

Comparing Model Parameters of Bulk Heterojunction and Nanoparticulate Photovoltaic Cells Using a Two-diode Model

Elisa Sesa^{1,2,*}, Ben Vaughan¹, M. Syahrul Ulum^{1,2}, Xiaojing Zhou¹, John Holdsworth¹, Warwick Belcher¹, and Paul Dastoor¹

¹*Centre for Organic Electronics, University of Newcastle, Callaghan, NSW 2308, Australia.*

²*Physics Dept., Tadulako University, Palu, Central Sulawesi, Indonesia*

* Email: elisa.sesa@uon.edu.au

Abstract. The performance of organic solar cells can be influenced by many factors such as device structure, active layer morphology, and active layer material. These performance differences can be seen through their characteristic electrical parameters. The aim of this article is to show the differences in electrical parameter properties that result from differences in active layer morphology. In particular, the differences between bulk heterojunction (BHJ) and nanoparticulate solar cells are determined using a two-diode circuit model. The simulation results show clear differences in photocurrent generation, serial resistance, and shunt resistance between the bulk heterojunction and nanoparticulate photovoltaic cells.

Keywords: organic solar cells, morphology, electrical parameter, two-diode circuit model

PACS: 88.40.jr

INTRODUCTION

For over two decades research into organic photovoltaics has been growing, especially since Tang (1986) reported a molecular thin film organic solar cell [1]. Following this result, many improvements to organic cells have been reported, including using small molecules [1,2], conjugated polymers [3], conjugated polymer blends [4-7], polymer-small molecule bi-layers [8,9], bulk heterojunctions (BHJ) [6,10,11] and combinations of organic-inorganic materials [12, 13].

Each of these improvements to organic solar cells produces altered device characteristics. These characteristics include exciton generation, exciton separation rate, charge mobility in the device's active layer and electron and hole transport to their respective electrodes. These device characteristics directly affect the performance of the photovoltaic cell.

While a large area, commercially viable organic photovoltaic module has yet to be realized, the efficiency of solar cells based on a BHJ of organic semiconductors has significantly increased in the last few years [14,15].

The BHJ approach to organic photovoltaics is well established and improving, however the nanoparticulate organic photovoltaics are a novel alternative that have only recently gained attention. Using a mini-emulsion technique [16], organic solar cells are processed using water rather than an organic

solvent. This approach has obvious environmental and safety benefits and most importantly also allows direct control of nano-scale morphology.

The morphological differences between BHJ and nanoparticulate devices are apparent in their electrical parameter properties. Applying the two-diode electrical model of a solar cell, an analysis of the J-V curve of each device type was performed.

EXPERIMENT

The active layer solution for the nanoparticulate device was prepared as follows. The polymer was first dissolved in a suitable solvent (which is not miscible with water) and added to an aqueous solution containing an appropriate surfactant. The surfactant was used for stabilizing the droplets against collisions [17] and to allow easier spreading as their action as a wetting agent lowers the surface tension at the solvent-aqueous two liquid interfaces. Applying high shear, for example by ultrasonication of the mixture, stable mini-emulsions containing small droplets of the polymer solution were obtained. Evaporation of the solvent resulted in a stable dispersion of solid polymer nanoparticles in water. However, this dispersion still contained individual surfactant molecules. Therefore a dialysis process was used to remove the excess surfactant.

Indium tin oxide (ITO) substrates were cleaned in an ultrasonic bath using detergent, acetone and isopropanol. After drying the slides, a 70 μl filtered poly (3,4-ethylenedioxythiophene) / (poly(styrenesulfonate) (PEDOT:PSS) solution was spin-coated onto each ITO slide at a speed of 4000 rpm for 1.5 minutes. The slides were then dried in the oven at 140 $^{\circ}\text{C}$ for 30 minutes. While drying the ITO/PEDOT:PSS slides, the active layer solution for the BHJ devices was prepared by blending the P3HT with (6,6)-phenyl-C61- butyric acid methyl ester (PCBM) in a 1:0.8 ratio. The blend was dissolved in a chloroform solution at a concentration of 18 mg/ml. The solution was then sonicated for 30 minutes.

The active layer solution for the nanoparticulate devices was spincoated onto the dry ITO/PEDOT:PSS slides in air. The P3HT:PCBM BHJ blend was spincoated on dry ITO/PEDOT:PSS slides in a nitrogen glove box. The nanoparticulate device was then dried on a hot plate at 110 $^{\circ}\text{C}$ for 4 minutes in the air but the BHJ slide was then dried on a hot plate at 50 $^{\circ}\text{C}$ for 4 minutes in the nitrogen glove box. Finally a metal (Al) back electrode (thickness 100 nm) was evaporated onto both nanoparticulate and BHJ slides.

A programmable sourcemeter (Model Keithley 2400) was used for the steady-state and time-dependent photocurrent measurements. These measurements obtained the J-V data which can be represented as a J-V curve.

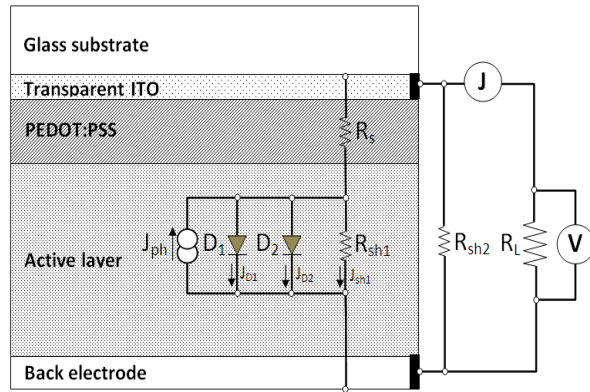


FIGURE 1. The two-diode electrical model equivalent circuit overlaid onto the organic photovoltaic device structure used in this study.

The two-diode electrical model of a solar cell was used to analyze the J-V data [18,19]. This model is represented by the equivalent solar cell circuit shown in Fig. 1. The model consists of a dc current source, two ideal diodes in parallel, a serial resistance, a shunt resistance in the active layer and a shunt resistance for the whole cell. The current density J that flows

through the device under voltage V is expressed in the following equation,

$$J = J_{o1} \left[\exp \left(\frac{q(V(1 + \frac{R_s}{R_{sh2}}) - J R_s)}{n_1 k T} \right) - 1 \right] + J_{o2} \left[\exp \left(\frac{q(V(1 + \frac{R_s}{R_{sh2}}) - J R_s)}{n_2 k T} \right) - 1 \right] + \frac{V(1 + \frac{R_s}{R_{sh2}}) - J R_s}{R_{sh1}} + \frac{V}{R_{sh2}} - J_{ph} \quad (1)$$

where J_{o1} = saturation current in diode D_1 ,
 J_{o2} = saturation current in diode D_2 ,
 J_{ph} = photocurrent
 n_1 = ideality factor of diode D_1
 n_2 = ideality factor of diode D_2
 R_s = serial resistance
 R_{sh1} = shunt resistance of active layer
 R_{sh2} = shunt resistance across the whole cell
 q = electrical charge
 k = Boltzmann constant.

From this equation, the main parameters for our model are J_{o1} , J_{o2} , J_{ph} , n_1 , n_2 , R_s and R_{sh1}

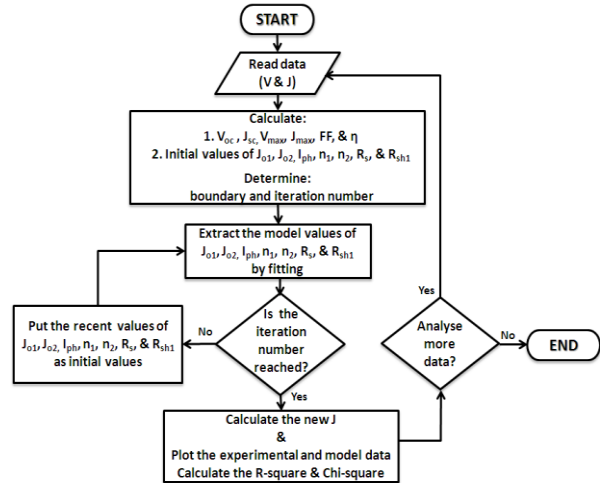


FIGURE 2. Flowchart of the two-diode electrical model program used in this study.

Figure 2 shows the flowchart of the program used to generate the two-diode electrical model of a solar cell. The program starts by reading the J-V data and generating an initial value for each parameter which is 2 for both ideality factors, n_1 and n_2 . The J-V data is then fitted using an iterative process, which is terminated after reaching a given iteration value.

In an organic solar cell, the series resistance (R_s) depends on the resistivity of the organic material(s), the metal electrodes and the electrode/organic interfaces. The shunt resistance (R_{sh}) represents geminate and bimolecular recombination and can also account for leakage from sources such as pinholes in the active layer [19].

RESULTS AND DISCUSSION

The comparison made in this study is between the best performing BHJ and nanoparticulate devices. Interestingly the best nanoparticulate device is unannealed while the best BHJ device is annealed at 140 °C for 4 minutes. Figure 3 shows the J-V curves of both devices. While their fill factors are similar, both the open circuit voltage, V_{oc} , and short circuit current, J_{sc} , of a nanoparticulate device are lower than in a BHJ device.

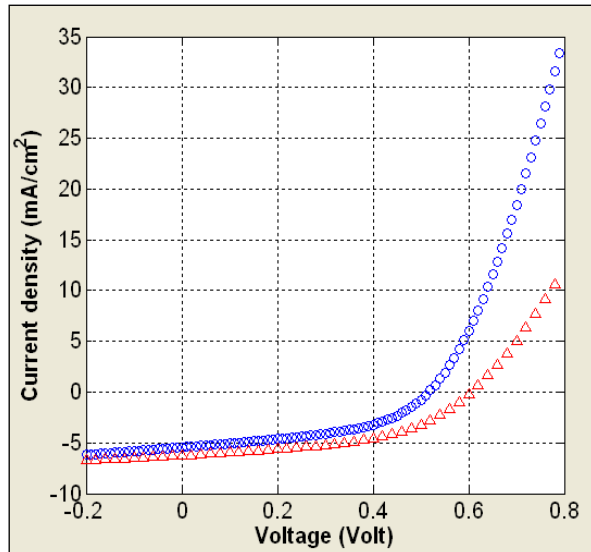


FIGURE 3. The J-V curves of unannealed nanoparticulate (blue circle) and annealed BHJ devices (red triangle)

TABLE 1. The main parameters extracted from the iterative fit-to-data for both nanoparticulate and BHJ devices.

Parameters	Device	
	Nano-particle	BHJ
J_{01} (mA/cm ²)	3.17e-4	2.82e-4
J_{02} (mA/cm ²)	4.55 e-4	5.07e-13
J_{ph} (mA/cm ²)	5.51	6.41
n_1	2.4	2.4
n_2	2.3	2.4
R_s (Ω)	77.73	188.45
R_{sh} (Ω)	5009.80	6056.00

The fitting results, shown in Figures 4a and 4b, had R-square values of 0.9999 and 0.9998 for nanoparticulate and BHJ devices respectively. The R-square value represents how close the model parameters fit to the experimental data. The fit parameters for each device are shown in Table 1.

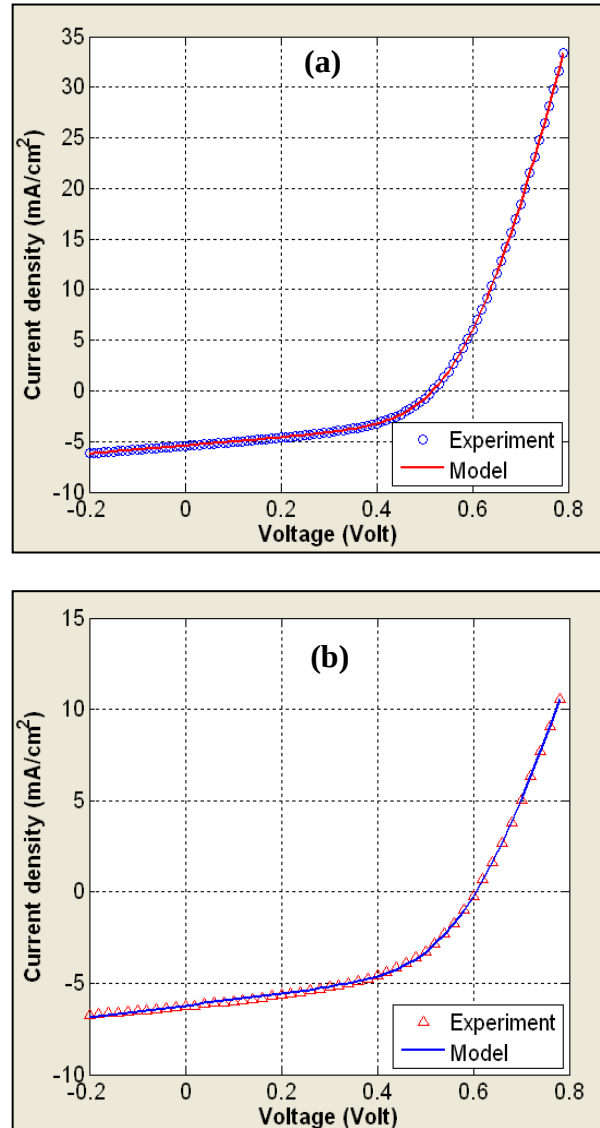


FIGURE 4. Model fitting results for J-V curves of the (a) nanoparticulate device and (b) BHJ device.

As seen in Table 1, the BHJ device produces more current than the nanoparticulate device, as shown by J_{ph} . Morphological differences between the devices could be a cause of this current generation difference.

The series resistance, R_s , of the BHJ device is also higher than nanoparticulate device. This could indicate that the contact between the electrodes and the active

layer is better in the nanoparticulate device as compared to the BHJ device. A lower series resistance will result in improved charge transport through the device.

The shunt resistance, R_{sh1} , in the BHJ device is higher than in the nanoparticulate device. This would indicate that less recombination occurs in the BHJ device. Lower recombination leads to increased current generation, as shown by the higher J_{ph} value for the BHJ device.

CONCLUSIONS

A comparison of J-V data has been presented for BHJ and nanoparticulate devices using the two-diode electrical model of a solar cell. It has been shown that the two-diode model can fit J-V data from both device types. Differences in the device parameters have been clearly shown which are attributed to the morphology of the devices. Further improvement in organic photovoltaic performance, in measurement and model, will come from understanding the complex relationship between morphology and device parameters.

ACKNOWLEDGMENTS

The authors would like to thank The Directorate General of High Education of Indonesia (DIKTI) for providing the overseas PhD scholarship. This paper is presented under funding support from the School of Mathematical and Physical Sciences of FSCIT University of Newcastle.

REFERENCES

1. C. W. Tang, *Appl. Phys. Lett.*, **48**, 183-185 (1986.).
2. D. Wohrle and D. Meissner, *Adv. Mater.* **3**, 129-138 (1991).
3. H. Antoniadis, et al., *Synthetic Metals* **62**, 265-271 (1994).
4. M. Granstrom, et al., *Nature* **395**, 257-260 (1998).
5. J. J. M. Halls, et al., *Nature* **376**, 498-500 (1995).
6. G. Yu, et al., *Science* **270**, 1789-1791 (1995).
7. L. S. Roman, et al., *Adv. Mater.* **9**, 1164-1168 (1997).
8. S. A. Jenekhe and S. Yi, *Appl. Phys. Lett.* **77**, 2635-2637 (2000).
9. A. J. Breeze, et al., *Appl. Phys. Lett.* **81**, 3085-3087 (2002).
10. J. J. Dittmer, E. A. Marseglia, and R. H. Friend, *Adv. Mater.* **12**, 1270-1274 (2000).
11. S. E. Shaheen, et al., *Appl. Phys. Lett.* **78**, 2996-2998 (2001).
12. N. C. Greenham, X. Peng, and A. P. Alivisatos, *Phys. Rev. B* **54**, 17628 (1996).
13. B. O'Regan and M. Gratzel, *Nature* **353**, 737-740 (1991).
14. M. M. Mandoc, L. J. A. Koster, and P. W. M. Blom, *Appl. Phys. Lett.* **90**, 133504-1 - 133504-3 (2007).
15. M. M. Mandoc, et al., *Adv. Func. Mater.* **17**, 2167 -2173 (2007).
16. T. Kietzke, et al., *Nature Materials* **2**, 408-U7 (2003).
17. K. Landfester, et al., *Adv. Mater.* **14**, 651-655 (2002).
18. A. Cheknane, et al., *Microelectron. J.* **39**, 1173-1180 (2008).
19. A. Moliton and J. M. Nunzi, *Polym. Int.* **55**, 583-600 (2006).