

Ordered Organic–Inorganic Bulk Heterojunction Photovoltaic Cells

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Abstract

Fabrication of bulk heterojunctions with well-ordered arrays of organic and inorganic semiconductors is a promising route to increasing the efficiency of polymer photovoltaic cells. In such structures, almost all excitons formed are close enough to the organic–inorganic interface to be dissociated by electron transfer, all charge carriers have an uninterrupted pathway to the electrodes, and polymer chains are aligned to increase their charge carrier mobility. Furthermore, ordered structures are interesting because they are relatively easy to model. Studies of ordered cells are likely to lead to better design rules for making efficient photovoltaic cells.

Keywords: ordered bulk heterojunctions, conjugated polymers, mesoporous titania, organic photovoltaic cells.

Introduction

As discussed in other articles in this issue, an attractive approach to improving the efficiency of organic photovoltaic (PV) cells is to use a bulk heterojunction, in which semiconductors with offset energy levels interpenetrate at approximately the 10 nm length scale. Most bulk heterojunction PV cells have been made by casting solutions containing the two semiconductors (e.g., a conjugated polymer and a fullerene derivative,¹ another polymer,² CdSe nanocrystals,³ titania nanocrystals,⁴ or ZnO nanocrystals⁵) to make blends. Although these blends are easy to fabricate, and it is desirable to use this simple process to manufacture PV cells, there are problems with the disordered nanostructures that are typically created. In some cases, the two semiconductors phase-separate on too large a length scale. Consequently, some of the excitons (electron–hole pairs) generated when light is absorbed are not able to diffuse to an interface to be dissociated by electron transfer before they decay. In other cases, there are dead ends in one of the phases that prevent charge carriers from reaching electrodes. In most

cases, charge transport is not fast enough to enable the charge carriers to reach the electrodes before the electrons and holes recombine with each other, unless the films are made so thin that they cannot absorb all of the incident light.

Ordered bulk heterostructure PV cells, such as the one shown schematically in Figure 1, are more difficult to fabricate than disordered blends, but there are several good reasons to do so. First, the dimensions of both phases can be controlled to ensure that every spot in a film is within an exciton diffusion length of an interface between the two semiconductors. Second, there are no dead ends in the structure. After excitons are dissociated by electron transfer, the electrons and holes have straight pathways to the electrodes. This geometry ensures that the carriers escape the device as quickly as possible, which minimizes recombination. Third, in an ordered structure it is possible to align conjugated polymer chains, which increases the mobility of their charge carriers. Another advantage, which is particularly important during the current stage

of organic photovoltaic cell research, is that ordered structures are much easier to model and understand.

Fabrication of Ordered Bulk Heterojunctions

Due to recent advances in nanotechnology, there are now many techniques available for patterning films at the 10 nm length scale. Making an efficient PV cell is still, however, a great challenge, since there are numerous properties the film needs to possess that place constraints on the materials that can be used. The films must be 200–400 nm thick, so that most of the light incident on the PV cell will be absorbed. The phases should be straight, aligned perpendicular to the electrodes, and ideally connected only to the appropriate electrodes. Furthermore, the energy levels of the semiconductors must be chosen carefully, so that most of the solar spectrum is absorbed, excitons are dissociated by electron transfer, and a significant voltage is generated. One of the most attractive approaches is to use a block copolymer that self-assembles to form an array of cylinders oriented perpendicular to the substrate.⁶ Well-ordered films with the desired nanostructure can be made with nonconjugated block copolymers, such as poly(methyl methacrylate)-polystyrene.^{7,8} Unfortunately, switching to conjugated blocks and keeping the desired structure is difficult because most of the polymerization routes used to make conjugated polymers do not result in low polydispersities, many conjugated blocks cannot be attached to each other, and stiff conjugated blocks do not form the same structures as flexible blocks. An easier approach at this time is to make a nanoporous film or an array of nanowires with an inorganic semiconductor, such as titania (TiO₂), zinc oxide, or cadmium sulfide, and then fill in the pores or the space between the wires with a conjugated polymer.^{4,9,10}

Titania films with arrays of nanopores can be made by evaporation-induced self-assembly.^{11–13} A solution containing a block copolymer that can self-assemble into an ordered structure and titanium ethoxide is dip-coated or spin-cast. As the solvent evaporates, the titania precursor and the more hydrophilic polymer block separate from the more hydrophobic block. The film is then heated to approximately 280°C to oxidize and remove the block copolymer. Finally, the film is heated to around 400°C to convert the amorphous titania into nanocrystalline anatase. A scanning electron micrograph of a film made this way is shown in Figure 2a. Cells have been made with the films shown in Figure 2a and will be discussed in the section titled “Performance of Photovoltaic Cells and the Need

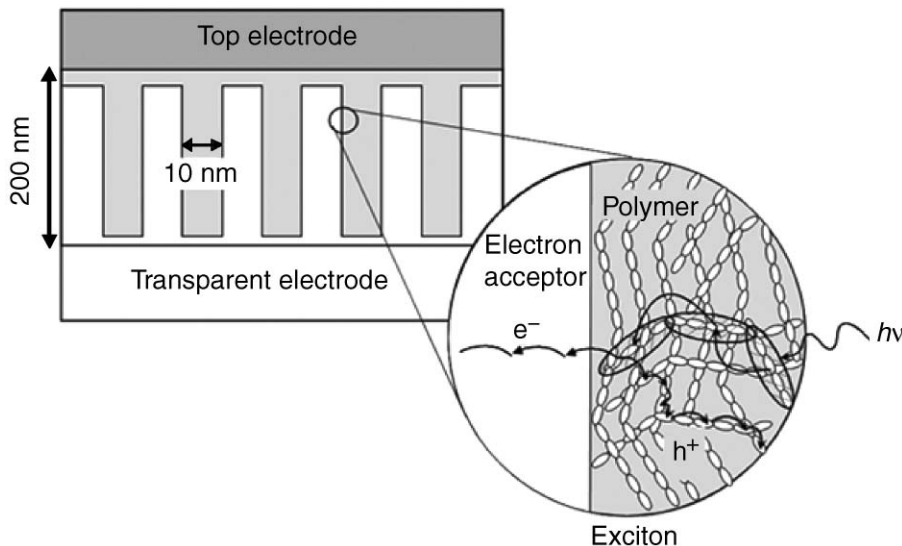


Figure 1. Schematic illustration of an ideal ordered bulk heterojunction photovoltaic cell. An incident photon is indicated by $h\nu$. The enlarged circle represents an exciton.

for Improved Hole Transport.^{9,14} Unfortunately, the films made so far do not have pores running straight from the top of the film to the bottom. Films with hexagonal arrays of straight pores can be made, but the pores run in the plane of the film.

In the last few years, there has been tremendous progress in synthesizing nanowires.¹⁵ Several research groups are growing ZnO nanowires on nanocrystal nucleation sites to create brushes of nanowires with nearly optimal dimensions.¹⁶ An example is shown in Figure 2b. We expect that photovoltaic cells will be made with these brushes in the near future.

Incorporating Polymers into Nanopores

There are several options for incorporating conjugated polymers into nanopores or the space between nanowires. Tolbert et al. demonstrated that poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) chains can be diffused from solution into mesoporous silica films with pores in the 3–5-nm-diameter range if the pore walls are coated with hydrophobic silylating agents.^{17,18} Furthermore, they used polarized absorption and emission spectroscopy to show that the chains are highly aligned in these

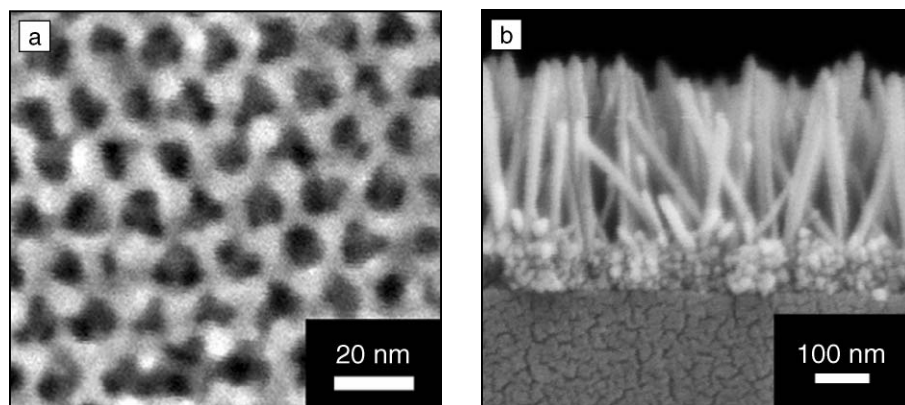


Figure 2. Scanning electron microscope images of (a) mesoporous titania (plan view) and (b) a brush of zinc oxide nanowires (cross-sectional view). (Figure 2a reprinted from Reference 11 with permission from the American Institute of Physics, copyright 2003; Figure 2b courtesy of S. Shaheen, National Renewable Energy Laboratory.)

narrow pores. We have found that regular poly-3-hexylthiophene (P3HT), a polymer often used in field-effect transistors because of its high charge carrier mobility, can be infiltrated into mesoporous titania films by spin casting a film and then heat-treating it at temperatures in the range of 100–200°C.¹⁴ More than 80% of the pore volume can be filled with this technique in just a few minutes. We have also shown that 3-methylthiophene can be electropolymerized in mesoporous titania from the bottom electrode up to the top of the film.¹⁹ Although this technique is great for completely filling the pores, a problem with it is that the polymer must be in contact with the bottom electrode. It is best to have a barrier between the polymer and the electron-withdrawing electrode, so that holes can only diffuse in the desired direction to the hole-withdrawing electrode.^{20,21}

Performance of Photovoltaic Cells and the Need for Improved Hole Transport

In a polymer–titania photovoltaic cell, the nanostructured film is sandwiched between a transparent, conducting-oxide bottom electrode and a high-work-function metal top electrode (Figure 3a).^{4,10} Fluorine-doped tin oxide is preferred for the transparent electrode over indium tin oxide because indium diffuses into the titania when it is heated to 400°C. We have found that open-circuit voltage and short-circuit current are higher if silver is used as the top metal instead of gold or aluminum, but the silver only works well if the devices are annealed for several hours at 150°C. The annealing probably oxidizes the metal at the interface with the polymer, which raises its work function. After the polymer absorbs light, excitons diffuse to the interface with the titania. Electrons then transfer to the titania because the bottom of its conduction band lies approximately 4.2 eV below vacuum level, while the lowest unoccupied molecular orbital (LUMO) of most polymers is around 3 eV below vacuum. From there, electrons travel through the titania to the bottom transparent electrode and holes travel through the polymer to the top electrode.

The short-circuit current and the quantum efficiency of the device depend on how many of the charge carriers reach the electrodes before recombination occurs by back-electron transfer from the titania to the highest occupied molecular orbital (HOMO) of the polymer. To see how far charge can travel in polymer-filled mesoporous titania films, like those shown in Figure 2a, before back transfer occurs, we have varied the depth of infiltration of the polymer into 200-nm-thick mesoporous titania films by

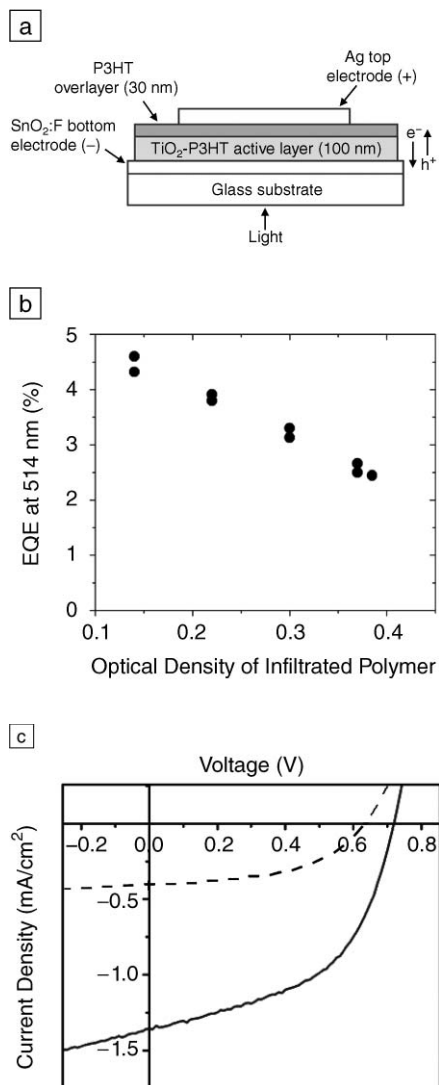


Figure 3. (a) Schematic illustration of a photovoltaic (PV) cell made with poly-3-hexylthiophene (P3HT) infiltrated into mesoporous titania. (b) External quantum efficiency (EQE) of photovoltaic cells made with varying amounts of infiltrated polymers. The amount of polymer is quantified by its optical density, i.e., how much light is absorbed at 514 nm. For each PV cell, both the mesoporous titania thickness and the P3HT overlayer thickness were held constant at 200 nm and 50 nm, respectively. (c) Current density–voltage curve under 33 mW/cm² 514 nm illumination for a PV cell made with P3HT infiltrated into a 100-nm-thick layer of mesoporous titania (solid curve). For comparison, the current density–voltage curve for a nonporous TiO₂-P3HT bilayer device is also shown (dashed curve). (Reprinted from Reference 11 with permission from the American Institute of Physics, copyright 2003.)

adjusting the time used for the melt infiltration.⁹ A 30-nm-thick polymer overlayer was used for each device to prevent electrons in the titania from reaching the top electrode. The amount of polymer in the pores was determined by measuring the optical density before the overlayer was spin-cast. The external quantum efficiency of the devices as a function of the amount of infiltrated polymer is shown in Figure 3b. Unfortunately, the efficiency of the device drops as more polymer is incorporated. This suggests that when light is absorbed near the bottom of the device, holes cannot travel through the film before back-electron transfer occurs. Holes are only able to escape if the excitons are formed within ~ 10 nm of the top of the titania film.

The best polymer–titania PV cell fabricated in our lab was made by infiltrating a 40 nm P3HT layer into a 100 nm mesoporous TiO₂ layer for 1 min at 200°C.⁹ A 30 nm thickness of the P3HT remained above the titania. The current density–voltage curves for 33 mW/cm² 514 nm illumination are shown in Figure 3c. The external quantum efficiency of this device was 10%. The open-circuit voltage was 0.72 V, and the fill factor was 0.51. The monochromatic power conversion efficiency was 1.5%. By analyzing the efficiency as a function of wavelength, we have estimated that the efficiency under solar AM 1.5 conditions would be approximately 0.5%. Figure 3c also shows a current–voltage curve for a device made with a solid titania film instead of a mesoporous one. The device with mesoporous titania is approximately three times more efficient.

To directly measure hole transport in polymers inside of mesopores, we have made mesoporous silica films, which are almost identical to the mesoporous titania films used in the PV cells, and filled them with P3HT.²² Because silica is a good insulator, all of the current that passes through these films travels in the polymer. We made diodes by sandwiching the film between two high-work-function electrodes, which can only inject holes. We measured the current through these diodes in the dark and found that it could be fit to a space-charge-limited current model.²³ The hole mobility we extracted from the fit was only 10^{-8} cm²/V s. For comparison, the mobility found in a space-charge-limited current diode with just P3HT between the electrodes was 3×10^{-4} cm²/V s. We attribute the extremely low hole mobility of the polymer in the mesopores to the chains being coiled and not π -stacked on each other. Evidence for this is a highly blue-shifted absorption and photoluminescence spectrum, which arises in conjugated polymers when chains are coiled

since the charge carriers are more confined.¹⁴ Another reason the mobility is low is that the diameter of the pores varies in the mesostructures, creating constrictions that the carriers have to pass through.

It is well known that regioregular P3HT can have a mobility as high as 0.1 cm²/V s in field-effect transistors (FETs).^{24,25} The mobility is higher in FETs than diodes because the polymer chains form a semi-ordered lamellar structure on the transistor's gate dielectric. Charge can move relatively easily in the plane of the film because it can travel along the polymer chain backbones or between the chains, which are π -stacked on each other.²⁶ Transport in the direction perpendicular to the substrate is more difficult because the non-conjugated side chains separate most of the conjugated backbones in this direction. With this in mind, we expected that the mobility of P3HT in nanopores could be significantly enhanced if the chains were aligned on the surface of straight pore walls. We made films with straight pores running from the bottom electrode to the top by anodizing alumina.²⁷ We then melt-infiltrated the P3HT as before and analyzed the current density–voltage curves in the space-charge-limited current regime. We found that for 75-nm-diameter pores, the mobility is 6×10^{-3} cm²/V s, which is a factor of 20 higher than in a film of just the polymer. Measurements of the transmission and reflection of polarized light through the films show that the chains are only partially aligned by the pores.²⁸ We think that better alignment and higher charge carrier mobilities can be achieved by treating the surface of the pore walls and optimizing the size of the molecules. We are in the process of making films with straight pores in a suitable semiconductor for a photovoltaic cell.

Outlook

Studies of films made with polymers infiltrated into nanoporous films^{9,29} have clearly shown the need for improving the hole mobility of the organic semiconductor and that this can be done by aligning polymer chains along pore walls. A key to raising device efficiency will be finding a way to fabricate films with straight pores of optimal diameter and spacing in suitable semiconductors. Other crucial issues, not addressed in this article, will be extending the range of exciton diffusion, slowing down back-electron transfer, using lower-bandgap semiconductors to absorb more light, and optimizing the energy levels to obtain the highest possible open-circuit voltage. The approach of making porous films and filling them with organic semiconductors will enable systematic studies of these issues since each component in the system

can be changed without affecting the geometry of the films. These studies should teach us how to design cells with energy conversion efficiencies approaching 20%.³⁰ We hope that these design rules will assist others in the field in finding a way to produce efficient, self-assembled photovoltaic cells.

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