Nanostructured Organic–Inorganic Hybrid Solar Cells

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The following article is based on the Outstanding Young Investigator Award presentation given by Michael McGehee of Stanford University on April 12, 2007, at the Materials Research Society Spring Meeting in San Francisco, California. McGehee was cited “for his innovation in the application of organic semiconductors in lasers, light-emitting diodes, transistors, and solar cells.” This article describes his research on organic solar cells.

Abstract

When light is absorbed in organic semiconductors, bound electron–hole pairs known as excitons are generated. The electrons and holes separate from each other at an interface between two semiconductors by electron transfer. It is advantageous to form well-ordered nanostructures so that all of the excitons can reach the interface between the two semiconductors and all of the charge carriers have a pathway to the appropriate electrode. This article discusses charge and exciton transport in organic semiconductors, as well as the opportunities for making highly efficient solar cells and for using carbon nanotubes to replace metal oxide electrodes.

Introduction

It is becoming increasingly clear that we must find a way to provide the world’s population with terawatts of power without releasing carbon into the atmosphere in order to prevent undesirable climate change. In his plenary talk at the Spring 2007 Materials Research Society Meeting, Nathan Lewis described this challenge and went on to show that solar cells are likely to be a significant part of the solution. Here, I focus on solar cells themselves.

Almost all solar cells installed today are made of crystalline silicon. The production of these cells is growing by approximately 35% each year, and the costs are dropping as the industry matures. In the next decade, we will likely see that obtaining electricity from solar cells will be cheaper than obtaining it from conventional power plants in certain areas such as my home state of California, where sunlight is abundant and electricity is expensive. This is great news for those of us striving to reduce carbon emissions. Nonetheless, it is irresistible to dream of even better technologies, for example, making solar cells in roll-to-roll coating machines similar to those used to make photographic film or newspapers. Such cells would be thin and flexible and could be incorporated directly into roofing shingles in order to reduce packaging and installation costs.

Organic semiconductors can be evaporated, printed, spin cast, or sprayed onto plastic substrates at low temperature and are therefore very attractive for solar cell applications. The January 2005 issue of MRS Bulletin focused on this subject and described the approaches that several prominent researchers around the world are taking to make organic solar cells. In the most common approach, two semiconductors with offset energy levels are patterned around each other at the nanometer length scale to form what is known as a bulk heterojunction (Figure 1). When one of the semiconductors absorbs light, a bound electron–hole pair known as an exciton is generated. The exciton travels to the interface either by diffusion or by Förster energy transfer. (In Förster energy transfer, an electronic excitation moves by dipole–dipole coupling between donor and acceptor molecules. It does not involve the transfer of radiation.) At the interface, the exciton dissociates by electron transfer. The electron then travels through the electron-accepting material to one electrode while the hole travels through the other material to the second electrode.

Most bulk heterojunction solar cells have been made by casting solutions containing the two semiconductors (e.g., a conjugated polymer and a fullerene derivative or nanocrystals) to make blends. Although these blends are easy to fabricate and use of this simple process to manufacture solar cells is desirable, there are problems that are typically created within the disordered nanostructures. In some cases, the two semiconductors phase separate on too large of a length scale. Consequently, some of the excitons are not able to make it to an interface to be split by electron transfer before they decay. In other cases, one of the phases can contain dead ends or islands that prevent charge carriers from reaching the electrodes.

Ordered bulk heterostructure solar cells, such as the one shown schematically in Figure 1d, are harder to fabricate than disordered blends, but there are several good reasons to make them. First, the dimensions of both phases can be controlled to make sure that every spot in the film is within an exciton diffusion length of the interface between the two semiconductors. Second, there are no dead ends in the structure. After excitons are split 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 solar cell research, is that ordered structures are much easier to model and understand.

Making Ordered Bulk Heterojunctions

Because of recent advances in nanofabrication, many techniques are now available for patterning films at the 10-nm length scale. Making an efficient solar cell, however, is still a great challenge because there are numerous essential properties that put constraints on the materials that can be used. One must make films that are 200–400 nm thick so that most of the incident light on the solar cell can be absorbed. The phases should be straight, aligned perpendicular to the electrodes, and connected only to the appropriate electrodes. Furthermore, the energy levels of the semi-
 conductors must be chosen carefully so that most of the solar spectrum is absorbed, excitons are split by electron transfer, and a significant voltage is generated.

The first approach my group chose for making ordered bulk heterojunction solar cells was to self-assemble nanoporous titania films and then infiltrate semiconducting polymers into the pores. Titania films with arrays of nanopores were made by evaporation-induced self-assembly.7–9 A solution containing a structure-directing block copolymer and titanium ethoxide was dip coated onto these films. As the solvent evaporated, the titania precursor and the more hydrophilic polymer block separated from the more hydrophobic block. The films were then heated to approximately 280°C to oxidize and remove the block copolymer. Finally, the films were heated to around 400°C to convert the amorphous titania into anatase nanocrystals. A scanning electron microscope image of a film made in this way is shown in Figure 2.

We found that regioregular poly(3-hexyl thiophene) (P3HT), a polymer that is often used in field-effect transistors (FETs) because of its high charge-carrier mobility, can be infiltrated into mesoporous titania films by spin casting a film and then heating it at temperatures in the range of 100–200°C.10 More than 80% of the pore volume can be filled by this technique in just a few minutes. We also found that 3-methyl thiophene can be electropolymerized in mesoporous titania from the bottom electrode up to the top of the film.11 Although electropolymerization is great for completely filling the pores, a problem with this approach 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-drawing electrode so that holes can diffuse only in the desired direction to the hole-withdrawing electrode.12,13

Figure 1. Polymeric solar cell heterojunctions. (a) Energy diagram of a heterojunction with an exciton in the polymer phase. (b) In a bilayer heterojunction, the semiconductor must be thin to utilize all excitons. In order to have every exciton separated, a heterojunction must exist within an exciton diffusion length. This can be achieved (c) in a bulk heterojunction or (d) in an ordered heterojunction. Note: PEDOT is poly(3,4-ethylenedioxythiophene), PSS is poly(styrene sulfonate), ITO is indium tin oxide, and FTO is fluorine-doped tin oxide.

Figure 2. Scanning electron microscope image of mesoporous titania (plan view). Reprinted from Reference 10. © 2003, American Institute of Physics.

Performance of Solar Cells and the Need for Improved Hole Transport

In a polymer–titania solar cell, the nanostructured film is sandwiched between a transparent conducting oxide bottom electrode and a high-work-function metal top electrode (Figure 3a).14 Fluorine-doped tin oxide is preferred for the transparent electrode over indium tin oxide because indium diffuses into the titania when the assembly is heated at 400°C. We found that silver is a better top metal than gold or aluminum, but it works well only 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. Silver is probably better than gold because of its higher reflectivity. After the polymer absorbs light, excitons diffuse to the interface with titania. Electrons then transfer to the titania because the bottom of titania’s conduction band lies approximately 4.2 eV below vacuum level, whereas the lowest unoccupied molecular orbital (LUMO) of most polymers lies 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 best solar cells made with P3HT and mesoporous titania convert only 0.5% of the energy in the solar spectrum into electricity. We tested cells with polymer infiltrated at varying depths into the titania and discovered that charge transport is so poor in the polymer that the holes cannot escape the device.14

Charge Transport in the Polymer

To directly measure hole transport in polymers inside mesopores, we made mesoporous silica films that were almost identical to the mesoporous titania films used in the solar cells and filled them with P3HT. 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 inject only 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. The hole mobility extracted from the fit was only 10−4 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).15 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 morphology
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is a highly blue-shifted absorption and photoluminescence spectrum, which arises in conjugated polymers when chains are coiled because the charge carriers are more confined. Another reason for the low mobility is that the diameter of the pores varies in the mesostructures, creating constrictions through which the carriers have to pass. It is well-known that regioregular P3HT can have a mobility as high as 0.1 cm²/(V s) in FETs.16,17 The mobility is higher in FETs than in 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.15 Transport in the direction perpendicular to the substrate is more difficult because the nonconjugated side chains separate most of the conjugated backbones in this direction.

With the direction of easy transport 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.19 We then melt infiltrated the P3HT as before and analyzed the current–voltage curves in the space-charge-limited current regime. We found that, for 75-nm-diameter pores, the mobility was 6 × 10⁻³ cm²/(V s), which is a factor of 20 higher than that in a film of just the polymer.20 Measurements of the transmission and reflection of polarized light through the films showed that the chains were only partially aligned by the pores. We believe 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.

Fabricating Nanostructures with Straight Pores

The studies of P3HT in anodic alumina pores showed that aligning polymer chains in straight pores enhances the charge-carrier mobility to a point that is thought to be adequate to remove charge from solar cells at the same rate as it is generated by the sun. This inspired us to make semiconductor films with straight smooth-walled pores having diameters in the range of 10–20 nm, lengths of 200 nm or more, and an orientation perpendicular to the substrate.

The first approach we took was nanoimprinting (Figure 4).20 We filled the pores of an anodic alumina film with poly(methyl methacrylate) (PMMA) to make a mold for nanoimprinting titania. This polymer was chosen because it is relatively stiff and not as prone to distortion as other polymers often used for embossing, such as poly(dimethylsiloxane) (PDMS). We found that the high-aspect-ratio pillars of PMMA could not be pulled out of the anodic alumina without tearing, so we etched away the alumina in sodium hydroxide. We then pressed the PMMA mold into a film of titania sol–gel precursor that was not yet dry or condensed. It was necessary to use a thin film of PMMA so that the ethanol solvent could pass through it and enable the titania film to dry. A thicker film of PDMS was used on top of the PMMA to give it mechanical support. Once the titania was solidified, we used toluene to dissolve the PMMA, leaving the desired nanoporous film. A scanning electron microscopy image of a film with 40-nm-diameter pores is shown in Figure 4 g. Unfortunately, we were not able to make the pores as narrow as we wanted in 200-nm-thick films because the PMMA molds were not mechanically stable enough. The pillars bent over and distorted the pattern.

We also used block copolymer lithography to make arrays of nanopillars, as shown in Figure 5.21 A poly(styrene–b–methyl methacrylate) block copolymer was cast onto a silicon substrate and annealed in such a way that a hexagonal pattern self-assembled. The PMMA blocks were removed by degrading the polymer in ultraviolet light and etching the film in acetic acid. A chromium etch mask was deposited into the holes that were left behind. The silicon was then reactive ion etched with NF₃ gas, leaving behind silicon nanopillars. Solar cells were made by infiltrating P3HT into nanoporous amorphous silicon. The efficiency was only 0.3% because the pores in the silicon were still too large for all of the excitons to diffuse to the interface. Furthermore, we found that when amorphous silicon absorbs light, the holes formed in it get trapped and are not transferred to the polymer to generate photocurrent.22 Amorphous silicon was chosen for the studies because it could be deposited onto transparent electrodes and etched easily. Work is under way to use reactive ion etching to deposit titania and other semiconductors that could perform better in solar cells.
Exciton Transport and Improving it with Energy Transfer

It would be much easier to fabricate well-ordered bulk heterojunction solar cells if the exciton diffusion length ($L_D$) were 20 nm or larger. Before one can even begin to optimize $L_D$, one must have a reliable method for measuring it. A popular method is to deposit organic semiconductor films of varying thickness onto glass and another substrate that can quench excitons by electron transfer, and then analyze the photoluminescence. In films much thinner than an exciton diffusion length on the quenching substrate, there is no photoluminescence because the excitons all reach the quencher. Curves of luminescence versus thickness can be fit to diffusion models to determine $L_D$.

Early applications of this method led many to believe that some common conjugated polymers had diffusion lengths of 20 nm. More recent work has shown that typical values of $L_D$ for conjugated polymers are around 6 nm. The precautions that need to be taken to obtain an accurate value include making sure that the two layers have a sharp interface, that Förster energy transfer does not occur between the two layers, and that interference effects are taken into account. A good way to measure $L_D$ accurately is to use a 5-nm-thick layer of titania on a glass as the quenching substrate. Titania does not diffuse into the organic semiconductor and cannot accept energy from the semiconductor because of its large bandgap. The thinness of the film enables the optical interference effects to be negligible.

It is interesting to estimate $L_D$ for semiconducting polymer films. If we first assume that there is no energetic disorder and that excitons hop from one site in the film to other neighboring sites by Förster energy transfer, simple diffusion theory suggests that $L_D$ should be between 40 and 160 nm, depending on how much overlap there is between the absorption and emission spectra and how well the polymer emits. $L_D$ is clearly much smaller than this estimate. The discrepancy almost certainly arises because there is energetic disorder, and excitons get stuck in low-energy sites. Evidence for this explanation is the observation in ultrafast spectroscopic measurements that luminescence shifts to lower energy over time after an initial excitation.

One strategy to collect excitons over a larger distance is to choose the donor and acceptor semiconductors such that Förster energy transfer can occur between the two. In this case, the exciton gets to the acceptor in one long movement instead of by a random walk of small steps. To demonstrate this technique, we deposited films of a strong emitting polymer, Dow Red, on a small-bandgap polymer and on titania. With the small-bandgap polymer, the photoluminescence in Dow Red can be quenched by either energy transfer to the substrate or exciton diffusion followed by electron transfer. With titania, the photoluminescence in Dow Red can be quenched only by exciton diffusion followed by electron transfer. Plots of the fraction of excitons harvested versus the Dow Red film thickness (Figure 6) show that the effective diffusion length is 27 nm when energy transfer is enabled and only 3 nm when it is not.

Transparent Electrodes

To revolutionize the way people obtain electricity with organic solar cells, it will

Figure 4. Schematic diagram of the processes involved in nanoimprinting titania: (a) preparing anodic alumina template, (b) infiltrating poly(methyl methacrylate) (PMMA), (c) coating on poly(dimethylsiloxane) (PDMS), (d) retrieving stamp by wet chemical etching, (e) embossing TiO$_2$ sol–gel, and (f) removing the stamp. (g) Scanning electron microscopy image of embossed TiO$_2$ structures on fluorine-doped tin oxide (FTO) substrate after calcinations (cross section). Reprinted with permission from Reference 20. © 2005, Chemical Society.
be necessary to manufacture them at a cost of about $30/m². To achieve this cost with high-throughput roll-to-roll coating machines, it will be essential to develop new ways to deposit an improved transparent conductor. Sputtering of metal oxides such as indium tin oxide (ITO) and Al-doped zinc oxide is currently too expensive because slow deposition on heated substrates is needed to obtain sufficient film quality. Moreover, ITO is unattractive because the supply of indium is already almost completely exhausted by the flat-panel display industry, which manufactures far less electrode area than a successful solar industry would. It is highly desirable to develop a method for depositing transparent conductors based on abundant (carbon) materials. One can do this, for example, by utilizing meshes of carbon nanotubes. We have made solar cells using carbon nanotube electrodes instead of ITO and found them to be only 17% less efficient. Cells with nanotube electrodes can be extremely flexible, as shown in Figure 7.28 It is likely that rapid progress will be made with this new approach to fabricating electrodes.

Outlook
Much progress has been made toward making efficient organic–inorganic hybrid solar cells. When inorganic films with straight pores are infiltrated with semicrystalline polymers, charge transport in both materials is adequate to extract charge at the same rate as it is generated by the sun without substantial recombination. It is still a challenge, however, to make structures with pores that are small enough to enable all of the excitons to be produced. This challenge will likely be met through advances in nanofabrication or through the new approach to harvesting excitons described in this work.

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Michael McGehee graduated from Princeton University with a degree in physics in 1994 after doing research on mesostructure self-assembly with Sol Gruner and Ilhan Aksay. He received a PhD in 1999 from the University of California at Santa Barbara (UCSB) for his research with Alan Heeger on the use of semiconducting conjugated polymers as materials for lasers and light-emitting diodes. After graduating, he studied self-assembly of block copolymer/metal oxide nanostructures in the research groups of Galen Stucky and Brad Chmelka at UCSB. In the spring of 2000, he joined the faculty of Materials Science and Engineering Department at Stanford University. McGehee won the MRS Gold Graduate Student Award in 1999, a Dupont Young Professor Award in 2001, and an NSF CAREER Award in 2001. He was a Gilbreth Lecturer at the National Academy of Engineering's 2006 National Meeting.

At Stanford, McGehee has led a group of students who make ordered organic–inorganic bulk heterojunction solar cells and study the electronic processes that occur in them. His group has also studied the effects of molecular packing on charge transport in polymer field-effect transistors and developed methods for improving light extraction from polymer light-emitting diodes. He teaches classes on nanotechnology, polymer science, organic electronics, and solar cells. McGehee is also Director of the Center for Advanced Molecular Photovoltaics, which is funded by the King Abdullah University of Science and Technology.

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