, where inexpensive fabrication of large-area devices is critical.

To date, several organic solar cell schemes have been investigated. Most are based on a heterojunction between an electron-donating molecule and an electron-accepting molecule. Various donor-acceptor pairs have been investigated, including polymer-fullerene [4,5], polymer-perylene [6,7], polymer-polymer [8], and polymer-quantum dot [9]. The design of devices based on these materials can fall into two broad categories: planar heterojunction and bulk heterojunction. Planar heterojunction devices rely on diffusion of excitons to the donor-acceptor interface in order to achieve charge separation. This provides a serious limitation on such devices, since exciton diffusion lengths in amorphous

organic semiconductors are typically limited to less than 10 nm. Higher efficiency devices have generally been achieved by blending the donor and acceptor species together into a phase segregated mixture. In such blends, the distance that an exciton must diffuse to reach an interface is typically very short, thus efficient charge separation is achieved for all absorbed photons. However, the blending of the donor-acceptor species allows for the free hole and electron charges to recombine in the bulk as they are transported toward their respective electrodes. Overcoming this obstacle by fabricating a nanostructured donor-acceptor interface without creating an intimate 3-dimensional blend of the two species is the subject of this work.

2. Current State-of-the-Art of the Bulk Heterojunction Plastic Solar Cell

In order for donor-acceptor heterojunction solar cells to work efficiently, the initial photoinduced charge separation process must be fast and efficient. In addition, the back reaction rate (recombination) must be a slow process, thus creating a stable charge-separated state. Such an asymmetry between forward and back electron transfer rates is observed for the conjugated polymer / fullerene interface [10]. Forward electron transfer times from excited conjugated polymers to a fullerene have been measured to be faster than 50 fs, while the back electron transfer rate is on the order of 1 μ s at room temperature [11]. This asymmetry of 9 orders-of-magnitude between forward and back electron transfer rates makes high efficiency bulk heterojunction solar cells

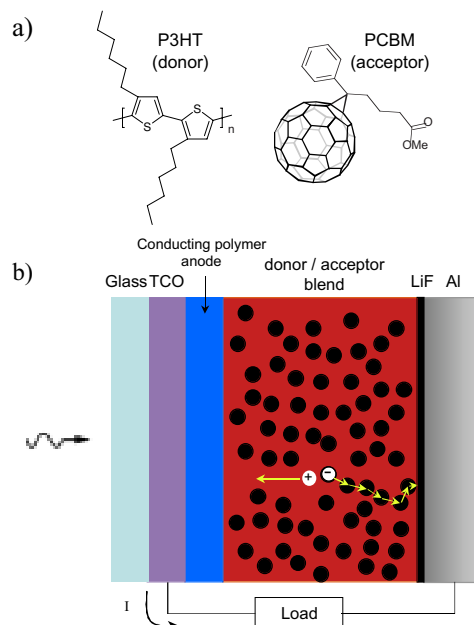


Figure 1. a) Molecular structures for P3HT and PCBM. b) Schematic of the device structure of the bulk heterojunction solar cell.

possible.

The device structure of a bulk heterojunction solar cell based on a blend between poly(3-hexylthiophene) (P3HT) as the donor and the fullerene derivative 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6]C₆₁ (PCBM) as the acceptor is shown in Fig. 1. Light is absorbed primarily by the conjugated polymer (the fullerene has little absorption in the visible spectrum). Excitons that are created on the polymer are quickly separated into free electrons and holes. These charges are then transported, through a combination of drift and diffusion, to their respective electrodes. Holes are transported by hopping between conjugated polymer segments, and electrons are transported by hopping between fullerene molecules. This device has shown power conversion efficiencies of 3.5% under AM1.5 illumination, with internal quantum efficiencies approaching 90% at peak absorption wavelengths [12]. P3HT appears to be the best material to date for such devices due to its low bandgap relative to most conjugated polymers ($E_g \sim 1.9$ eV) and high degree of intermolecular ordering leading to high charge carrier mobility ($\mu_{\text{hole}} \sim 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ measured in FET geometry) [13]. The morphology and degree of molecular ordering has previously been shown to be an important parameter in the operation of these devices [14].

There are several limiting factors on the efficiency of these devices, including the size of the optical bandgap, which leads to poor overlap with the solar spectrum, as well as poor alignment of the donor-acceptor molecular orbital levels leading to a loss in open-circuit voltage. Additionally, as discussed before, the intimate mixture of donors and acceptors leads to charge recombination in the bulk. This ultimately limits the thickness of the device, and therefore the amount of light that is absorbed.

3. Nanostructured Oxides as Substrates for Polymer Based Solar Cells

An alternative device geometry is to create a large interfacial area between the donor and acceptor species by using a nanostructured, porous, inorganic material as the electron collecting cathode [15]. This would act as a 'scaffolding' onto which the acceptor molecules can be attached. Once this is constructed, an electron-donating, hole transporting, polymer can be intercalated into the porous volume to create the heterojunction. Optimally, there would be some free volume remaining into which a conducting polymer, acting as the anode, could be infiltrated. In such a device, excitons created by light absorption within the polymer would have a small distance to diffuse before reach a donor-acceptor interface. The electron donated to the acceptor would then immediately be injected into the cathode, and the hole remaining on the polymer would have a short distance to travel before reaching the anode. Figure 2a) illustrates the conceptual design of such an optimal device.

As a first step toward realizing this device, we fabricated porous, nanostructured SnO₂ materials. Films

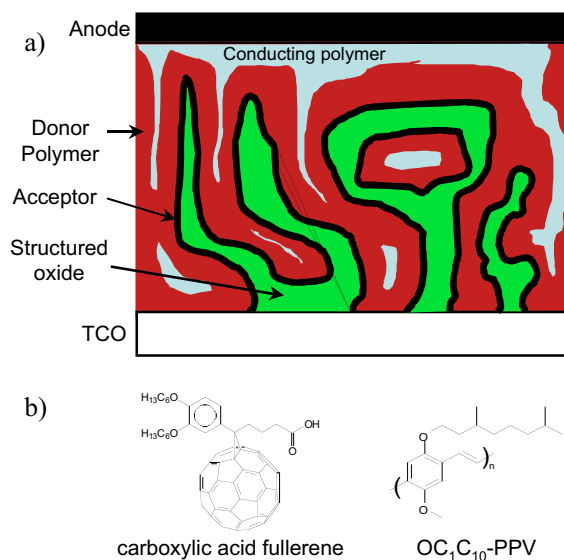


Figure 2. a) 2-dimensional slice through an idealized nanostructured oxide – conjugated polymer composite photovoltaic device. b) Molecules used in this study.

were fabricated by spin coating SnO₂ nanoparticles (diameter ~ 9 nm) blended with polystyrene microspheres (diameter ~ 100 nm). Upon annealing the films to 450 °C, the SnO₂ nanoparticles sintered together, and the polystyrene spheres decomposed and were baked out of the material. The resulting structure formed a continuous network of SnO₂ with a porosity of approximately 50% and pore sizes of ~ 100 nm. Figure 3 shows SEM images of the resulting porous SnO₂ structure at two magnifications.

The pore volumes were chosen to be this size in order to facilitate intercalation of polymers into the structure by adsorption from solution. Polymers with relatively weak interactions between segments take on an 'unperturbed' random coil shape when in solution. This is the case, to a first approximation, for the conjugated polymers with which we are working. The root-mean-square radius (the radius of gyration R_g) of the coil can be approximated from the molecular weight of the polymer [16]. For the polymer used in this study (OC₁C₁₀-PPV), $M_w \approx 1.2 \times 10^6$ and $R_g \approx 17$ nm.

4. Polymer Intercalation into Porous SnO₂

Intercalation of the porous SnO₂ structure was performed by submerging it in a solution containing the conjugated polymer OC₁C₁₀-PPV, shown in Fig. 2b), at 85 °C for 12 hours. Several thermodynamic factors contribute to the degree of adsorption of the polymer onto the oxide surface [17]. Osmotic pressure drives the polymer chains into the pores. However, the entropic force is in the other direction due to the reduced number of configurational states available to the confined polymer. The force that can tip the scales in either direction is the interaction energy between the polymer and oxide surface. A strong attractive force between the polymer and the oxide can overcome the entropic drive and result in adsorption of many monolayers of polymer onto the surface. This is particularly true if the

polymer is dissolved in a poor solvent. For this study, chlorobenzene was used as the solvent. Light scattering measurements have revealed that chlorobenzene is a poor solvent for OC₁C₁₀-PPV; the polymer chains are not truly dissolved but instead are suspended in solution [18].

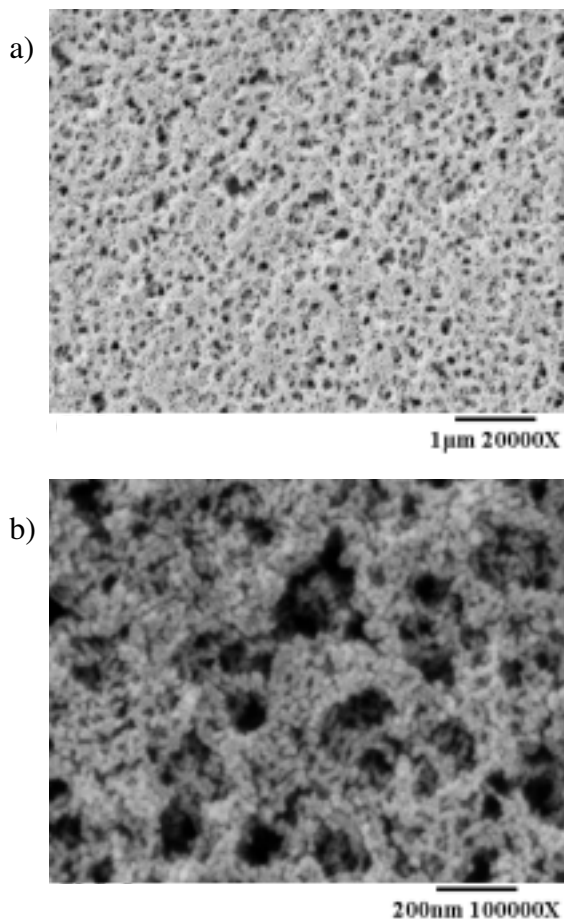


Figure 3. SEM images of nanoporous SnO₂ at magnifications of a) 20000× and b) 100000×.

Figure 4 shows an SEM image of the porous SnO₂ intercalated with OC₁C₁₀-PPV using this technique of adsorption from solution. Using optical density, film thickness, and film porosity measurements, it was estimated that the polymer filled ~75% of the free volume in the porous structure. Optical characterization of the composite structure was performed and compared to a 65 nm thick film of pure OC₁C₁₀-PPV (Fig. 5). Absorption and luminescence spectra exhibited a shift to higher energies in the composite structure, indicating a possible reduction in π -conjugation of the polymer chains when they are intercalated into the pores of the oxide.

5. Adsorption of an Acceptor onto the Oxide Surface

Preliminary investigations of the adsorption of an acceptor molecule onto the oxide surface were carried out using a carboxylic acid fullerene derivative, shown in Fig. 2b). Adsorption was carried out in a solution of THF at 50 °C for 1 hour. Kelvin probe measurements

indicated a shift in vacuum level of -0.3 eV (further from vacuum) of the surface of the oxide upon fullerene adsorption. Such vacuum level shifts can arise from a dipole moment in the adsorbed species or charge transfer between the adsorbate and the surface, or both [19]. These effects can strongly effect the direction and degree of charge transfer across the interface, and provide a way of tuning the interface to achieve optimal device performance.

Besides fullerenes, there are several other possible acceptor species that can be adsorbed onto the oxide surface. Perylene molecules and quantum dots [20], for example, have both shown electron-accepting character and may be good candidates for adsorption onto a nanostructured oxide. Such species would have the added advantage of contributing to the light absorbed within the device.

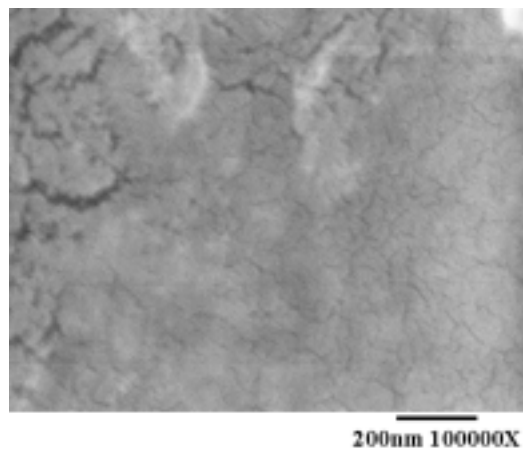


Figure 4. SEM images of polymer-intercalated, nanoporous SnO₂ at a magnification of 100000×.

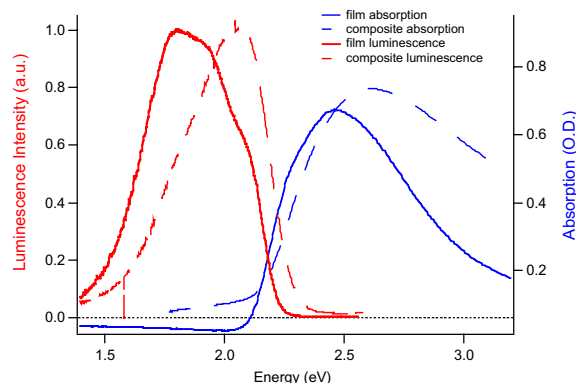


Figure 5. Optical absorption (blue) and luminescence (red) of a 65 nm thick film of OC₁C₁₀-PPV (solid) and the SnO₂ – OC₁C₁₀-PPV composite structure (broken).

6. Conclusions

Porous, nanostructured oxides have been fabricated with pore diameters of ~100 nm. Efficient intercalation of a conjugated polymer into the structure has been demonstrated, and an acceptor molecule has been adsorbed onto the surface of the oxide. These results are the first steps towards fabricating a nanostructured donor – acceptor heterojunction without intimate mixing of the two species. Such a device is expected to have high quantum efficiency

and a large optical density, leading to improved power conversion efficiencies. Additionally, the polymer-intercalated oxide structure is expected to have greater thermal stability and mechanical robustness than a polymer film.

Further efforts are underway to optimize the density and charge transfer characteristics of the adsorbed acceptor molecules, and to fill in the remaining free volume of the composite material with a conducting polymer.

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