Hybrid organic/inorganic solar cells

Summary

In this chapter, solar cells with active layers consisting of MDMO-PPV and inorganic semiconductor materials are discussed. One method to obtain such blends is to spin cast a co-solution of the polymer and an organic precursor for either TiO$_2$ or ZnO. The performance of MDMO-PPV/prec-TiO$_2$ devices was quite poor, probably due to a lack of crystallinity of the TiO$_2$. Although the efficiency of the MDMO-PPV/prec-ZnO devices was quite reasonable, the hole transport through the polymer phase clearly suffered from the addition or formation of the ZnO.

Another approach is to make nanocrystalline ZnO $ex$ $situ$ and add this to the MDMO-PPV solution. It is demonstrated that the hole transport through the thus-formed blends is not affected by the presence of nc-ZnO. The electron mobility in these MDMO-PPV/nc-ZnO blends also is quite decent (one order of magnitude larger than the hole mobility), consequently, the hole transport through the polymer phase is identified as the limiting factor in these devices.
Chapter 5. Hybrid organic/inorganic solar cells

5.1 Introduction to hybrid organic/inorganic solar cells

So far, several electron acceptors have been shown to yield efficient devices: conjugated polymers,\(^1\) fullerenes,\(^2\) and inorganic nanocrystals.\(^3\) In the class of inorganic acceptors, metal oxides are among the most studied materials. Titanium dioxide has been studied in several forms: nanoparticles,\(^4,5\) porous networks,\(^6\) and \textit{in situ} formation of titanium dioxide from a precursor.\(^7\) Recently, zinc oxide nanoparticles (nc-ZnO) have also been used as electron accepting material, in combination with MDMO-PPV, with an AM1.5 efficiency of 1.6\%.\(^8,9\) Zinc oxide has several merits: Zinc oxide is a cheap and environmentally friendly material that can be made in crystalline form at low temperature. Furthermore, it displays good transport properties, even in films consisting of nanoparticles.\(^10\)

5.2 Hybrid solar cells with acceptors from a precursor

One of the challenges in making BHJ solar cells is obtaining a suitable morphology; this is especially so for hybrid devices since a common solvent for both components is not easily found.

5.2.1 Using a precursor for titanium dioxide

Van Hall \textit{et al.} chose an attractive approach to circumvent this problem by mixing a solution of MDMO-PPV with an organic precursor for TiO\(_2\).\(^7\) By spin casting the film in ambient conditions, the precursor (titanium(IV) isopropoxide) reacts with moisture from the air, thereby forming TiO\(_2\) (at least 65\% was converted) in an MDMO-PPV matrix. They found that efficient charge transfer from the polymer phase to the TiO\(_2\) phase occurs, although the photoluminescence was not fully quenched;\(^7\) the residual emission was attributed to photoexcitations that do not reach the interface with TiO\(_2\). This is supported by scanning electron microscopy measurements on these blends performed by Slooff \textit{et al.}\(^11\) They demonstrated that the TiO\(_2\) phase in blend with MDMO-PPV shows typical dimensions of 10–20 nm, which is somewhat larger than the exciton diffusion length in PPV.\(^12\)

Figure 5.1(a) shows the current-voltage characteristics of a solar cell based on MDMO-PPV and TiO\(_2\) formed by the precursor route (prec-TiO\(_2\)). The efficiency of these devices is rather limited, typically 0.2\%. A strong correlation was found between the performance of these devices and the relative humidity during processing, which is not surprising given the hydrolysis reaction necessary to form TiO\(_2\). Slooff \textit{et al.} have demonstrated that the best devices are obtained at a relative humidity of around 50\%.\(^13\) Unfortunately, MDMO-PPV/prec-TiO\(_2\) films made at this level of humidity were inhomogeneous and very rough, with root-mean-square roughnesses approximately equal to half the active layer thickness. Moreover, the best performing solar cells displayed
strong hysteresis in their current-voltage characteristics in dark, therefore, charge transport studies could not be executed. The intensity dependence of $J_{\text{sc}}$ gives a hint though: Figure 5.1(b) shows that $J_{\text{sc}}$ is linearly dependent on intensity. As demonstrated in chapter 4 this indicates that the mobilities of electrons and holes cannot differ much. Figure 5.1(b) also shows the intensity dependence of $V_{\text{oc}}$. Surprisingly, the intensity dependence of $V_{\text{oc}}$ is much stronger than what is to be expected on basis of Eq. (3.11) ($S = 2.0 V_t$), which may indicate that recombination is not only bimolecular. It should be mentioned that the p-n junction model, Eq. (3.3), also cannot explain the observed behavior since the ideality factor is equal to 2.4.

Why is the efficiency of these devices so modest? One possible explanation is that the conversion of titanium(IV) isopropoxide does not yield crystalline TiO$_2$, since this reaction has to be performed at low temperature due to the presence of the polymer. As crystalline TiO$_2$ is only obtained at temperatures of more than 350°C, it is to be expected that only amorphous TiO$_2$ is formed, thereby limiting the transport of electrons. Moreover, Van Hall et al. observed a blue-shift in the absorption spectrum of MDMO-PPV upon addition of TiO$_2$,[7] suggesting that the polymer is also affected.

### 5.2.2 Using a precursor for zinc oxide

In contrast to TiO$_2$, zinc oxide (ZnO) is known to crystallize at much lower temperatures.[15] Beek et al. have shown that BHJ solar cells based on MDMO-PPV and ZnO formed from a precursor (prec-ZnO) can formed by using diethylzinc.[16] As the hydrol-
Figure 5.2: Current-voltage characteristics of an illuminated \((I = 877 \text{W/m}^2)\) MDMO-PPV/prec-ZnO device with an efficiency of 1.0\%, \(J_{sc} = 21.5 \text{A/m}^2\), \(V_{oc} = 1.00 \text{V}\), and FF = 42\%. The thickness of the active layer is 100 nm, with a root-mean-square roughness of 8 nm.

Analysis and condensation of diethylzinc take place very rapidly when diethylzinc is exposed to air, it is necessary to moderate these reactions by adding tetrahydrofuran, which can stabilize diethylzinc by coordination of the zinc atom. By spin casting a co-solution of diethylzinc and MDMO-PPV and subsequent thermal annealing at a moderate temperature (110°C), crystalline ZnO is formed in the MDMO-PPV matrix. Although the photoluminescence of the resulting films is not completely quenched, long-lived photogenerated charges are indeed formed.\[16\]

Figure 5.2 shows the current-voltage characteristics of an illuminated MDMO-PPV/prec-ZnO (15 vol.-% ZnO, assuming full conversion) with an efficiency of 1.0\%. It is remarkable that the optimal devices are obtained with only 15 vol.-% prec-ZnO. When the concentration of prec-ZnO is increased, the films become very rough and inhomogeneous. Fortunately, devices with 15 vol.-% prec-ZnO are relatively smooth (the device of Fig. 5.2 has a roughness of 8 nm) and do not show hysteresis in the \(J_D-V_a\) characteristics. Therefore, charge transport studies were undertaken. Although it was possible to study the transport of holes, unfortunately, it turned out to be very difficult to make reproducible electron-only devices.

In order to study the transport of holes through the MDMO-PPV/prec-ZnO layer, the standard LiF/Al cathode was replaced by palladium. Figure 5.3 shows the current-voltage characteristics of such a device, together with the characteristics of a pristine MDMO-PPV hole-only device with a comparable thickness of the active layer. The strong bias dependence of the current through the MDMO-PPV/prec-ZnO device is striking. When fitted to Eq. (1.8), a zero-field mobility of \(1.4 \times 10^{-12} \text{m}^2/\text{V s}\) and a field activation parameter \(\gamma = 1.35 \times 10^{-3} \text{ (m/V)}^{0.5}\) are found (fit not shown). Such high values of \(\gamma\) are difficult to rationalize within the framework of trap-free space-charge-
5.2. Hybrid solar cells with acceptors from a precursor

limited currents. Furthermore, as is evident from Fig. 5.3, the currents through the pristine MDMO-PPV film and the MDMO-PPV/prec-ZnO device seem to converge at high bias. That this difference in current is not caused by the annealing treatment of the MDMO-PPV/prec-ZnO blend, was confirmed by annealing and processing a pristine MDMO-PPV device in the same way as the blend devices. No difference between an annealed and a not annealed MDMO-PPV device was observed, therefore, the strong bias dependence of MDMO-PPV/prec-ZnO devices must be linked to the presence or formation of ZnO.

What can be the cause of the strong dependence on bias? One possible explanation might be the presence of neutral traps for charge carriers, since this is known to cause a strong dependence on field strength. For example, one has for traps with an exponential distribution in energy of width $E_{tr}$,[17]

$$J \propto \mu V^{r+1} \frac{1}{L^{2r+1}},$$

where $r = E_{tr}/k_B T$. However, it was found that in order to obtain a good fit to the data, it was still necessary to incorporate a high field dependence of the mobility. In addition, the predicted temperature and active layer thickness dependence was not in accordance with the measurements. The possibility of a barrier to hole injection was dismissed for the same reasons.

Another possible candidate is field-assisted detrapping of charge carriers, the so-called Poole-Frenkel (PF) mechanism.[18] The PF mechanism describes the enhancement of the escape rate of a carrier from an oppositely charged trap by the presence of an electric field, see Fig. 5.4(a). This detrapping results in a larger free carrier density, thereby

*Varying the active layer thickness is somewhat cumbersome, since this may affect the chemical reaction of the precursor.
increasing the conductivity of the film. The resulting current density $J_{PF}$ is given by

$$J_{PF} \propto F \exp\left(\frac{\eta \sqrt{F}}{k_B T}\right),$$  

(5.2)

where $\eta$ is the detrapping parameter. In the PF theory, $\eta$ is equal to\[^{18}\]

$$\eta_{PF} = \sqrt{\frac{q^3}{\pi \epsilon}}.$$  

(5.3)

Figure 5.4(b) shows current-voltage data of an MDMO-PPV/prec-ZnO hole-only diode at various temperatures fitted to Eq. (5.2). Table 5.1 lists the thus obtained values for $\eta$. Clearly, the values obtained for $\eta$ are close, albeit somewhat smaller, than those predicted by Eq. (5.3). That there is a difference between the PF model and the data is not surprising: The PF model, as presented here, considers only a Coulomb potential in one dimension, while the actual potential may be different and the escape of the trapped carrier will be a three dimensional process.

What can be learnt from the seeming success of the PF model? In any case, the blue-shift of the absorption spectrum of MDMO-PPV/prec-ZnO films as compared to pristine MDMO-PPV observed by Beek \textit{et al.} is notable.\[^{16}\] As this blue-shift was also observed for MDMO-PPV redissolved from an MDMO-PPV/prec-ZnO film, it is connected to degradation of the polymer and indicates that the conjugation of the backbone is partly destroyed. Possibly, the double bond of the vinylene group in the PPV backbone (see Fig. 1.2) reacts with ZnO$^{-}$ anions, thereby breaking the conjugation. As a side-effect,
negative charges may be present in the polymer phase, which can act as charged traps for holes. Alternatively, there may be negative groups on the surface of the ZnO phase in the blend with MDMO-PPV. P3HT is expected to be more stable against a chemical reaction with ZnO$^-\text{anions}$ and may lead to better performing solar cells. These observations indicate that considerable care is required when designing polymer solar cells with an acceptor formed \textit{in situ} from a precursor.

### Table 5.1: The values of \( \eta \), relative to \( \eta_{PF} \) as given by Eq. (5.3), used in the fits shown in Fig. 5.4(b)

<table>
<thead>
<tr>
<th>( T [K] )</th>
<th>( \eta / \eta_{PF} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>0.92</td>
</tr>
<tr>
<td>275</td>
<td>0.88</td>
</tr>
<tr>
<td>255</td>
<td>0.87</td>
</tr>
<tr>
<td>235</td>
<td>0.87</td>
</tr>
<tr>
<td>215</td>
<td>0.84</td>
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</tbody>
</table>

5.3 Polymer solar cells with zinc oxide nanoparticles

By preparing the inorganic acceptor \textit{ex situ}, it is possible to have greater control over the reaction conditions and purity of the obtained materials. This comes at the cost of having to provide a means for mixing the acceptor with the polymer. Beek \textit{et al.} have developed a method for making polymer solar cells with nc-ZnO as acceptor material.\^[8] Zinc oxide nanoparticles approximately 5 nm in diameter (see Fig. 5.5) were synthesized by hydrolysis and condensation of zinc acetate dihydrate by potassium hydroxide in methanol, using the method of Pacholski \textit{et al.}\^[8,19] The zinc oxide particles were dispersed in a mixture of methanol and chlorobenzene without the aid of additional surfactants or ligands.

Figure 5.6(a) shows the current-voltage characteristics of an MDMO-PPV/nc-ZnO solar cell under illumination. Typically, the open-circuit voltage ranges from 0.7 V to 0.8 V. As the conduction band of nc-ZnO (4.2 eV) lies deeper than the LUMO of PCBM (approximately 3.8 eV), it is easy to understand that the open-circuit voltage of MDMO-PPV/nc-ZnO solar cells is slightly lower than the open-circuit voltage of MDMO-PPV/PCBM devices (\( V_{oc} = 0.80-0.85 \text{ V} \)).\^[20,21] Since the effective masses of electrons and holes in ZnO is relatively low, quantum confinement effects already start to play a role at a diameter of approximately 8 nm.\^[22] Moreover, considerable influence of surface conditions is to be expected, rendering the exact positions of the electronic levels of nc-ZnO quite sensitive to the circumstances during synthesis. Figure 5.6(b) shows the short-circuit current density as a function of light intensity of an MDMO-PPV/nc-ZnO solar cell. When fitted to \( J_{sc} \propto I^\alpha \), \( \alpha = 1.03 \pm 0.02 \) is obtained, showing that the short-circuit current density is linear in the intensity.
Figure 5.5: Transmission electron micro-graph of nc-ZnO. The length of the scale bar corresponds to 20 nm.

Figure 5.6: (a) Current-voltage characteristics of an illuminated MDMO-PPV/nc-ZnO solar cell with an active layer thickness of 130 nm (symbols); the line denotes the numerical modeling result. (b) The incident light intensity dependence of the short-circuit current density of an MDMO-PPV/nc-ZnO photovoltaic device (symbols) and a fit to the relation $J_{sc} \propto I^\alpha$, where $\alpha = 1.03 \pm 0.02$ (line).
5.3. Polymer solar cells with zinc oxide nanoparticles

5.3.1 Charge transport in MDMO-PPV/nc-ZnO blends

In order to assess to the transport of holes in MDMO-PPV/nc-ZnO solar cells, the cathode is replaced by a high work function electrode, thereby blocking the injection of electrons from the contact. This results in space-charge-limited current flow by holes. Figure 5.7(a) shows current-voltage characteristics of a pristine MDMO-PPV hole-only diode with an active layer of 90 nm thickness. By fitting the experimental data to Eq. (1.8) and using $V_{bi} = 0.4 \, V$, a value of $4.0 \times 10^{-10} \, \text{m}^2/\text{V s}$ is obtained for the zero-field mobility, together with $\gamma = 3.5 \times 10^{-4} \, (\text{m/V})^{0.5}$. Note that this batch of MDMO-PPV, synthesized via the sulfinyl route, has a ten times higher hole mobility than previously reported for MDMO-PPV.\textsuperscript{[23]} Figure 5.7(a) also shows current-voltage measurements of an MDMO-PPV/nc-ZnO hole-only diode, with an active layer thickness of 130 nm. Although the blend layer is somewhat thicker than the layer of MDMO-PPV discussed previously, the current densities are very similar. In fact, using $V_{bi} = 0.3 \, V$ a zero-field mobility of $5.5 \times 10^{-10} \, \text{m}^2/\text{V s}$ is obtained and $\gamma = 3.5 \times 10^{-4} \, (\text{m/V})^{0.5}$, showing that, within experimental error, the hole mobility in the polymer phase of the blend is not affected by the presence of nc-ZnO.

To study the transport of electrons, the bottom- and top electrode were made of samarium, a metal with a low work function. Spin casting on samarium requires some care, since it is a reactive metal, but extensive testing showed no significant degradation of the bottom electrode. However, in this configuration the samarium bottom electrode is not used to inject electrons into the active layer, but only to suppress the injection of
holes, while the top electrode supplies the electrons.∗

The current-voltage characteristics of an electron-only device with a 115 nm thick active layer consisting of the MDMO-PPV/nc-ZnO blend is depicted in Fig. 5.7(b). No built-in voltage is subtracted, since the bottom and top electrode are made of the same metal. Using Eq. (2), we find $\mu_0 = 2.8 \times 10^{-9} \text{m}^2/\text{Vs}$ and $\gamma = 0.5 \times 10^{-4} \text{m/(V)}^{0.5}$, so the electron mobility is an order of magnitude larger than the hole mobility of the polymer phase. Transport of electrons in nc-ZnO films has also been studied using an electrochemically gated transistor[10,15] showing that the electron mobility in these films shows a strong dependence on the number of electrons per particle. In these measurements, the mobility ranged from $10^{-7} \text{m}^2/\text{Vs}$ to $10^{-5} \text{m}^2/\text{Vs}$. These values are in good agreement with photocurrent measurements performed on electrochemical cells.[24] However, it is difficult to compare these values to the values reported here, since the volume fraction of ZnO present in the film is much lower in our case (25 vol.%). Furthermore, the electron concentration in a bulk heterojunction solar cell under operating conditions (see chapter 2) is several orders of magnitude lower than those reported in Refs. [10] and [15]. On the basis of these observations, it is reasonable to expect that the mobilities found in Refs. [10], [15], and [24] represent an upper limit to electron mobility through the nc-ZnO phase in MDMO-PPV/nc-ZnO devices.

In chapter 4 it was shown that the intensity dependence of the short-circuit current is determined by the ratio of electron- to hole mobility, leading to different values of the exponent $\alpha (J_{sc} \propto I^\alpha)$. When the electron mobility is much larger (typically more than two orders of magnitude) than the hole mobility, buildup of net space charge results in $0.75 < \alpha < 1$. [25] On the other hand, if the mobilities of electrons and holes are comparable, the transport is balanced and $\alpha$ is equal to unity. The linear dependence of the short-circuit current density on light intensity (see Fig. 5.6(b), $\alpha = 1.03 \pm 0.02$), supports our findings of the electron- and hole mobilities. It should be noted that Beek et al. have reported a lower value for $\alpha$, i.e., 0.93.[8] However, in their investigation, the MDMO-PPV was synthesized via a different route, probably leading to a lower hole mobility, thereby leading to a lower value of $\alpha$.

### 5.3.2 Improving the efficiency of MDMO-PPV/nc-ZnO solar cells

In order to identify the factors limiting the performance of MDMO-PPV/nc-ZnO solar cells, the numerical model presented in chapter 2 was applied to the data of Fig. 5.6. Note, that a field-dependent generation rate of free electrons and holes was not considered, since it is not expected that this results in a significant field-dependence in the limited voltage range considered here, due to the high dielectric constant of ZnO. Using $\mu_p0 = 5.5 \times 10^{-10} \text{m}^2/\text{Vs}$ and $\gamma = 3.5 \times 10^{-4} \text{m/(V)}^{0.5}$ for the mobility of holes, $\mu_n0 = 3.7 \times 10^{-9} \text{m}^2/\text{Vs}$ and $\gamma = 0.5 \times 10^{-4} \text{m/(V)}^{0.5}$ for the electrons, and a generation rate of

*Solar cells with an MDMO-PPV/nc-ZnO or P3HT/PCBM blend with samarium as a top contact (instead of LiF (1 nm)/Al) show a good performance and, most importantly, an open-circuit voltage equal to devices with LiF/Al as top electrode.
free carriers $G = 1.26 \times 10^{27} \text{ m}^{-3} \text{s}^{-1}$, a good agreement between experimental data and numerical modeling is obtained (see Fig. 5.6 (a)), allowing for a detailed investigation of the factors governing the performance of these solar cells.

**Comparing MDMO-PPV/PCBM with MDMO-PPV/nc-ZnO solar cells**

A striking feature of the MDMO-PPV/PCBM system is that the best performing solar cells contain 80 wt.-% PCBM (corresponding to 70 vol.-% PCBM, using the densities of MDMO-PPV and PCBM of Ref. [26]), although PCBM hardly contributes to the absorption of light. Two main reasons for the need for such high PCBM loadings can be given:[27] Surprisingly, it has been demonstrated that the hole mobility of the MDMO-PPV/PCBM blend actually increases upon addition of PCBM. At 80 wt.-% PCBM, the hole mobility amounts to $2.0 \times 10^{-8} \text{ m}^{2}/\text{V s}$, which is an increase of more than two orders of magnitude as compared to pristine MDMO-PPV.[28,29] Additionally, the performance of MDMO-PPV/PCBM solar cells benefits from a higher dielectric constant associated with the addition of PCBM, since this facilitates the dissociation of bound electron-hole pairs across the polymer-PCBM interface.[27]

Interestingly, the performance of MDMO-PPV/PCBM solar cells with only 25 vol.-% PCBM, corresponding to the composition of the best performing MDMO-PPV/nc-ZnO cells, is markedly worse with an efficiency of only 0.2%.[27] Moreover, at that composition, the electron mobility in the PCBM phase is equal to approximately $3 \times 10^{-10} \text{ m}^{2}/\text{V s}$ and the hole mobility equals the pristine MDMO-PPV value. Therefore, the electron mobility of the MDMO-PPV/nc-ZnO system is higher at this composition, as is the efficiency (1.6%). The generation of free charge carriers under operating conditions in the MDMO-PPV/nc-ZnO system is more efficient ($G = 1.26 \times 10^{27} \text{ m}^{-3} \text{s}^{-1}$, for the device of Fig. 5.6) than in the MDMO-PPV/PCBM (3:1 by volume) devices, where $G = 5 \times 10^{26} \text{ m}^{-3} \text{s}^{-1}$.[27] Since the volume ratio of MDMO-PPV in both systems is the same (75 vol.-%), this lowering of the carrier generation is attributed to the less efficient electron-hole pair dissociation due to the lower dielectric constant of PCBM. Model calculations show that this changes the dissociation efficiency by more than a factor of 2.

**Improving the performance of MDMO-PPV/nc-ZnO solar cells**

As already mentioned, the open-circuit voltage of MDMO-PPV/nc-ZnO is lower than the open-circuit voltage of MDMO-PPV/PCBM devices due less favorable energetic position of the conduction band of nc-ZnO. However, as will be demonstrated below, the main cause for a lower efficiency, as compared to optimized MDMO-PPV/PCBM devices, lies in the lower charge carrier mobilities.

The concentration of nc-ZnO in these blends is limited by the film forming properties: when more than 33 vol.-% of nc-ZnO is added, the film quality becomes very poor.[8] The fact that one is limited to rather low nc-ZnO content, complicates a good comparison between both systems. For example, it is at this moment unclear whether the spectacular enhancement of the hole mobility upon addition of PCBM will also be
induced by nc-ZnO addition, if it were possible to maintain a good morphology. Additionally, in view of the high mobilities reported for nc-ZnO electrodes,[10,15,24] it is reasonable to assume that the electron mobility through the nc-ZnO phase would also benefit from a larger volume percentage of nc-ZnO. Additionally, Beek et al. have shown that the photoluminescence of an MDMO-PPV/nc-ZnO containing 25 vol.% nc-ZnO is not completely quenched, probably due to large polymer domains in the film morphology.[8] The need for a better control over the morphology of the blend is obvious, and one option would be the use of additional ligands that improve the dispersability of the nanocrystals. However, Greenham et al. have demonstrated that the use of a ligand can seriously hamper the charge transfer from conjugated polymers to inorganic nanocrystals.[3] Huynh et al. were able to control the morphology of films consisting of cadmium selenide nanocrystals blended with poly(3-hexylthiophene) through the use of the weakly binding ligand pyridine.[30] After deposition of the blend film, the ligand could be removed by heating the sample under vacuum. Another approach is to use an electroactive ligand, which mediates the electron transfer between cadmium selenide nanoparticles and conjugated polymers.[31,32] These results show the potential of the use of ligands for controlling the properties of polymer/inorganic nanoparticles blends.

To show that higher efficiencies can indeed be obtained once the hole mobility is improved, the effect is calculated of enlarging the hole mobility up to the MDMO-PPV/PCBM (1:4 by weight) value, $2.0 \times 10^{-8} \text{m}^2/\text{Vs}$, on the current-voltage characteristics of an MDMO-PPV/nc-ZnO solar cell, see Fig. 5.8. As expected, the efficiency of MDMO-PPV/nc-ZnO solar cells benefits from this improvement of the charge transport,
and the efficiency would be enhanced by 35%. The fact that the hole mobility is equal to the pristine MDMO-PPV value represents a limit to the efficiency that may be relieved by replacing MDMO-PPV with another, more suitable, polymer.

Although bulk ZnO is a very good electron conductor, the electron mobility in the nc-ZnO phase is lower than the electron mobility of PCBM. Since electron mobilities that are at least comparable to or higher than the electron mobility of PCBM have been reported, it is to be expected that by fine-tuning the processing conditions, the electron mobility in the nc-ZnO phase can be improved. However, since the hole mobility is lower than the electron mobility, it is to be expected that not much is to be gained by improving the mobility of electrons. Therefore it comes as no surprise, that also increasing the electron mobility to the PCBM value \(2.0 \times 10^{-7} \text{ m}^2/\text{V s}\) yields an only slightly higher efficiency, which is 44% higher than the efficiency of the actual devices (see Fig. 5.8).

The main increase in the efficiency for the system with enhanced mobilities lies in an increase in fill factor due to better transport of charges. As the open-circuit voltage depends on the bimolecular recombination strength [see Eq. (3.11)], \(V_{oc}\) decreases slightly when the charge carrier mobilities are increased, see Fig. 5.8. Because of this increase of the mobilities, the carrier densities in the bulk of the device are lowered, since the carriers flow out of the device more easily. The field and carrier densities in the device, therefore, come closer to their values in dark (in other words, the quasi-Fermi potential splitting becomes less) and hence the open-circuit voltage decreases.∗ This implies that there is an optimum for the charge carrier mobilities, depending on light intensity and active layer thickness. At intensities around 1 Sun, the optimal values of the mobilities is in the order of \(10^{-8}–10^{-6} \text{ m}^2/\text{V s}\), according to the numerical model.

In a recent study, P3HT has been used to replace MDMO-PPV as the electron donor material. It is well known that, depending on processing conditions, the hole mobility in the P3HT phase of P3HT/PCBM solar cells can be very high, resulting in very efficient devices. In the case of P3HT/nc-ZnO solar cells, it was found that the efficiency increased up to 0.9% upon thermally annealing of the devices, which is not an improvement as compared to MDMO-PPV/nc-ZnO devices, despite the supposedly higher hole mobility. It is, however, unclear whether the hole mobility in the P3HT phase of the hybrid device is as high as in the P3HT/PCBM devices, since the presence of nc-ZnO may influence the crystallization of P3HT. The sublinear (\(\alpha = 0.9\)) intensity dependence of the short-circuit current suggests that there exists at least a large difference between electron and hole mobility. Additionally, it was found that not all of the P3HT was in close proximity to ZnO, because of an unfavorable morphology, which limits the exciton quenching process and thereby the charge generation process. This observation clearly demonstrates the need for greater control over the film morphology.

∗As can be seen from Eqs. (2.2) and (2.3), when \(\mu_n,\mu_p: G = \text{constant}\) the current-voltage characteristics have the exact same shape and only the magnitude of the current changes. This already implies that \(V_{oc}\) decreases when the mobilities become larger, since this is equivalent to a solar cell with lower mobilities but illuminated with a lower intensity. It is, therefore, not desirable to have near-infinite charge carrier mobilities.
Modifying the ZnO nanoparticles

The exact positions of the energy levels of nc-ZnO are sensitive to processing circumstances through their size and surface conditions. It was tried to advantageously use this sensitivity to enhance the performance of MDMO-PPV/nc-ZnO solar cells. Attempts to obtain smaller particles, giving rise to higher open-circuit voltages, were largely unsuccessful. Although obtaining smaller particles is in itself not difficult, the growth can simply be quenched, for example, by cooling the reaction mixture, it proved very hard to keep a small particle size while washing the ZnO particles. This washing step is crucial, since the material purity plays an important role in photovoltaic devices.

Beek et al. observed that the use of a small ligand, in this case $n$-propylamine, improves the film forming properties of the MDMO-PPV/nc-ZnO mixture.\(^{[9]}\) Since this is such a small molecule, the use of $n$-propylamine may not be detrimental to the charge transfer processes. Unfortunately, they found that this ligand resulted in a decrease of $J_{sc}$ and $V_{oc}$. The decrease in $J_{sc}$ could be slightly restored by increasing the amount of nc-ZnO in the blend, but this reduced $V_{oc}$ even further. In order to try to circumvent this loss in $V_{oc}$, the effect of ligands with an opposite dipole (with respect to $n$-propylamine) was studied (see Experimental). Although the film quality indeed improved, this did not lead to an enhancement of the efficiency.

5.4 Conclusions

In this chapter, solar cells with active layers consisting of a polymer (MDMO-PPV) and inorganic semiconductor materials were investigated. One method to obtain such blends is to spin cast a co-solution of the polymer and an organic precursor for either TiO$_2$ or ZnO. Although the efficiency of the MDMO-PPV/prec-ZnO devices was quite reasonable, the hole transport through the polymer phase clearly suffered from the addition or formation of the ZnO.

Another approach is to make nanocrystalline ZnO \textit{ex situ} and add this to the MDMO-PPV solution. It is demonstrated that the hole transport through the thus-formed blends is not affected by the presence of nc-ZnO. The electron mobility in these MDMO-PPV/nc-ZnO blends also is quite decent, although not as high as reported for electrochemical cells. By replacing the MDMO-PPV by a polymer with a higher hole mobility, while maintaining a favorable morphology, and by further optimizing the processing of nc-ZnO, it should be possible to reach significantly higher efficiencies.

5.5 Experimental

In order to make MDMO-PPV/prec-TiO$_2$ blends, a 3 mg/mL solution of MDMO-PPV in toluene was prepared in nitrogen. To this solution, titanium(IV) isopropoxide (Aldrich) was added, such that the final ratio MDMO-PPV:prec-TiO$_2$ corresponded to 4:1 by volume (assuming full conversion). After spin casting the active layer in air, the samples
were kept in dark for one hour in order to let the of the precursor take place. This was followed by one hour in vacuum at 40°C to remove any residual solvents or reaction products.

Blends of MDMO-PPV/prec-ZnO were made as follows: A stock solution of 0.4 M diethylzinc in toluene and tetrahydrofuran was prepared by adding 1.8 mL of diethylzinc (1.1 M in toluene, Aldrich) to 3.2 mL of dry tetrahydrofuran under a nitrogen atmosphere. Assuming full conversion, 1 mL of this stock solution gives 32 mg ZnO. The correct amount of diethylzinc stock solution was added to a 3mg/mL MDMO-PPV solution in chlorobenzene. Spin casting, and subsequent aging and annealing, of the active layer was performed in a nitrogen atmosphere with a relative humidity of approximately 40%. The samples were aged for 15 minutes, followed by annealing at 110°C for 30 minutes.

The nc-ZnO sols were used within a week after synthesis. Typically, 2.95 g of zinc acetate dihydrate was dissolved in 125 mL methanol, kept at 60°C. A solution of 1.48 g potassium hydroxide (87%) in methanal was prepared at room temperature. The hydroxide containing solution was added to the zinc ions containing solution in 8 minutes, under constant stirring. All glassware was dried in an oven. After addition of the potassium hydroxide solution, a clear solution was obtained. The solution was allowed to react for 135 minutes, and was subsequently allowed to cool down for 2 h to room temperature without stirring, causing a white powder to precipitate. Precipitate and mother-liquid were separated and the precipitate was washed twice with 50 mL of methanol. In order to disperse the particles, 10 mL of chlorobenzene was added to the washed precipitate. After filtration (1 µm), the concentration of nc-ZnO was determined by weighing the solid residue after solvent evaporation. Typically, the concentration of nc-ZnO was 60 mg/mL. A 6 mg/mL MDMO-PPV solution in chlorobenzene was prepared. A mixture of methanol and chlorobenzene (1:9 by volume) and the appropriate amount of nc-ZnO sol were added to bring the MDMO-PPV concentration to 3 mg/mL. This blend was spin cast in a nitrogen-filled glove box. The following substances were tried as ligands: 2,3,4,5,6-pentafluoraniline, 2,2,3,3,3-pentafluoropropylamine, and 1H,1H-pentadecafluoroctylamine.
Chapter 5. Hybrid organic/inorganic solar cells

References


