PTEBS application in photovoltaic devices

QIQUAN QIAO AND JAMES T. MCLESKEY, JR.
Energy Conversion Systems Laboratory, Department of Mechanical Engineering
Virginia Commonwealth University, Richmond, VA 23284, USA
E-mail: jtmcleskey@vcu.edu

Over the last decade, conjugated polymer-based semiconductors have been developed as a novel class of photovoltaic materials that have the potential to lower costs. Solvent based polymers MEH-PPV, MDMO-PPV, P3HT, and P3OT have been reported as electron donors in photovoltaic devices. In this research, we studied the use of a water soluble polythiophene[1] - Sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate]) [PTEBS] in photovoltaic devices. Solar cells in two different configurations were fabricated: bilayer heterojunctions with TiO_2 and bulk heterojunctions with carbon nanotubes. The water-soluble polythiophene showed significant photoresponse and the potential for use in photovoltaics.

The thiophene polymer (PTEBS) was obtained from American Dye Source[1]. In addition the obvious environmental benefits, using water as the solvent offers other potential advantages. A primary advantage of this water-soluble polymer is its tuneability. Acidic solutions of PTEBS develop a new absorption band in the near-IR and films made from the self-acid form of the polymer show the same optical characteristics[2]. In our experiments, three solutions with 1% PTEBS by weight were prepared: a basic solution, a fresh acidic solution and an acidic solution that was left exposed to the air for a few days. The basic solution was made by adding a few drops of DMF to the PTEBS solution dissolved in deionized water. For acidic solutions, PTEBS was dissolved in a 3:1 volume ratio solution of hydrochloric acid (HCl, 35%) and deionized (DI) water. Thin films made from the three solutions were investigated. Figure 1 shows the appearance of the three films (fresh acidic (green), exposed acidic (orange), basic (dark orange)).

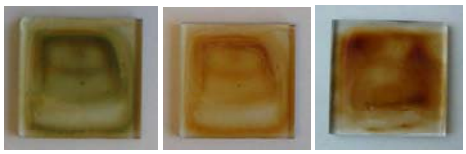

Fig. 1 The appearance of the fresh film from fresh HCl solution (green), HCl films exposed to air for several days (orange) and the basic solution of PTEBSNa (dark orange)

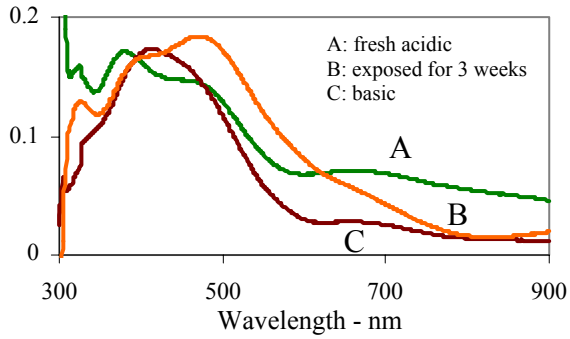

Fig. 2 The absorption spectra of the fresh acidic, exposed acidic and basic films

The absorption spectra were measured by the Lambda 40 UV-Vis spectrometer. As are shown in Fig. 2, our group has observed a new absorption band in the ultraviolet both in the fresh acidic film and the film after being exposed to air for three weeks. This is in addition to the red-near infrared (IR) absorption band reported by Tran-Van et al.[2]. After being exposed to the air for three weeks, the ultraviolet and red-near IR absorption bands in the acidic films had weakened somewhat, but are still stronger than in the films made from the basic solution. In addition, the absorption peak in the blue range has broadened to include both the ultraviolet and yellow bands, which will increase the total light absorption. Interestingly, we observed that the orange exposed acidic film changed its appearance back to green when exposed to HCl vapor. However, it turns orange again after staying in the air for a few days.

We used the PTEBS polymer as the electron donor and TiO_2 as the acceptor to fabricate bilayer heterojunction solar cells. The device configuration is Glass/FTO/TiO_2/PTEBS/Au and is shown in Fig. 3. Glass squares (2.5 cm x 2.5 cm) coated with fluorinated tin oxide (FTO) were used as substrates. The FTO coated glass has a resistance of 12.5-14.5 ohms/square and layer thickness of 400 nm. An anatase TiO_2 powder with a particle diameter of 22-25nm was suspended in acetic acid with pH value of 3-4 and then deposited by spin coating. The layer is then sintered at 500°C for an hour.

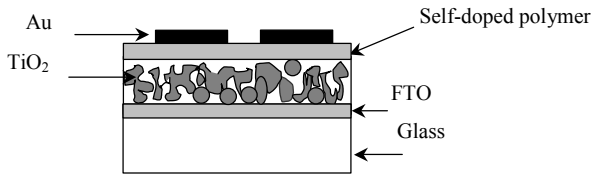

Fig. 3 Schematic of Glass/FTO/ TiO_2/polymer/Au solar cells

Solar cells were made using the PTEBS polymer from both acidic and basic solutions. After being stirred and centrifuged, the solution is dropped onto the TiO_2, and a clean glass rod is then swept back and forth across the polymer film until it dries on a 50°C heating plate. The sample is 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 2mm×5mm device area and 50nm of gold is sputter coated onto the polymer to serve as the electrode.

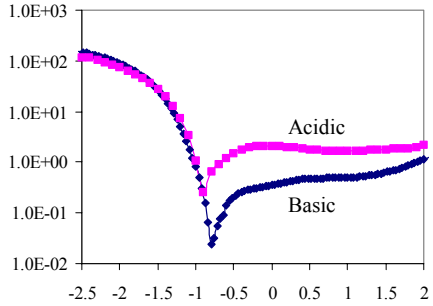

Fig. 4 The semi-log J-V characteristics in the light of solar cells made using acidic and basic polymer

The devices were tested in the dark and under illumination through the FTO electrode using AM1.5 spectral illumination with an intensity of approximately 80 mW/cm^2. The current density-voltage (J-V) curve was measured using Keithley 236 source generator sourcing the voltage from –2.5 V to +2.0 V in 0.04 V steps across the FTO and gold electrodes. The results are shown in Fig. 4. Both the basic samples and the exposed acidic samples showed noticeable photovoltaic effects and the results are summarized in Table 1. The improved output with the polymer dissolved in acid may be due to the increased absorptivity of the acidic films. Limited photovoltaic effects were observed in the fresh acidic (green) samples. This is likely because the high conductivity of the doped polymer causes the shunting. The conductivity decreases when the acidic sample is exposed to air for several days.

In addition to the TiO_2 / PTEBS bilayer cells, bulk heterojunctions using carbon nanotubes in the PTEBS have been tested. The cells do show some photoresponse and results are given in Table 1. To date, the results have not been as promising as with the TiO_2 cells, but further study is being done under way.

Table 1: Characteristics of PTEBS Solar Cells

Cell type	Open circuit voltage (V_{OC})	Short circuit current density(J_{SC})	Fill factor(FF)	Power conversion efficiency (η)
Basic bilayer	0.81 V	0.35 mA/cm^2	0.4	0.13 %
Acidic bilayer	0.9 V	2.12 mA/cm^2	0.41	0.92 %
SWNT bulk	0.65 V	0.47μA/cm^2	0.35	1.35×10^{-4} %

In addition to the obvious environmental benefits of using water as the solvent, the PTEBS polymer offers other potential advantages and opportunities for further study. Further performance improvement may be achievable by building a polymer/TiO_2 bulk heterojunction structure because both are soluble in water. In addition, acidic solutions of the polymer develop a new absorption band in the near-IR and films made from the self-acid form of the polymer show the same optical characteristics. This opens the possibility for building tandem junction cells with layers made using both acidic and basic solutions in order to absorb a greater portion of the solar spectrum.

[1] American Dye Source, Water Soluble Thiophene Polymer, http://www.adsdyes.com/products/pdf/polythiophene/ADS2000P.pdf, (2004).
[2] F. Tran-Van, M. Carrier, C. Chevrot, *Synthetic Metals* 142 (2004) 251-258.