Device physics of organic bulk heterojunction solar cells
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Summary

In the pursuit of developing new technologies that can provide environmental safe energy with unlimited material availability, the photovoltaic (PV) technology has attracted considerable attention in the past few years, owing to its potential of harvesting energy directly from sunlight without having a harmful effect on the natural balance of our planet. Plastic solar cells bear the potential for large-scale power generation based on materials that provide the possibility of flexible, lightweight, inexpensive, and efficient solar cells. Since the discovery of the photoinduced electron transfer from a conjugated polymer to fullerene molecules, followed by the introduction of the bulk heterojunction concept in 1990s (Figure 1), this material combination has been extensively studied in organic solar cells leading to several breakthroughs in efficiency, with a current power conversion efficiency approaching 5%. The efficient photoresponse of these devices depends on the balance of charge generation, transport and recombination [Figure 1(b)].

![Figure 1: (a) Device configuration of an bulk heterojunction solar cell with a photoactive layer consisting of a blend of a conjugated polymer (MDMO-PPV) and fullerene molecules (PCBM). (b) The corresponding (schematic) band diagram of the device under illumination at short-circuit condition. The dotted lines represent the energy levels of the PCBM (acceptor), while the full lines indicate the energy levels of the MDMO-PPV (donor). The numbers refer to the operation processes as follow: (1) exciton creation, (1’) exciton decay, (2) exciton diffusion, (3) charge transfer at donor/acceptor interface ⇒ metastable electron-hole (e-h) pairs across the interface, (3’) ground state recombination of e-h pairs, (4) dissociation of e-h pairs to free charge-carriers, (4’) bimolecular recombination of free e and h, (5) transport of free charge-carriers, and (6) collection.

This thesis discusses the processes and limitations that govern the device operation of polymer:fullerene bulk heterojunction solar cells, with respect to the charge-carrier transport and photogeneration mechanism. The preparation and electrical characterization of the devices were mainly done for the most
effective material combination used in polymer:fullerene bulk heterojunctions at present [Figure 1(a)]. The results of these studies provide a better understanding of the operation principle, and offer a way to design new materials that can further improve the power conversion efficiency of these solar cells.

For the understanding of the opto-electronic properties of bulk heterojunction devices made from polymer (MDMO-PPV) and fullerene molecules (PCBM), first the transport of electrons in PCBM and holes in MDMO-PPV:PCBM blends is investigated in Chapter 2. The occurrence of space-charge-limited current enables a direct determination of the electron mobility from current-voltage characteristics. The resulted electron mobility in pristine PCBM is found to be more that three orders of magnitude larger than the hole mobility measured in the pristine MDMO-PPV. The observed field- and temperature dependence of the electron mobility in pristine PCBM films can be described by the correlated Gaussian disorder model, which is based on hopping of charge carriers between localized state that are subjected to energetic and spatial disorder. This model provides information about the energetic disorder of the transport-sites in PCBM. On the relative comparison with films of pristine MDMO-PPV, the higher electron mobility in PCBM-based devices is due to less energetic disorder of the transport sites in PCBM. Furthermore, on the bases of this result, the charge transport in MDMO-PPV:PCBM solar cells is strongly unbalanced and the experimental photocurrent is expected to be strongly limited by the build-up of space-charge. However, the space-charge limited conduction, admittance spectroscopy, and transient electroluminescence measurements, reveals that hole mobility for the MDMO-PPV phase of the blend is enhanced by a factor of 400 in the presence of PCBM. Consequently, the charge-carrier transport in the MDMO-PPV:PCBM solar cells is much more balanced than previously assumed, which is a necessary requirement for the experimental observed high photon-to-electron conversion efficiencies in these blends.

In Chapter 3, the photocurrent generation in polymer:fullerene solar cells is discussed. When the transport is balanced, the photocurrent is dominated by the dissociation efficiency of electron-hole pairs formed after photoinduced charge transfer across the donor/acceptor interface. A model based on Onsager’s theory of geminate charge recombination explains the field and temperature dependence of the photocurrent in the large voltage regime. Under short-circuit condition, at room temperature, only 60% of the bound electron-hole pairs are separated from the interface and contribute to the generated photocurrent in 20:80 weight percentage MDMO-PPV:PCBM blends. For an unbalanced transport of electrons and holes in the blend, caused by a large difference in their mobilities, the charge-carriers of the slowest species accumulate stronger in the device and result in the build-up of space-charge. Here, it is demonstrated that the experimental photocurrent reaches the fundamental space-charge limit when the difference between electron and hole mobility in the blend exceeds two orders of magnitude. For such a limitation, the photocurrent scales with the square-root on voltage and three-quarter dependence on light intensity. Consequently, the maximum electrostatically allowed fill factor of the solar cells does not exceed 42%.

Chapter 4 discusses the variation of the device performance as a function of
the nature of the metal top electrode in polymer:fullerene bulk heterojunctions. In contrast to the present understanding, it is demonstrated that the open-circuit voltage of the solar cells with non-Ohmic contacts is determined by the work function difference of the electrodes. For Ohmic contacts, the open-circuit voltage is governed by the LUMO (acceptor) and HOMO (donor) difference, which pin the Fermi levels of the cathode and anode. Furthermore, we have shown that the photocurrent obtained from the active layer of a solar cell with different metal work function shows a universal behavior when scaled against the effective voltage across the device. Consequently, for any given metal, only the device’s open-circuit voltage is required in order to be able to predict the remaining solar cell parameters, such as fill factor, short-circuit current, and maximum output power of the device.

The dependence of the performance of MDMO-PPV:PCBM bulk heterojunction solar cells on their composition has been investigated in Chapter 5. With regard to the charge transport, it is demonstrated that with increasing PCBM weight ratio the electron mobility gradually increases up to 80 weight percentage and subsequently saturates to its bulk value. The hole mobility in the MDMO-PPV phase shows an identical behavior and saturates beyond 67 weight percentage PCBM, at a value which is more than two orders of magnitude higher than the one of the pristine polymer. Subsequently, the experimental electron and hole mobilities are used to study the photocurrent generation of MDMO-PPV:PCBM solar cells as a function of composition. From the numerical calculations it is shown that the optimum performance obtained at 80 weight percentage PCBM is due to the best compromise between light absorption, spatial averaged dielectric constant, and charge transport (especially hole mobility in the blend).

In Chapter 6, the photogeneration and transport of charge carriers in blends of regioregular poly(3-hexylthiophene) (P3HT) and a fullerene derivative (PCBM) have been investigated. This material combination has shown an increase of the photovoltaic efficiency upon thermal annealing of the devices, as follows from measurements of external quantum efficiency and current-voltage characteristics. It is demonstrated that the electron mobility dominates the transport of the cell, varying from $10^{-8}$ m$^2$/Vs in as-cast devices to $\approx 3 \times 10^{-7}$ m$^2$/Vs after thermal annealing. The hole mobility in the P3HT phase of the blend increases more than three orders of magnitude, to reach a value up to $\approx 2 \times 10^{-8}$ m$^2$/Vs after the annealing process, as a result of an improved crystallinity of the film. Moreover, upon annealing the absorption spectrum of P3HT:PCBM blends undergoes a strong red-shift, improving the spectral overlap with the solar emission, which result in an increase of more than 60% in the generation rate of charge carriers. Subsequently, the experimental electron and hole mobilities were used to study the photocurrent generation in P3HT:PCBM devices as a function of thermal annealing temperature. The results indicates that the most important factor leading to a strong enhancement of the efficiency, compared with non-annealed devices, is the increase of the hole mobility in the P3HT phase of the blend.

In conclusion, the transport of electrons and holes in the blend is a crucial parameter and needs to be controlled (e.g., by controlling the nanoscale morphology) and enhanced in order to allow for fabrication of thicker films to max-
imize the absorption, without significant recombination losses. Concomitantly, a balanced transport of electrons and holes in the blend is needed to suppress the build-up of the space-charge which, subsequently, will significantly reduce the power conversion efficiency. Understanding of charge transport leads to a good description of the observed photocurrent generation in polymer:fullerene bulk heterojunctions. Dissociation of electron-hole pairs at donor/acceptor interface is an important process that limits the charge generation efficiency under normal operation condition. Both electrodes should form Ohmic contacts in order to maximize the open-circuit voltage of the cell. Based on the findings of this theses, there will be a compromise between charge generation (light absorption) and open-circuit voltage, when attempting to reduce the band gap of the polymer (or fullerene). Therefore, an increase in open-circuit voltage of polymer:fullerene cells, for example by rising the LUMO level of the fullerene, will bring much more benefit to the cell performance since both fill factor and short-circuit current simultaneously increase, and the resulting power conversion efficiency will therefore vary super linearly with open-circuit voltage.