Photovoltaic cells made from conjugated polymers infiltrated into mesoporous titania

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We have made photovoltaic cells by infiltrating the conjugated polymer regioregular poly(3-hexylthiophene) into films of mesoporous titania, which are self-assembled using a structure directing block copolymer. The mesoporous titania films were chosen because they have pores with a diameter slightly less than 10 nm, which is the exciton diffusion length in many conjugated polymers, and because they provide continuous pathways for electrons to travel to an electrode after electron transfer has occurred. The photovoltaic cells have an external quantum efficiency of 10% and a 1.5% power conversion efficiency under monochromatic 514 nm light. Experiments that vary the amount of polymer in the titania films suggest that the performance of the cells is limited by poor hole transport in the polymer. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1616197]

An important challenge in making efficient organic photovoltaic (PV) cells is preventing the geminate recombination of excitons. Since a built-in electric field is usually not sufficient to split excitons, a popular approach for achieving charge separation in organic films is to incorporate an electron accepting material, such as a C_{60} derivative,[1–3] sintered TiO_2 nanocrystals,[4–7] CdSe nanocrystals,[8,9] or another conjugated polymer,[10,11] into the film. Because excitons in organic films can typically travel less than 20 nm before recombining,[12,13] the electron acceptor must be intermixed on the nanometer length scale with the organic semiconductor in order to obtain a high charge separation yield. After electron transfer occurs, the electron and hole must be transported to the electrodes of the device before back recombination occurs. Since in many cases the electron accepting network is formed by randomly interspersing nanocrystals or molecules into the organic film, charge transport in the photovoltaic cell can be limited by the hopping of electrons along a poorly formed network. In both the processes of charge separation and charge transport in these films, it is apparent that the precise geometrical arrangement of the electron accepting network is tantamount to making efficient photovoltaic devices. Previously we have demonstrated that 50- to 300-nm-thick mesoporous films of titania with fairly well ordered arrays of uniformly sized pores can be made using a block copolymer structure directing agent and that the pores can be filled with the semiconducting polymer regioregular poly(3-hexylthiophene) (P3HT).[14] In this letter, we report on the photovoltaic properties of these films. In PV cells of this type, the P3HT absorbs light, carries excitons to the polymer/TiO_2 interface, and transports holes to the metal top electrode. The mesoporous TiO_2 accepts electrons from the conjugated polymer and transports them to the transparent bottom electrode.

We make mesoporous TiO_2 films by first dip coating a titanium ethoxide–block copolymer precursor mixture on a conducting glass substrate, and then calcining the films at 400–450 °C to remove the structure-directing block copolymer and partially crystallize the TiO_2.[15] Figure 1 shows a top view high-resolution scanning electron microscope (HRSEM) image of a mesoporous TiO_2 film that has been deposited on a fluorine-doped tin oxide (SnO_2:F) substrate and calcined at 400 °C. We used SnO_2:F as the transparent electrode in these studies instead of indium tin oxide (ITO), which had been used previously, because indium diffuses out of ITO electrodes during the calcination of TiO_2. Although mesoporous TiO_2 is not as well-ordered on SnO_2:F as it is on ITO following calcination, the pore size is still highly uniform. Each pore has a radius of less than 5 nm, which is smaller than a typical exciton diffusion length in a semiconducting polymer.

After making a mesoporous TiO_2 film, we spin cast a P3HT layer from a THF solution on top of the film and infiltrate the conjugated polymer into the mesoporous layer by heating the sample in a nitrogen atmosphere. Figure 2(a) shows the structure of photovoltaic cells made by infiltrating a 40-nm-P3HT layer into a 100-nm-mesoporous TiO_2 layer for 1 min at 200 °C. The optical density of the infiltrated P3HT in the pores of the TiO_2 is 0.1 at the peak of its absorption spectrum. In order to prevent electrons in the TiO_2 from reaching the silver electrode, the total thickness of the P3HT layer was chosen so that a 30-nm P3HT overlayer remained on top of the TiO_2 film following infiltration. Fig-

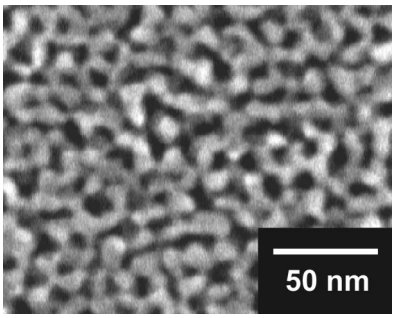

FIG. 1. HR SEM top view image of a mesoporous TiO_2 film following calcination at 400 °C. The pore diameter in the plane of the film is ~10 nm.

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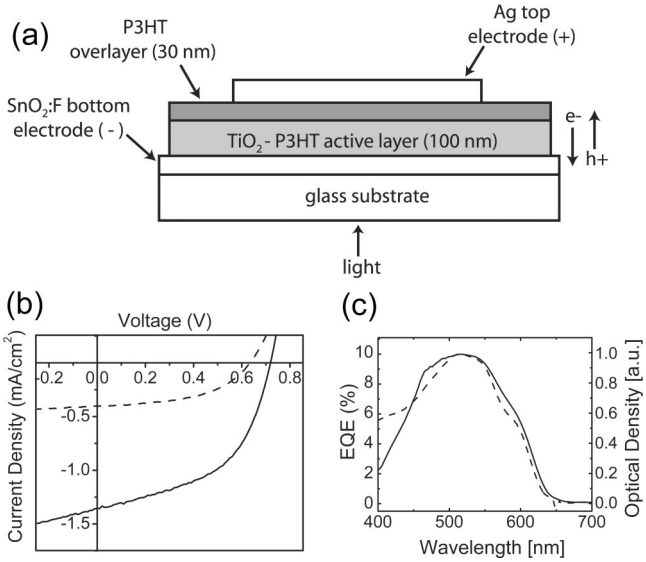

FIG. 2. Device structure and performance for photovoltaic cells made from mesoporous TiO_2 and P3HT: (a) Optimized device geometry. The electrode area was 5 mm^2; (b) $I-V$ curves for mesoporous TiO_2 (solid line) under 33 mW/cm^2 514 nm illumination. The $I-V$ curve of a sample made using nonporous TiO_2 (dashed line) is included for comparison; (c) external quantum efficiency vs wavelength (solid line) and absorption spectrum (dashed line) for a PV cell made from mesoporous TiO_2 and P3HT.

ure 2(b) shows the $I-V$ curve under 33 mW/cm^2 514 nm monochromatic illumination for a photovoltaic cell made with this structure. The external quantum efficiency (EQE) corresponding to 1.4 mA/cm^2 photocurrent is $\sim 10\%$. Multiplying the photocurrent by the fill factor (0.51) and open-circuit voltage (0.72) of the PV cell yields a power efficiency of 1.5%. By integrating the spectral response [Fig. 2(c)] of the PV cell over the solar spectrum, we estimate that the power efficiency of the cell would be $0.45 \pm 0.05\%$ under AM1.5 conditions.

In order to determine the relative contribution of excitons formed in the polymer overlayer and in the infiltrated polymer region to the photocurrent, we measured the EQE under 514 nm illumination from a series of PV cells with varying amounts of infiltrated polymer (Fig. 3). In these PV cells the optical density of infiltrated polymer was controlled by infiltrating P3HT into 200-nm-TiO_2 films for periods of time ranging between 0 and 10 min at 170 °C. Although PV cells made from these relatively thick TiO_2 films produce smaller photocurrents than PV cells made from thin films, a wider range of infiltrated polymer optical densities can be achieved using thick films. In order to achieve a constant total device thickness following infiltration of the polymer, the remaining polymer overlayer was rinsed off using toluene and replaced by a spin cast 50-nm-P3HT layer. Figure 3 shows that there is a monotonic decrease in EQE as the optical density of infiltrated polymer is increased. This is an indication that the charge generation in the cell occurs predominantly near the top of the TiO_2 film, and that polymer chains located in the bottom of the TiO_2 layer effectively act as a filter that prevents light from reaching the top interface.[16,17] This strongly suggests that the photocurrent in these cells is limited by the transport of holes to the top electrode of the device, and that holes generated more than 10–20 nm below the top of the TiO_2 film undergo back recombination with an electron on the TiO_2 before escaping the polymer-TiO_2 region. We believe that the poor hole transport on the infiltrated polymer chains results from an inability of the chains to π stack (crystallize) in the 8–10 nm TiO_2 pores. This hypothesis is supported by previously reported spectroscopy measurements,[14] which show a blueshift in the absorption and emission spectra from infiltrated P3HT chains.

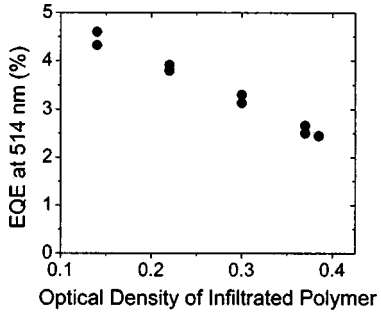

FIG. 3. EQE at 514 nm for PV cells with varying optical densities of infiltrated polymer. For each PV cell, both the mesoporous TiO_2 thickness and the P3HT overlayer thickness were held constant at 200 and 50 nm, respectively.

Despite the fact that holes in the polymer cannot traverse the entire TiO_2 film before recombining with electrons in the TiO_2, we have observed that photovoltaic cells made using mesoporous TiO_2 produce a larger photocurrent than devices made from nonporous TiO_2 [Fig. 2(b)], if the optical density of infiltrated polymer in the mesoporous film is kept below 0.1. Using a sample size of ten devices of each type, we found the 514 nm EQE of devices made with mesoporous TiO_2 to be $9.2\% \pm 0.8\%$, while the EQE of devices made with nonporous TiO_2 was $3.3\% \pm 0.4\%$. Both sets of devices had 40-nm-thick layers of P3HT and 100-nm-thick TiO_2 films. This demonstrates that the increased surface area of a mesoporous film enhances the photocurrent if the P3HT chains are not infiltrated too deeply into the TiO_2. Further optimization of this type of photovoltaic cell will require an improvement in the polymer chain morphology in the pores of the TiO_2 or modification of the interface between the TiO_2 and the polymer to reduce the rate of back electron transfer.

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