JOURNAL OF MATERIALS SCIENCE **40** (2005) 1455– 1458

Water soluble polymer/carbon nanotube bulk heterojunction solar cells

J. A. RUD, L. S. LOVELL, J. W. SENN, QIQUAN QIAO, J. T. MCLESKEY, JR.*
Energy Conversion Systems Laboratory, Department of Mechanical Engineering, Virginia Commonwealth University, P.O. Box 843015, Richmond, VA 23284, USA
E-mail: jtmcleskey@vcu.edu

We report the characteristics of polymer/quantum dot solar cells fabricated using a water-soluble polymer and carbon nanotubes in a bulk heterojunction configuration. The water-soluble polythiophene polymer showed significant photoresponse and the potential for use in photovoltaics. The addition of carbon nanotubes to the polymer resulted in an order of magnitude increase in the photoconductivity. Improved charge separation and collection was evidenced by the large difference between light and dark conductivities as well as the increase in both open circuit voltage and short circuit current. Finally, photovoltaic cells using aligned nanotubes showed further improvement in the photoconductivity and IV characteristics.

1. Introduction

In order for photovoltaics to become competitive with other sources of terrestrial power generation, the cost per Watt must come down. One possible solution is the use of polymer-based semiconductors that have the potential to lower costs by utilizing inexpensive liquid based processing [1]. Conjugated polymers such as PPV [poly-(phenylene-vinylene)] [2] and its derivatives (e.g. MEH-PPV [1], MDMO-PPV [3], etc.) have been widely studied as photovoltaic materials in recent years [4]. Other groups have reported on results using the thiophene derivatives P3HT [poly(3-hexylthiophene)] [5] and P3OT [poly(3-octylthiophene)] [6].

In addition to low cost processing, photovoltaics made from polymers offer several prospective advantages. By modifying the chemical structure, the band gap and ionization potential can be tuned to the desired energies [7]. They are generally flexible which offers the possibility for integration into building materials and appliances [8]. However, while the absorption coefficients for these materials are high, they tend to absorb over a narrow spectral range compared to the solar spectrum [8]. In addition, because the excitons are strongly bound, they tend not to dissociate into separate charges. This means that the collection of charges is poor and devices made from homogeneous layers of these polymers have been inefficient [9]. Furthermore, these materials suffer from low charge mobility and short exciton diffusion lengths [10].

Quantum dots offer a potential solution to these deficiencies. Carrier generation in the polymer materials was improved with the discovery that charge separation tends to occur at a material interface [11]. Blending nano-crystals or quantum dots into a polymer creates a heterogeneous composite with a high interface surface area allowing for improved charge separation. If the polymer and quantum dot materials have different electron affinities, this will result in carrier transport in the different materials with a low likelihood of recombination [9]. Quantum dots have been fabricated from a number of materials including TiO_2 [10], CdSe [7, 9], CdS [12], carbon fullerenes [2], and carbon nanotubes [5, 6]. Conversion efficiencies approaching 4% have been achieved [1] and 5% appears to be within reach [8].

Nonetheless, many challenges remain to be solved in the fabrication of polymer/quantum dot composite photovoltaics before they become commercially viable. In particular, charge generation, carrier transport, and exciton dissociation have yet to be well understood and optimized [1]. In conjunction with poor light absorption, this leads to low photocurrents in comparison with inorganic cells [8].

This paper reports on two unique experiments. First, the polymer/quantum dot solar cells discussed in the paper have been fabricated using a water-soluble polymer. Though more study is needed, the water-soluble polythiophene polymer showed potential for efficient photovoltaic response. The use of this polymer would allow safe, environmentally friendly processing. In addition, the absorption range of the polymer is tunable by utilizing changes in the pH of the solvent [13] and could lead to tuneability within the solar cells. Second, single wall carbon nanotubes (SWNTs) have been added to form a bulk heterojunction and improve charge separation and transport. The addition of nanotubes to the polymer improved the output of the solar cells. The characteristic shape of the nanotubes is particularly conducive

*Author to whom all correspondence should be addressed.

to alignment and cells made with nanotubes aligned using an electric field [14, 15] have shown a further increase in photoconductivity as compared to non-aligned samples.

2. Sample preparation

Three different types of samples were fabricated: homojunctions consisting of only the water-soluble polymer sandwiched between tin oxide and aluminum contacts, bulk heterojunctions with carbon nanotubes added to the polymer, and bulk heterojunctions where the carbon nanotubes have been aligned (Fig. 1). The polymer used for all samples is a water soluble thiophene (Sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate]) obtained from American Dye Source [13] (see Fig. 2).

The carbon nanotubes used in the heterojunctions are single-wall CarboLex AP-grade with a diameter of 1.2–1.5 nm from Sigma-Aldrich [16] (see Fig. 2). The bulk length of the nanotubes is given as 20 μm but the individual length is not reported [16]. The polymer was first wetted with Dimethylacetamide (DMAc) and then dissolved in deionized water to a concentration of 3%. The nanotubes were added to 1% by weight. The solution was slightly basic. The polymer/nanotube solution was then sonicated and drop cast onto 2.5 × 2.5 cm fluoride doped tin oxide (FTO) coated glass substrates. The thickness of the FTO layer is 400 nm with resistivity of 12.5–14.5 ohms per square. The samples were cured on a hot plate at 150°C for 30 min. For some of the samples an electric field was used to align the nanotubes during curing [14]. Finally, a 250 nm thick aluminum rear contact was applied by horizontal sputtering. The rear contact was approximately 1 cm^2 for all samples. Sample thickness was checked with an Alpha-step 500 stylus profilometer and found to range between 2.5 and 8.5 μm. These relatively large thicknesses were necessary to avoid complete shunting of the cells by the nanotubes. Work is underway to fabricate and test thinner samples.

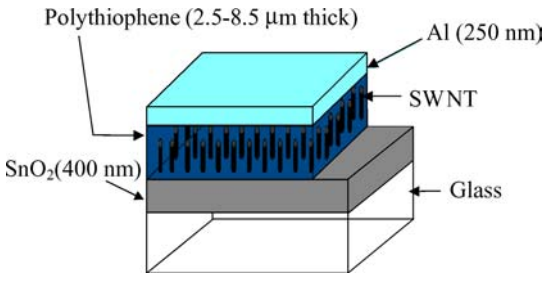

Figure 1 Schematic of SnO_2/polymer - SWNT/Al solar cells.

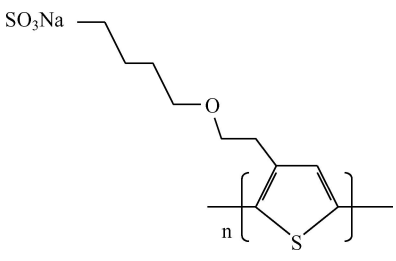

Figure 2 Water soluble thiophene (Sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate]) obtained from American Dye Source [13].

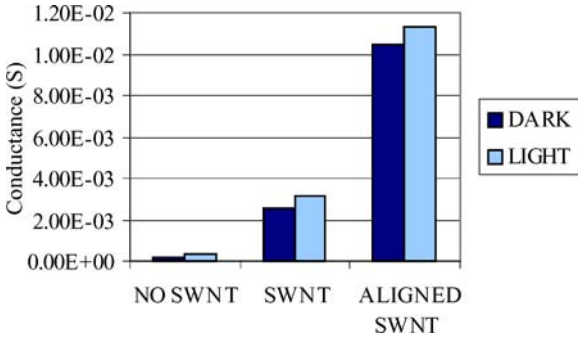

Figure 3 Dark and Light conductance in Siemens of homojunction, non-aligned heterojunction, and aligned heterojunction.

3. Characterization and results

All devices were illuminated through the glass using a tungsten halogen light source with an intensity of approximately 50 mW/cm^2. Light and dark conductances were measured using an HP 4284 Precision LCR meter. As shown in Fig. 3, the conductance of the neat polymer in the homojunction is quite low and the addition of carbon nanotubes greatly increased both the light and dark conductance. This is to be expected given the high conductivity of the nanotubes. More interesting, however, is the nearly order of magnitude increase in the conductance when the nanotubes are aligned. This provides indirect evidence that the alignment is, in fact, taking place.

The current-voltage (I-V) characteristics for each sample were tested using a Keithley 236 Source Generator by sourcing the voltage from –3 to + 3V in 0.1 V steps both in the dark and under illumination. Forward bias means that positive voltage is applied to the SnO_2. The I-V curves for each type of cell are shown in Figs 4a–c. In each case, the higher current in forward bias is evidence of diode behavior. This agrees with results of tests on similar cells made using solvent based polymers [17]. In Fig. 4a, the light current under reverse bias is less than the dark current—perhaps due to sample heating by the light source. The figure does show that, although the output is quite low, this water-soluble polymer does display a photovoltaic response and can be used to fabricate solar cells. Output is expected to increase with improved construction techniques. As can be seen in Fig. 4b, the addition of nanotubes doubles the forward current as compared to the pristine polymer. This is likely due to improved charge separation from the nanotube-acceptor [18]. When the nanotubes are aligned (Fig. 4c), they not only aid in charge separation, they also provide a better path to the electrodes and thus provide improved charge transport. This is evident in the order of magnitude increase in forward bias current at 3 Volts compared to that in Fig. 4b.

The open circuit voltage (V_{oc}) values and short circuit current (I_{sc}) values are given in Figs 5 and 6 respectively. The absolute magnitudes are quite low but the relative magnitudes show some interesting trends. The typical homojunction had a $V_{oc} = 0.9$ mV. The addition of nanotubes increased the V_{oc} to 3.0 mV in the non-aligned heterojunction. This three-fold increase is in line with that previously reported by Kymakis and Amartunga [17] for the solvent based polythiophene.

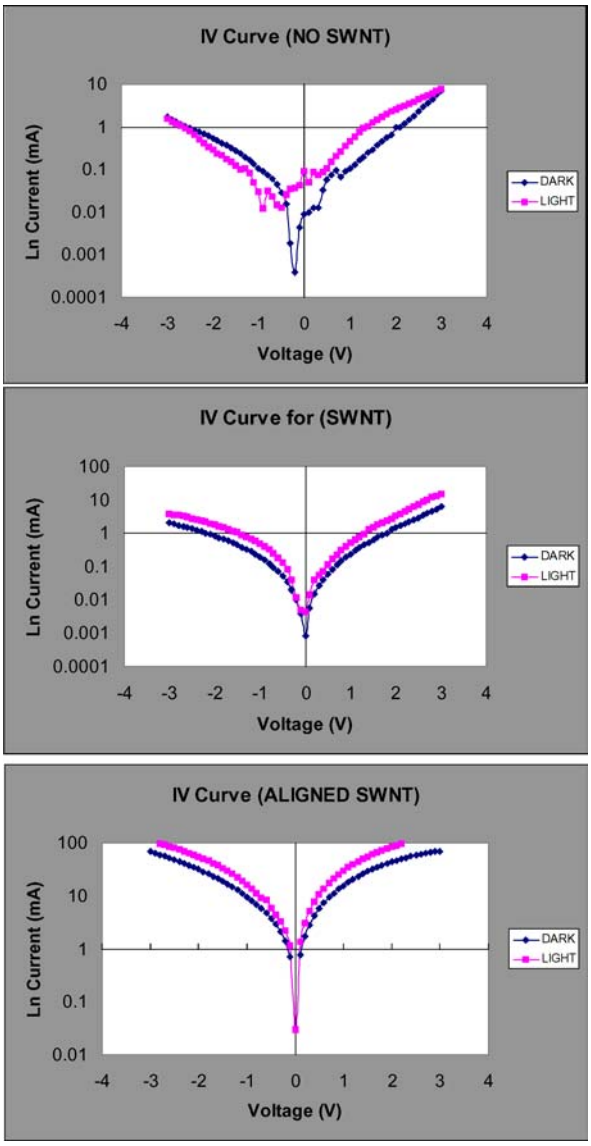

Figure 4 (a) I-V characteristics of homojunction in dark and under illumination. (b) I-V characteristics of non-aligned heterojunction. (c) I-V characteristics of aligned heterojunction.

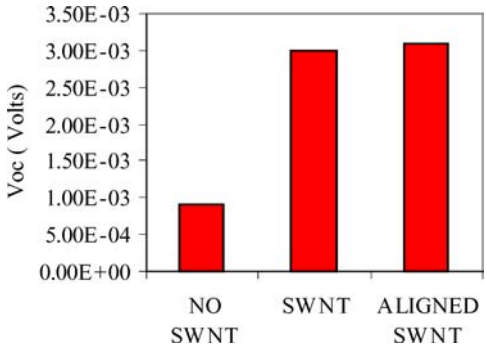

Figure 5 Comparison of open circuit voltage for homojunction, non-aligned heterojunction, and aligned heterojunction.

It has been postulated that the open circuit voltage is based on the work functions of the various materials [17] and so it is not surprising that alignment of the nanotubes had little effect on the V_{oc} (=3.1 mV for the aligned heterojunction). However, while the work function of the nanotubes is known to be approximately 4.5 eV [18], the HOMO value of the polymer is not yet

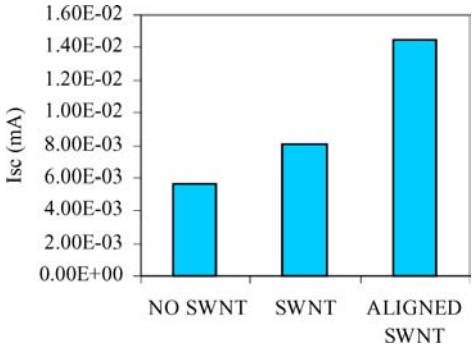

Figure 6 Comparison of short circuit current for homojunction, non-aligned heterojunction, and aligned heterojunction.

available and it is therefore not yet possible to determine the theoretical relation between the work functions of the constituent materials and the open circuit voltage for the cells described here.

The short circuit current density of the homojunction was $I_{sc} = 5.7\ \mu A/cm^2$—comparable to that for a solvent based polymer [17]. The addition of non-aligned nanotubes increased the current density by approximately 40% to $I_{sc} = 8.1\ \mu A/cm^2$. Aligning the nanotubes nearly doubled the short circuit current ($I_{sc} = 14.5\ \mu A/cm^2$), but the values are still quite low. It is believed that thinner samples and improved techniques for dispersing the nanotubes will improve these results.

4. Conclusions and future work

A water-soluble polythiophene polymer has shown photovoltaic response and has the potential to be used in applications where other organic polymers are used. This may lead to lower cost, environmentally friendly processing for organic polymer solar cells. Blending of SWNTs into the polymer as the electron acceptor improved the exciton dissociation caused by the built in potential [18]. Alignment of SWNT further enhances PV response and forms a better path for the carriers to reach the electrodes.

While these results are promising, there is tremendous opportunity for further study. The low V_{oc} and I_{sc} values need to be explained and work is underway to determine the HOMO value of the polymer films to allow theoretical calculations of the V_{oc}. While in solution, the absorption spectrum of the polymer changes with the pH of the solution. However, the absorption spectrum for polymer films made using water as the primary solvent have been found to be the same, regardless of the pH of the solution. In the future, using other solvents or adding other constituents to the solution may make it possible to fabricate films with different absorption spectra.

The nanotube alignment needs to be quantified using SEM or similar techniques. The thickness, purity, and uniformity of the samples can be improved. Shunting is a potential problem in heterojunction cells made using nanotubes. For the samples tested here, complete shunting was avoided by fabricating relatively thick samples. For future work, the use of a thin buffer or insulator layer will keep the nanotubes from contacting the SnO_2 electrode.

In characterizing the cells, the absorption characteristics have not been measured. An AM 1.5 light source needs to be used to obtain comparable output readings and the cells need to be modeled in order to better understand the charge separation and transport characteristics.

Acknowledgements

The authors would like to thank Dr. Zoubeida Ounaies for use of several pieces of equipment including the LCR meter. Funding from VCU School of Engineering was used to purchase materials. Sumanth Banda and David Callahan offered valuable suggestions and insight.

References

1. A. J. BREEZE, Z. SCHLESINGER and S. A. CARTER, *Phys. Rev. B* **64** (2001) 1.
2. T. PIOK, R. SCHROEDER, C. BRANDS, J. R. HEFLIN, G. LEISING and W. GRAUPNER, *Syn. Metals* **121** (2001) 1589.
3. M. T. RISPENS, A. MEETSMA, R. RITTBERGER, C. J. BRABEC, N. S. SARICIFTCI and J. C. HUMMELEN, *Chem. Comm.* (2003) 2116.
4. H. MATTOUSSI, L. H. RADZILOWSKI, B. O. DABBOUSI, E. L. THOMAS, M. G. BAWENDI and M. F. RUBNER, *J. Appl. Phys.* **83** (1998) 7965.
5. S. B. LEE, T. KATAYAMA, H. KAJII, A. ARAKI and K. YOSHINO, *Syn. Metals* **121** (2001) 1591.
6. E. KYMAKIS and G. A. J. AMARATUNGA, *Solar Eng. Mat. Solar Cells* **80** (2003) 465.
7. N. C. GREENHAM, X. PENG and A. P. ALIVISATOS, in Proceedings of Future Generation Photovoltaic Technologies: First NREL Conference, A CdSe Nanocrystal/MEH-PPV Polymer Composite Photovoltaic (1997) p. 295.
8. J. NELSON, *Materials Today* **5** (2002) 20.
9. W. U. HUYNH, X. PENG and A. P. ALIVISATOS, *Adv. Mater.* **11** (1999) 923.
10. A. C. ARANGO, S. A. CARTER and P. J. BROCK, *Appl. Phys. Lett.* **74** (1999) 1698.
11. G. YU and A. J. HEEGER, *J. Appl. Phys.* **78** (1995) 4510.
12. N. C. GREENHAM, X. PENG and A. P. ALIVISATOS, *Phys. Rev. B* **54** (1996) 17628.
13. American Dye Source, Water Soluble Thiophene Polymer, http://www.adsdyes.com/OLEDS/ads2000p.pdf (2004).
14. S. BANDA, Z. OUNAIES, J. WILKINSON, C. PARK and J. HARRISON, in Proceedings of the SPIE, Aligned Carbon Nanotube-Polymer Composites: Investigating Their Electrical and Physical Characteristics (2004) p. 5387.
15. P. COLLINS and P. AVOURIS, *Sci. Amer.* **283** (2000) 62.
16. Sigma-Aldrich, 519308 Carbon Nanotube, Single-Walled, https://www.sigmaaldrich.com (2004).
17. E. KYMAKIS and G. A. J. AMARATUNGA, *Appl. Phys. Lett.* **80** (2002) 112.
18. E. KYMAKIS, I. ALEXANDROU and G. A. J. AMARATUNGA, *J. Appl. Phys.* **93** (2003) 1764.