Nanoparticle – polymer and polymer – polymer blend composite photovoltaics

A.J. Breeze[a], Z. Schlesinger[a], S.A. Carter[a], H. H. Hörhold[b], H. Tillmann[b], David S. Ginley[c], P.J. Brock[d]

[a] University of California, Santa Cruz, Physics Dept, Santa Cruz, Ca 95064
[b] Friedrich-Schiller-Universitat, Jena, Germany
[c] NREL, 1617 Cole Blvd, Golden, Co. 80401
[d] IBM Almaden Research Center, San Jose, Ca. 95120

Abstract

The main factors inhibiting higher conversion efficiencies in plain polymer layer sandwich photovoltaic devices are the low exciton dissociation efficiency and the low carrier mobilities in the polymer. We consider two different blend approaches for increasing these qualities. NiO (or LiNiO) hole transporting nanoparticles are blended into the photoactive polymer MEH-DOO-PPV in an attempt to increase hole mobility across the device. Improvements to device performance were not significant at these blend concentrations. Devices made using blends of hole and electron transporting polymers M3EH-PPV and CN-ether-PPV showed increased dissociation efficiency and gave power conversion efficiencies of up to 0.6% with stable electrodes.

Keywords: polymer photovoltaic, TiO_2 solgel, nanoparticle – polymer composite photovoltaic, polymer – polymer composite photovoltaic, M3EH-PPV, CN-ether-PPV, MEH-DOO-PPV

1. Introduction

Although work over the past several decades has allowed silicon solar cells to achieve power conversion efficiencies on the order of 30%, the high manufacturing and materials cost significantly limits their widespread usage. Organic based solar cells such as dye sensitized electrochemical [1], small molecule organic [2-4] and polymer composite photovoltaics have been proposed as alternatives. Soluble conjugated polymers allow for the possibility of good quality films deposited via spin casting, ink jet or screen printing. In addition, polymers offer the possibility of low costs, less toxic manufacturing methods, tunable optical properties, and the possibility of large area, light weight, flexible panels. Nonetheless, polymer-based photovoltaics are not yet efficient enough to compete with the more traditional inorganics. Recent results suggest that polymer-nanoparticle and polymer-polymer blends may be promising for obtaining more competitive efficiencies [5,6]. In this paper, we discuss the impact of electrode configuration and polymer blend composition on achieving higher energy conversion efficiencies.

2. Electrode configuration

In order to create a favorable direction of the internal electric field in our device, we use non-dye sensitized TiO_2 sol-gel as our semi-transparent electron collecting electrode in conjunction with gold as a top electrode [7,8]. This electrode configuration allows the majority of the electrons created at the transparent electrode to be immediately transferred to the TiO_2 rather than having to transport through the bulk of the low electron mobility polymer. For plain, single polymer layer devices, exciton dissociation tends to be limited to the regions within an exciton diffusion length of the electrodes, with most of the useful current being produced next to the transparent electrode, in our case, the TiO_2 layer. With exciton diffusion lengths of approximately 15 nm and polymer absorption coefficients on the order of 100 nm, only about 15% of the incoming light is absorbed in the most active dissociation area. Most polymers absorb perhaps 1/3 of the solar spectrum, and as a result only about 5% of the incoming light is usefully absorbed. Clearly, it would be advantageous to be able to extend the dissociation region throughout the entire polymer layer, thereby eliminating the large amount of recombination occurring in the bulk of the photoactive region. Furthermore, improvements in the carrier mobility and the absorption of the polymers are needed to improve performance.

3. Polymer blends

Nanoparticle - polymer and polymer - polymer blends are two approaches for extending the exciton dissociation region from next to the electrodes to throughout the polymer layer. In addition, nanoparticle blends have the potential to improve carrier mobility. Whether a nanoparticle blend will improve the size of the dissociation region, improve carrier mobility, or both depends on the types of nanoparticles and polymers used. We blend hole transporting nanoparticles such as

NiO or LiNiO into these polymers with the goal of increasing the hole mobility of the device. The TiO_2 - polymer interface still acts as the main dissociation site, but if holes can be transferred from the polymer to nanoparticles with higher mobilities, both short circuit current density and fill factors can be improved. Higher nanoparticle concentrations are expected to give better results. At lower concentrations, where there are many isolated nanoparticles, charges transferred to the nanoparticles are then trapped with no way to reach the appropriate electrode. This will decrease the efficiency rather than increase it, especially at lower light intensities.

The use of hole transporting nanoparticles in hole transporting polymers is not expected to improve the device performance through increased exciton dissociation. While it is possible that the nanoparticles act as dissociation sites in the middle of the polymer layer, charges dissociated in this manner will not exit the device efficiently; holes will be transferred to the nanoparticle pathway but the low mobility electrons will be left to travel through the rest of the polymer layer. Electron transporting nanoparticles, on the other hand, should be able to increase the exciton dissociation by creating dissociation sites throughout the polymer layer, as well as improving the electron mobility. Electrons will be transferred to the nanoparticle pathways, leaving holes to travel through the polymer.

Previous experiments [5] using electron transporting C_{60} and CdSe nanoparticle blends with ITO and Al electrodes have achieved improved peak external quantum efficiencies of 12% and 29%, respectively, but only at very high concentrations (~90%) of nanoparticles. At such high concentrations, light absorption by the nanoparticles themselves make a significant contribution to the photocurrent. At lower concentrations (~50%), the peak quantum efficiencies of these devices are on the order of 6%, comparable to our earlier results using rough TiO_2 nanoparticle layers with a plain polymer layer [8]. This suggests that except for very high blend concentrations, a rough TiO_2 layer in a device with a favorably directed internal field is just as effective at dissociation of electrons as interpenetrating blends with ITO and Al electrodes.

In order to explore the effects of increased hole mobility pathways, we examine blends of hole transporting NiO and LiNiO nanoparticles in the polymer MEH-DOO-PPV in concentrations of 1:1 by weight. As can be seen in Figure 1, no significant improvements are apparent in the current density - voltage curves for a 1:1 NiO - MEH-DOO-PPV blend device as compared to a plain MEH-DOO-PPV control device. Short circuit currents for the blend devices are slightly improved, but this is balanced by slightly lower open circuit voltages and fill factors. Similar results are obtained for LiNiO blends (Figure 2).
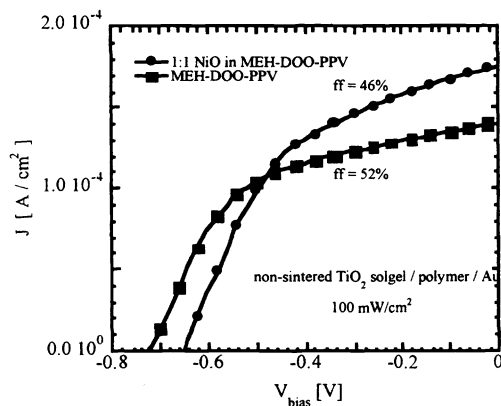
Figure 1: Current density as a function of applied voltage comparing a control ITO/TiO_2/MEH-DOO-PPV/Au device (closed squares) with an ITO/TiO_2/1:1 NiO : MEH-DOO-PPV/Au blend device (closed circles).
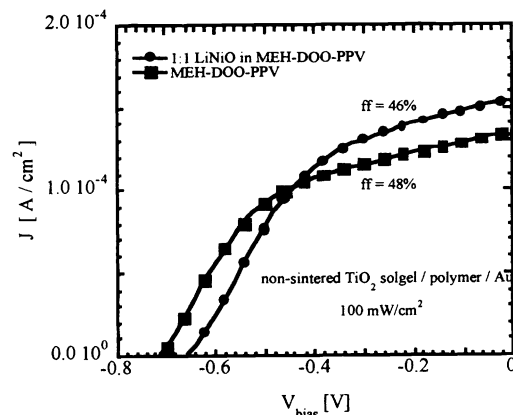
Figure 2: Current density as a function of applied voltage comparing a control ITO/TiO_2/MEH-DOO-PPV/Au device (closed squares) with an ITO/TiO_2/1:1 LiNiO : MEH-DOO-PPV/Au blend device (closed circles).

Photoaction current spectra comparing the control and the nanoparticle blend devices show that, contrary to expectations given by the J-V curves, the external quantum efficiencies for the blend devices are approximately an order of magnitude lower than that of the control (Figure 22). The MEH-DOO-PPV control device, which peaks with 1.2% efficiency around 470 nm, is comparable to other non-sintered solgel devices made with MEH-PPV. However, NiO and LiNiO blend device efficiencies peak at only 0.15%. These results are most likely due to the difference in the light intensity used to take J-V curves compared to that used for the photoaction current spectra; the photoaction spectra setup provides much lower light intensity. At these low intensities, it is likely that a significant fraction of the (small amount of) charge produced in the blend devices is trapped on isolated nanoparticles, leading to lower photocurrents and hence lower quantum efficiencies. It is possible that external quantum efficiencies measured at light intensities more comparable to normal sun would show that nanoparticle - polymer blends at these concentrations are on the whole comparable to those of the plain polymer devices. Based on our results, as well as others' results with C_{60} and CdSe, it would seem that nanoparticle - polymer blends must have higher concentrations of nanoparticles in order to significantly improve over nanoparticle - polymer layered devices. The surface chemistry of our NiO and LiNiO particles would have to be altered to make them more soluble in order to increase their concentration and test this assumption.
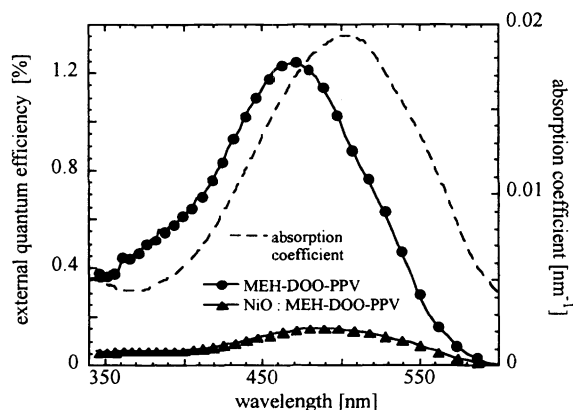

Figure 3: External quantum efficiency as a function of wavelength for ITO/ TiO$_2$/MEH-DOO-PPV/Au (closed circles) and ITO/TiO2/1:1 NiO : MEH-DOO-PPV/Au (closed triangles) devices. The absorption coefficient spectrum of MEH-DOO-PPV is shown for comparison (dashed line).

Polymer - polymer blends of electron and hole transporting polymers show strong promise for increasing exciton dissociation efficiency. By blending polymers of appropriate energy levels directly together in a common solvent and spin casting a single solution, phase separation on the nanometer scale can be achieved, creating dissociation interfaces throughout the entire polymer layer (Figure 23a). Figure 23b shows the energy level diagram for blends of hole transporting M3EH-PPV with electron transporting CN-ether-PPV. Excitons are produced in both polymers, with dissociation occurring at the phase separation boundaries. The relative HOMO levels and the direction of the internal field are both favorable for the transfer of holes from CN-ether-PPV to M3EH-PPV. Likewise, electrons created in M3EH-PPV are transferred to the CN-ether-PPV. By immediately separating the charge carriers to their respective polymers, recombination in the bulk of the polymer layer is drastically reduced, leading to high increases in current density. Figure 24 shows current density - voltage curves comparing a control device of M3EH-PPV with a 1:1 by weight M3EH-PPV : CN-ether-PPV blend. (The current densities measured for CN-ether-PPV control devices degraded too quickly to make reasonable measurements.) All devices use sintered TiO$_2$ solgel layers.

M3EH-PPV is by itself a good photovoltaic material, yielding short circuit current densities of 1.2 mA/cm^2 at 100 mW/cm^2 light intensity. Mobility measurements of an ITO/PEDOT/annealed M3EH-PPV/Al device taken in the range of 3.8-6.1 V yield an average hole mobility of 5.1 x 10^{-7} cm^2/Vs, just under twice the hole mobility of annealed MEH-PPV. This increase in mobility is not high enough to completely account for the improvement in current over MEH-PPV devices; likely, the M3EH-PPV devices also have slightly increased absorption and exciton dissociation efficiency due to their improved structure.

A 1:1 M3EH-PPV : CN-ether-PPV blend device of corresponding thickness has a short circuit current density of 3.0 mA/cm^2. Given the exciton diffusion length of roughly 15-20 nm, this factor of 2.5 increase in J_{sc} is consistent with exciton dissociation occurring through a majority of the polymer thickness for the blend devices. Our best M3EH-PPV : CN-ether-PPV blend devices have achieved high short circuit current densities of up to 3.3 mA/cm^2 and an open circuit voltages of –0.65V, leading to an overall power efficiency of 0.6% with ITO/TiO2 and Au as electrodes.

There is a drawback, however, to the use of polymer - polymer blends. While the exciton dissociation is drastically increased, leading to high increases in current, there is no corresponding increase in the carrier mobility. Since the fill factor can be thought of as roughly proportional to the majority carrier mobility and inversely proportional to the short circuit current, the increase in current density with no corresponding mobility increase leads to much lower fill factors, on the order of 25 to 30%. Even so, polymer - polymer blends have higher overall power conversion efficiencies compared to normal polymer devices; an M3EH-PPV : CN-ether-PPV device has up to 0.6% overall conversion efficiency, compared to a plain M3EH-PPV device with 0.3% efficiency. Earlier research done by other groups using MEH-PPV : CN-PPV blends have shown peak external quantum efficiencies of 5% [6]. Our best blend device to date has a peak quantum efficiency of 23%. The external quantum efficiency for the polymer blend devices shows definite improvement over that of the plain M3EH-PPV device, as shown in Figure 26. The plain ITO/sintered TiO$_2$ solgel/40 nm M3EH-PPV/Au device achieves a maximum external quantum efficiency of 7%, as compared to the 23% of the blend device.
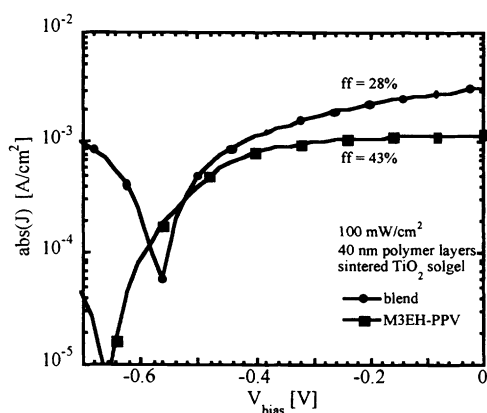

Figure 4: The absolute value of the current density as a function of applied voltage for ITO/TiO$_2$/M3EH-PPV:CN-ether-PPV/Au (closed circles) and ITO/TiO$_2$/M3EH-PPV/Au (closed squares) devices under solar conditions. Both devices use sintered TiO$_2$ sol-gel and have 40 nm polymer layers.
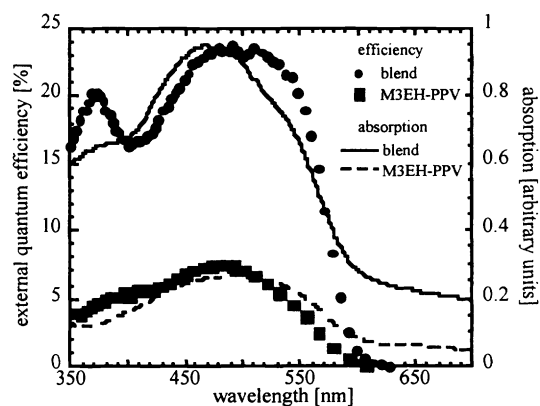
Figure 5: The external quantum efficiency as a function of wavelength for plain M3EH-PPV (squares) and 1:1 M3EH-PPV : CN-ether-PPV (circles) devices. The absorption coefficient spectra for M3EH-PPV (dashed line) and blend (line) are also shown.

4. Conclusions

In conclusion, we have discussed several different approaches towards improving exciton dissociation and carrier mobility, some of the main factors limiting power conversion efficiencies in polymer photovoltaic devices. Nanoparticle – polymer blends, depending on the types of materials used, have the potential to increase carrier mobility and/or exciton dissociation. Hole transporting nanoparticles blended into hole transporting polymers should result in increased effective hole mobilities. We have demonstrated that concentrations of 1:1 hole transporting nanoparticles : hole transporting polymer by weight are insufficient for significantly improving device performance. In contrast, 1:1 polymer – polymer blends achieve noticeable improvements in short circuit current densities and power conversion efficiencies due to the increased exciton dissociation and corresponding decrease in recombination. Preliminary measurements suggest that exciton dissociation is extended throughout the polymer layer, in contrast to plain polymer devices where the dissociation is limited to the regions

within the exciton diffusion length of either electrode. Low carrier mobilities are still strong limiting factors for the polymer – polymer blend devices, however, leading to fill factors on the order of 25-30%. Our most efficient devices are achieved using blends of M3EH-PPV and CN-ether-PPV, giving short circuit current densities of up to 3.3 mA/cm^2 and corresponding power conversion efficiencies of 0.6%.

5. Acknowledgements

6. References

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