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Water-soluble polythiophene/nanocrystalline TiO₂ solar cells

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We report the characteristics of polymer/nanocrystalline solar cells fabricated using an environmentally friendly water-soluble polythiophene and TiO₂ in a bilayer configuration. The cells were made by dropping the polymer onto a TiO₂ nanocrystalline film and then repeatedly sweeping a clean glass rod across the polymer as it dried. The devices showed an open circuit voltage of 0.81 V, a short circuit current density of 0.35 mA/cm², a fill factor of 0.4, and an energy conversion efficiency of 0.13%. The water-soluble polythiophene showed significant photovoltaic behavior and the potential for use in solar cells. © 2005 American Institute of Physics. [DOI: 10.1063/1.1900300]

Organic semiconductors, including conjugated polymers^{1,2} and small molecular organic materials,^{3,4} have recently attracted much attention and show great promise in the ongoing effort to lower the cost of solar cells. These materials are usually soluble in common solvents. This leads to the possibility of making large area thin film solar cells using inexpensive liquid based processing techniques such as spin coating,⁵ doctor blading,⁶ ink jet printing, and screen printing.⁷ Often, the band gap and ionization potential can be tuned to the desired energies by modifying the chemical structure⁸ and solar cells made from polymers are commonly lightweight and flexible.

In these polymers, however, photogenerated excitons are strongly bound and resist dissociation into separate charges. Furthermore, these materials suffer from low charge mobility and short exciton diffusion lengths.⁹ Therefore, the performance of the solar cells made from homogenous polymer layers has been limited. This problem has been resolved in part by building bilayer and bulk heterojunction structures with phase separation between the polymer and certain inorganic nano-particles such as TiO₂ (Ref. 10) and CdSe.¹¹ Device efficiencies have increased steadily over the last decade and an external power conversion efficiency of 1.7% under AM1.5 illumination has been achieved.¹¹

Solvent-based polymers such as poly(2-methoxy-5-(2-ethyl-hexyloxy)-*p*-phenylenevinylene) [MEH-PPV],¹⁰ poly(3-hexylthiophene) [P3HT],¹² poly(3-octylthiophene) [P3OT],¹³ and poly(2-methoxy-5-(3,7-dimethyl-octyloxy)-*p*-phenylenevinylene) [MDMO-PPV] (Ref. 14) have been reported as electron donors in the TiO₂ based solar cells. The solvents typically used include toluene, chloroform, chlorobenzene, tetrahydrofuran (THF), xylene, and dichloromethane. The influence of the solvent on the performance of solar cells has been investigated by several groups^{12,15} and it has been found that by dissolving the polymer in the optimal solvent, extended polymer chains can be formed. When these solutions are then cast into thin solid films, the chains remain extended. As reported by Shi, Liu, and Yang,¹⁵ the effect of the solvent is more pronounced in high concentration solutions than in diluted solutions because of the inter-chain interactions.

In this work, we fabricated bilayer heterojunction solar cells using a water-soluble thiophene polymer (sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate]) [PTEBS], a polythiophene derivative, as the electron donor and TiO₂ as the electron acceptor. The device configuration was glass/FTO/TiO₂/PTEBS/Au and is shown in Fig. 1. Fluorinated tin oxide (FTO) coated glass squares (2.5 cm × 2.5 cm) were used as substrates. The FTO coated glass has a resistance of 12.5–14.5 Ω/square and layer thickness of 400 nm. The substrates were cleaned in ultrasonic baths first with acetone and then with deionized water.

To make the TiO₂ films, an anatase TiO₂ powder was first suspended in acetic acid (pH 3–4) and then stirred and heated for three hours. The TiO₂ films were made by spin coating onto the FTO twice at 2000 rpm. In our experiments, devices made with a single TiO₂ layer tended to develop shorts between the electrodes and therefore two layers of TiO₂ were deposited to prevent shunting. The TiO₂ was then sintered at 500 °C for one hour. This high temperature treatment of the TiO₂ film has two effects. First, it enhances the electronic contact between the TiO₂ particles and FTO electrode. Second, it results in a porous nanocrystalline network of interconnected TiO₂ particles.¹⁶ Atomic force microscopy of sintered nanocrystalline layers has revealed films with an average particle size of 80 nm and pore diameters of more

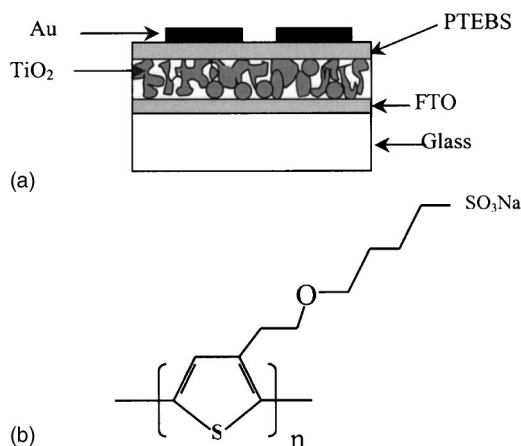


FIG. 1. (a) Schematic of glass/FTO/TiO₂/polymer/Au solar cells; (b) chemical structure of the water-soluble polythiophene (sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate]).

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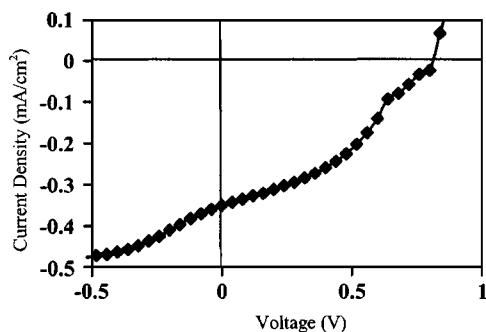


FIG. 2. Linear J - V curve in the fourth quadrant under 80 mW/cm^2 AM1.5 illumination.

than 20 nm .⁹ This pore diameter is large enough for the polymer to penetrate into the film.

The thiophene polymer (PTEBS) was obtained from American Dye Source¹⁷ and dissolved in deionized water to a concentration of 1%. A few drops of dimethylformamide were added in order to enhance dissolution. The solution was stirred for two days and then left for 24 h to allow undissolved particles to settle out. The chemical structure of the thiophene polymer is shown in Fig. 1(b).

Spin coating the polymer film is difficult due to the low viscosity of the water solution. Instead, a variation of the doctor blade technique was employed. The TiO_2 coated substrate was placed on a 50°C heating plate. The polymer solution was dropped onto the TiO_2 , and a clean glass rod was swept back and forth across the polymer film until it dried. The sample was then further dried in a vacuum oven at 150°C overnight to remove any remaining water. Finally, a mask was applied to the sample to define a $2 \text{ mm} \times 5 \text{ mm}$ device area and 50 nm of gold was sputter coated onto the polymer to serve as the electrode.

The devices were tested in the dark and under AM1.5 illumination with an intensity of approximately 80 mW/cm^2 through the FTO electrode. The current density-voltage (J - V) curve was measured using a Keithley 236 source generator by varying the voltage from -3 to 3 V in 0.04 V steps across the FTO and gold electrodes. The device has a rectification ratio of more than one order of magnitude in the dark, indicating diode behavior.

Figure 2 shows the linear current-voltage curve in the light in fourth quadrant. This indicates a short circuit current density of 0.35 mA/cm^2 and an open circuit voltage of 0.81 V . From the curve in Fig. 2, we calculated a fill factor (FF) of 0.40 using $\text{FF} = P_{\text{max}} / (I_{\text{SC}} V_{\text{OC}}) = (I_{\text{MP}} V_{\text{MP}}) / (I_{\text{SC}} V_{\text{OC}})$, where I_{MP} and V_{MP} are the current and voltage at the point of maximum power output of the device.

The energy conversion efficiency is defined as the ratio of the electric power output of the cell at the maximum power point to the incident optical power, which can also be expressed in terms of I_{SC} , V_{OC} , and FF as: $\eta = (\text{FF} \cdot V_{\text{OC}} \cdot I_{\text{SC}}) / P_{\text{light}}$. An energy conversion efficiency of 0.13% has been obtained for the water-soluble polythiophene solar cells described here.

The optical absorption of a homogeneous PTEBS film was measured with a Lambda 40 spectrometer and is shown in Fig. 3. The maximum absorption occurred at 480 nm . The onset of the absorption occurred at 620 nm , from which the band gap was estimated to be approximately 2.0 eV . Based on cyclic voltamperometry measurements made by Tran-

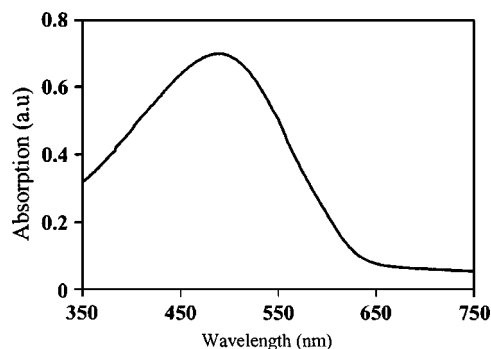


FIG. 3. Absorption spectrum of the water-soluble polythiophene in the visible spectrum.

Van, Carrier, and Chevrot¹⁸ in PTEBS thin films, the oxidation onset occurs at $\sim +0.3$ – $+0.4 \text{ V}$ versus saturated calomel electrode (SCE). The Highest Occupied Molecular Orbital (HOMO) level of the polymer can be estimated at the onset point. Typically, an adjustment factor of 4.4 to 4.7 eV is used in converting the energy values versus SCE into energy values versus vacuum. Therefore, the HOMO level is estimated to be between -4.7 and -5.1 eV . The optical gap of 2 eV results in a Lowest Unoccupied Molecular Orbital (LUMO) level between -2.7 and -3.1 eV .

Although the exact origin of the open circuit voltage in this type of device structure is not fully understood, it has been demonstrated¹³ that V_{OC} can be estimated by the difference of the work functions of the electrodes. This same estimate can be applied here. As seen in Fig. 4, the difference between the work functions of gold (5.2 eV) (Ref. 19) and of FTO (4.4 eV) (Ref. 20) matches the measured open circuit voltage ($V_{\text{OC}} = 0.81 \text{ V}$). In this particular case, however, the work function of the gold contact is very close to the HOMO level of the polymer (5.1 eV) and the work function of the FTO is close to the conduction band energy of the TiO_2 (4.2 eV).¹⁰ This makes it difficult to ascertain the influence of the polymer and the TiO_2 on the V_{OC} .

Interestingly, devices fabricated at room temperature show limited photovoltaic behavior, but devices fabricated on a 50°C hot plate performed well. This difference is not yet fully understood, but other studies have shown that solvent evaporation rates can have a significant influence on the performance of the devices due to changes in film morphology.^{12,21} Another possibility may be related to the solubility of the TiO_2 . Under standard conditions, the slowly evaporating water may interfere with the TiO_2 nanocrystalline network and therefore inhibit the electron transport path

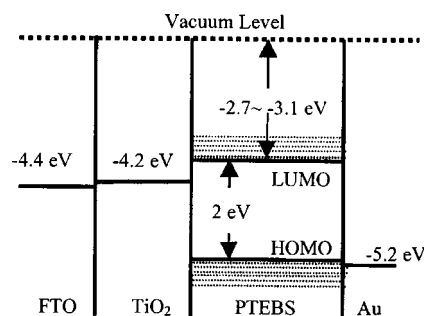


FIG. 4. Energy band diagram relative to vacuum level for FTO/ TiO_2 /PTEBS/Au devices. The work functions of FTO, TiO_2 , and gold are 4.4 eV (Ref. 20), 4.2 eV (Ref. 10), and 5.2 eV (Ref. 19), respectively.

in the completed devices. However, at 50 °C, the water evaporates much more quickly and does not have time to destroy the TiO₂ nanocrystalline structure.

One advantage of this water-soluble polymer is that the absorption spectrum can be “tuned” by changing the pH of the solution from basic to acidic. When the polymer is dissolved in water, the solution is orange in color and has an absorption band from 400 to 650 nm—similar to that shown in Fig. 3. However, if an acid such as HCl is added to solution, the color changes to green and a new absorption band from 600 to 800 nm is created. Films made from these basic and acidic solutions show similar optical characteristics.¹⁸ The additional absorption band in the infrared region offers the opportunity for improved light harvesting by building tandem junction cells. These cells would have layers made using both acidic and basic solutions in order to absorb a greater portion of the solar spectrum.

In summary, solar cells with a power conversion efficiency of 0.13% have been fabricated using a water-soluble polythiophene. The results show that the polymer provides significant photovoltaic response and has the potential to be used as an electron donor in solar cells, replacing solvent-based organic polymers. This may lead to lower costs and environmentally friendly processing for organic polymer solar cells. Further improvement may be achievable by building a bulk heterojunction structure since both PTEBS and TiO₂ are soluble in water. Work is underway to study this possibility.

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