Charge carrier transport and energetic disorder in poly (3-hexylthiophene):methanofullerene photovoltaic blends

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In this paper, the charge carrier transport and energetic disorder in photovoltaic blends of regioregular poly(3-hexylthiophene) (P3HT) and methanofullerene (PCBM) with different annealing temperatures have been studied. It is demonstrated that the current density versus voltage ($J-V$) characteristics of both P3HT hole-only device and PCBM electron-only device can be accurately described by using our recently introduced improved mobility model. Furthermore, the $J-V$ characteristics of P3HT:PCBM blends that were measured in hole-only and electron-only devices for different annealing temperatures can also be accurately described by the improved mobility model. Additionally, we find that the width of the Gaussian density of states σ and zero-field mobility of holes and electrons in P3HT:PCBM blends are the function of thermal annealing temperature. For both hole-only and electron-only devices based on P3HT:PCBM blends, the hole and electron mobilities gradually increase with increasing the annealing temperature, while the width of the Gaussian density of states σ gradually decreases with increasing the annealing temperature, indicating the mobility is closely related to the energetic disorder. These results suggest that the amount of energetic disorder in disordered organic semiconductors appears to govern the charge transport.

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Keywords: Charge transport, Energetic disorder, Disordered organic semiconductors

1. Introduction

Organic photovoltaics (OPVs) have been expected to provide next generation energy sources owing to their low costs, large printable areas, and flexibility [1-4]. The active layer of OPV devices is generally based on a bulk-heterojunction (BHJ) structure consisting of semiconducting electron donor (p-type) and acceptor (n-type) materials. A promising OPV device candidate is based on the regioregular poly(3-hexylthiophene) (P3HT) as the electron donor and the methanofullerene [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) as the electron acceptor due to the commercial availability of these materials [5]. In this donor/acceptor OPV device, light absorption results in the formation of excited electron-hole pairs that dissociate at the heterojunction interface by an ultrafast charge transfer from the donor to the acceptor [6]. These photogenerated free holes and electrons are then transported through the donor and acceptor phases towards the anode and cathode, respectively, resulting in an external photocurrent density. As a result, the external photocurrent does not solely depend on the photogeneration rate of free holes and electrons, but also on the transport properties of the holes and electrons in the donor and acceptor, respectively. Consequently, for the understanding of the optoelectronic properties and further improvement of the performance of P3HT:PCBM-based photovoltaic devices, knowledge about the charge transport of the individual components and P3HT:PCBM blends is indispensable.

For pristine P3HT, much work has been done to measure the hole mobility by using time-of-flight (TOF) photocurrent measurements and space charge limited (SCL) current in a sandwich structure as solar cells or light emitting diode configurations, and a measured hole mobility of 1.4×10^{-8} m^2/Vs at room temperature has been reported [7, 8]. For pristine PCBM, it was demonstrated that the electron current is a space charge limited current and an electron mobility of 2×10^{-7} m^2/Vs at room temperature has been obtained [9]. It can be found that at room temperature the electron mobility in PCBM is about one order of magnitude larger than the hole mobility in P3HT. However, in contrast to the charge transport in pristine P3HT and PCBM, the hole mobility in P3HT:PCBM blends is almost four orders of magnitude lower than the electron mobility [10], making the charge transport in P3HT:PCBM blends strongly unbalanced and the current is fully dominated by the electrons, which is detrimental to the photovoltaic device performance. Fortunately, it was found that the hole mobility in P3HT:PCBM blends can be significantly enhanced by controlled thermal annealing [10], which can dramatically

improve the degree of crystallinity and orientation of polythiophene polymer chains in blend films. The interplay between the charge transport and morphology in photovoltaic blends has been extensively studied [11-15]. Based on the Monte Carlo simulation, Frost et al. have investigated the impacts of morphology on the charge transport and photocurrent generation by varying the interaction energies between the polymer chains [12]. Moreover, Groves et al. have studied the effects of composition, domain size, and energetic disorder on the mobility [13]. On the other hand, Koster have studied the influences of morphology, energetic disorder, electric field, and carrier concentration on blend mobility and found the important differences between neat materials and blends by the numerically solving the Pauli master equation [14]. However, they do not explicitly describe the electric field, carrier density, and temperature dependence of blend mobility, especially neglect the importance of carrier density dependence of mobility for describing the charge transport.

In this paper, the charge transport in P3HT:PCBM photovoltaic blends will be investigated by using our recently introduced improved mobility model in which the mobility depends on the electric field, carrier density, and temperature [16]. Compared with Monte Carlo simulation and the master equation approach, the model and method in this paper are convenient for considering carrier density dependent effect and are numerically more efficient. Furthermore, it is worth mentioning that in this work we focus on using energetic disorder as a method for modeling the charge transport in neat organic semiconductors and polymer/fullerene blends, indicating that the use of a Gaussian disorder reduces the effects of many processes to a single disorder parameter without describing them explicitly.

2. Model and method

Based on the extended Gaussian disorder model (EGDM) [17], we recently proposed an improved mobility model in which the dependences of the mobility μ on the electric field E, carrier density p, and temperature T can be described as follows [16]:

$$\mu(T,p,E)=\mu(T,p)^{g(T,E)}\exp[c_4\big(g(T,E)-1\big)], \quad (1)$$

$$\mu(T,p)=\mu_0(T)\exp[\frac{1}{2}\Big(\hat{\sigma}^2-\hat{\sigma}\Big)\Big(2pa^3\Big)^{\delta}], \quad (2a)$$

$$\mu_0(T)=\mu_0 c_1\exp(c_2\hat{\sigma}-c_3\hat{\sigma}^2), \quad (2b)$$

$$\delta\equiv 2\frac{\ln(\hat{\sigma}^2-\hat{\sigma})-\ln(\ln 4)}{\hat{\sigma}^2},\ \ \mu_0\equiv\frac{a^2\nu_0 e}{\sigma}, \quad (2c)$$

$$g(T,E)=[1+c_5(Eea/\sigma)^2]^{-1/2}, \quad (3)$$

with $c_1=0.48\times10^{-9}$, $c_2=0.80$, and $c_3=0.52$, where $\mu_0(T)$ is the mobility in the limit of zero carrier density and zero electric field, $\hat{\sigma}\equiv\sigma/k_BT$ and σ is the width of the Gaussian density of states (DOS), a is the intersite distance, ν_0 is the attempt frequency, c_4 and c_5 are weak density dependent parameters, given by

$$c_4=d_1+d_2\ln(pa^3) \quad (4a)$$

$$c_5=1.16+0.09\ln(pa^3) \quad (4b)$$

$$d_1=28.7-36.3\hat{\sigma}^{-1}+42.5\hat{\sigma}^{-2} \quad (5a)$$

$$d_2=-0.38+0.19\hat{\sigma}+0.03\hat{\sigma}^2 \quad (5b)$$

Using the above mobility model and following coupled equations, the current density versus voltage ($J-V$) characteristics of organic electron devices based on neat organic semiconductors and polymer/fullerene blends can be exactly calculated by employing a particular uneven discretization method introduced in our previous paper [18-20].

$$J=p(x)e\mu(T,p(x),E(x))E(x), \quad (6a)$$

$$\frac{dE}{dx}=\frac{e}{\varepsilon_0\varepsilon_r}p(x), \quad (6b)$$

$$V=\int_0^L E(x)dx, \quad (6c)$$

where x is the distance from the injecting electrode, $\varepsilon_0\varepsilon_r$ is the permeability of the organic semiconductors, and L is the organic semiconductor layer thickness sandwiched between two electrodes.

3. Results and discussion

Prior to the investigation of the charge transport in P3HT:PCBM photovoltaic blends, knowledge about the hole transport in pristine P3HT and electron transport in pristine PCBM is indispensable. We firstly display the temperature dependent $J-V$ characteristics of P3HT hole-only device and PCBM electron-only device in Fig. 1 and Fig. 2, respectively. The charge transport is modeled by using the improved mobility model and numerical method as described in Sec. 2. Apparently, the temperature dependent experimental $J-V$ measurements from Ref. [21] for P3HT hole-only device with a layer thickness of 95 nm can be excellently described using a single set of parameters, $\sigma=0.1$ eV, $a=1.2$ nm, and $\mu_0=550$ m^2/Vs. The parameters σ, a, and μ_0 are determined in such a way that an optimal overall fit is obtained. It is clear that our numerical results are in good agreement with experimental measurements. This indicates that the improved mobility model is suitable to study the $J-V$ characteristics of P3HT, and captures the physical essence of the charge transport in this polymer. As for the

parameters, the width of the DOS, 0.1 eV, is very close to the value obtained by Tanase et al. in Ref. [21]. The value of the lattice constant, $a = 1.2$ nm, obtained in this work is approximately equal to the result reported by Martens et al. as optimal fitting parameter [22], and smaller than the result used by Pasveer et al. for PPV derivatives in Ref. [17]. Furthermore, it appears from Fig. 2 that the temperature dependent experimental $J-V$ measurements from Ref. [9] for PCBM electron-only device with a layer thickness of 170 nm can also be excellently described by using the improved mobility model with a single set of parameters, $\sigma = 0.066$ eV, $a = 4.4$ nm, and $\mu_0 = 1500$ m^2/Vs. The width of the Gaussian density of states σ is considerably smaller than usually obtained for disordered organic semiconductors, indicating a low degree of energetic disorder in PCBM. The weak disorder is in agreement with the high value obtained for the electron mobility of 2×10^{-7} m^2/Vs [9]. In addition, it is worth noting that previous studies of the electron transport in organic semiconductors have included specific modeling of shallow traps or traps combined with energetic disorder in order to account for apparent temperature and thickness dependences of mobility [23, 24], with such models giving excellent agreement with experimental measurements. However, the above results suggest that models based solely on energetic disorder can also account for such effects, indicating that organic semiconductors can be described simply by a single value of energetic disorder, without needing to refer to an explicit distribution of trap states. As a result, the accurate description of the experimental $J-V$ measurements for P3HT and PCBM devices with the numerical simulations suggests that the improved mobility model can be used for both positive and negative charge carriers in organic semiconductors, leading to simplified modeling of the charge transport.

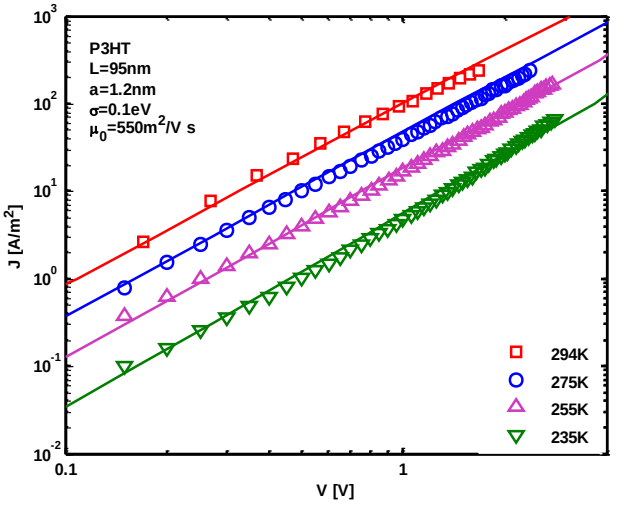

Fig. 1. Temperature dependent $J-V$ characteristics of P3HT hole-only device with a layer thickness of 95 nm. Symbols are the experimental measurements from Ref. [21]. Lines are the numerically calculated results from Eqs. (1) – (6) (color online)

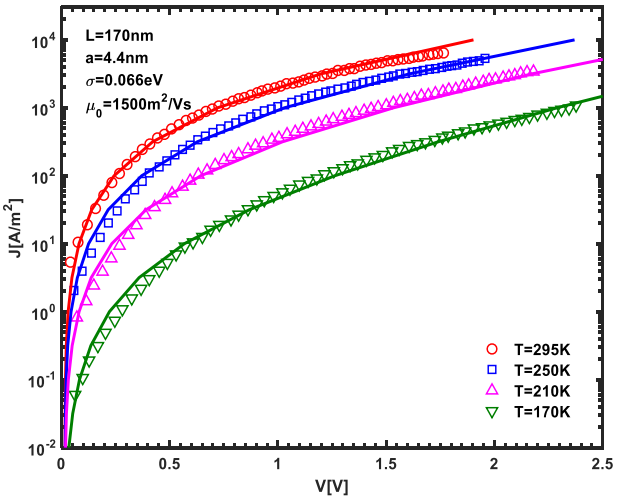

Fig. 2. Temperature dependent $J-V$ characteristics of PCBM electron-only device with a layer thickness of 170 nm. Symbols are the experimental measurements from Ref. [9]. Lines are the numerically calculated results from Eqs. (1) – (6)(color online)

Fig. 3 shows the $J-V$ characteristics of hole-only devices based on the 50:50 wt.-% P3HT:PCBM blends with different annealing temperatures performed on the completed device, and the dependences of the width of the Gaussian DOS and hole zero-field mobility in 50:50 wt.-% P3HT:PCBM blends on the annealing temperature. The values of the width of the Gaussian DOS σ obtained in present work are 0.146 eV, 0.112 eV and 0.101 eV for P3HT:PCBM blends correspond to the different annealing temperatures as follow: as-cast, 90 °C, 120 °C, respectively. Fig. 4 shows the $J-V$ characteristics of electron-only devices based on the 50:50 wt.-% P3HT:PCBM blends with different annealing temperatures performed on the completed device, and the dependences of the width of the Gaussian DOS and electron zero-field mobility in 50:50 wt.-% P3HT:PCBM blends on the annealing temperature. The obtained values of the width of the Gaussian DOS σ are 0.098 eV, 0.078 eV and 0.07 eV for P3HT:PCBM blends with the annealing temperatures of as-cast, 90℃, 120 °C, respectively. It can be seen from Fig. 3 and Fig. 4 that our simulated results are in fairly good agreement with the original experiment measurements for all the annealing temperatures in the entire range of applied fields. This demonstrates that our improved mobility model is also applicable to the charge transport in P3HT:PCBM blends. Furthermore, it appears from Fig. 3 and Fig. 4 that the width of the Gaussian DOS σ and zero-field mobility of holes and electrons in P3HT:PCBM blends are the function of thermal annealing temperature. The hole mobility gradually increases with increasing the annealing temperature, while the width of the Gaussian DOS σ gradually decreases with increasing annealing temperature. From as-cast to 120 °C of annealing temperature, the hole mobility increases almost four orders of magnitude from 4

$\times 10^{-12}$ m^2/Vs to 1×10^{-8} m^2/Vs, whereas the width of the Gaussian DOS decrease from 0.146 eV to 0.101 eV. The electron mobility and the values of the Gaussian DOS σ for the electron-only devices based on P3HT:PCBM blends show a similar behavior. From as-cast to 120 ^{o}C of annealing temperature, the electron mobility increases by a factor of 20 from 1.4×10^{-8} m^2/Vs to 2.8×10^{-7} m^2/Vs, whereas the width of the Gaussian DOS decrease from 0.098 eV to 0.07 eV. From these results it can be found that the mobilities in both hole-only and electron-only devices based on P3HT:PCBM blends are closely related to the energetic disorder.

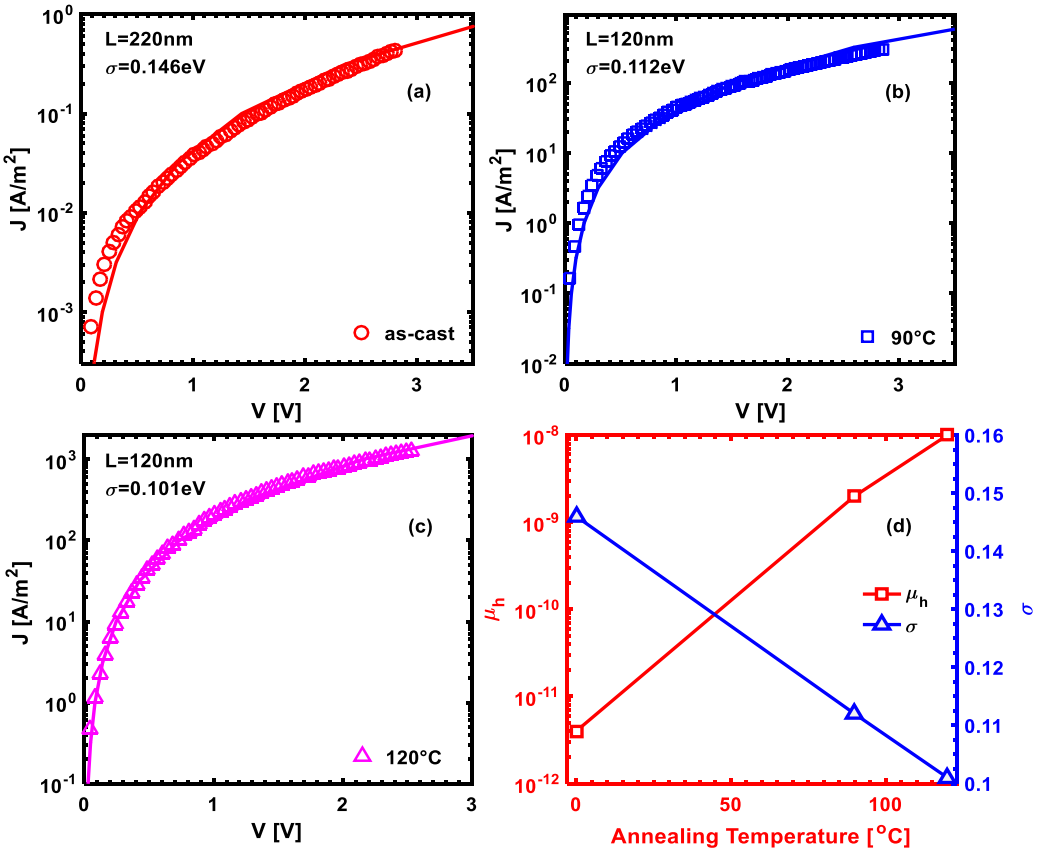

Fig. 3. (a)-(c) The $J-V$ characteristics of hole-only devices based on the 50:50 wt.-% P3HT:PCBM blends with different annealing temperatures, and (d) the width of the Gaussian DOS and hole zero-field mobility in 50:50 wt.-% P3HT:PCBM blends as a function of the annealing temperature. The symbols in (a)-(c) are the experimental measurements from Ref. [10] and lines are the numerically calculated results from Eqs. (1) – (6). The mobility in (d) is calculated from the space charge limited (SCL) current presented in (a), (b) and (c), respectively (color online)

Apparently, it can be found from Fig. 3 and Fig. 4 that in as-cast P3HT:PCBM blends the hole mobility is almost four orders of magnitude lower than the electron mobility, making the charge transport in P3HT:PCBM blends strongly unbalanced and the current is fully dominated by the electrons. Upon thermal annealing, however, the hole mobility in P3HT:PCBM blends is enhanced more strongly than the electron mobility, which making the charge transport in P3HT:PCBM blends annealed at 120 ^{o}C almost balanced. It has been shown that an enhanced degree of crystallinity and orientation of polythiophene polymer chains in P3HT:PCBM blends can be induced by thermal annealing [10]. The change in film morphology upon thermal annealing results in an enhanced intermolecular interaction and an improved charge transfer between adjacent polymer molecules. As a consequence, the molecular conformation and strongly ordered stacking of the molecules should be the origin of the excellent charge transport properties in disordered organic semiconductors, and the charge carrier mobility is closely related to the energetic disorder. This indicates that the amount of energetic disorder in disordered organic semiconductors appears to govern the charge transport properties. From above results, it can be found that the use of a Gaussian disorder in mobility model can reduce the effects of many processes (chain distortions, impurities, and trapping effects and so on) to a single disorder parameter without describing them explicitly. Generally, by reducing a number of unknown properties to a single disorder parameter, the improved mobility model provides

a simple yet adequate method for describing the charge transport in a range of complex disordered systems and can be included in device models with the inclusion of a minimal set of model parameters.

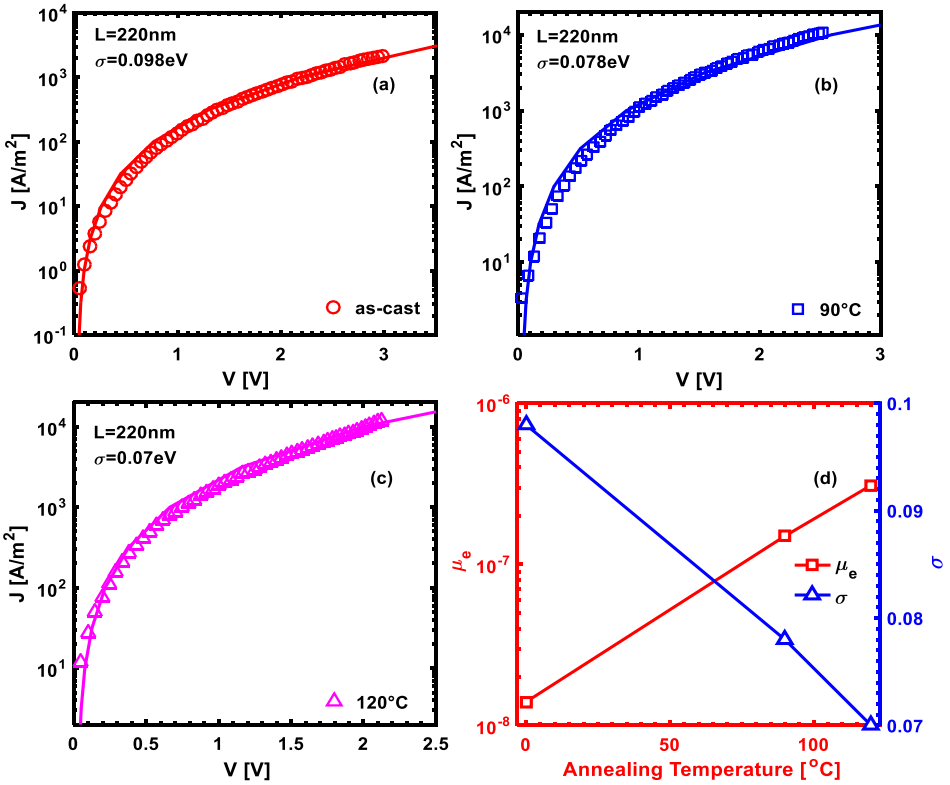

Fig. 4. (a)-(c) The $J-V$ characteristics of electron-only devices based on the 50:50 wt.-% P3HT:PCBM blends with different annealing temperatures, and (d) the width of the Gaussian DOS and electron zero-field mobility in 50:50 wt.-% P3HT:PCBM blends as a function of the annealing temperature. The symbols in (a)-(c) are the experimental measurements from Ref. [10] and lines are the numerically calculated results from Eqs. (1) – (6). The mobility in (d) is calculated from the space charge limited (SCL) current presented in (a), (b) and (c), respectively (color online)

4. Summary and conclusions

In conclusion, the charge transport and energetic disorder in P3HT:PCBM blends with different annealing temperatures have been characterized. We have implemented an improved mobility model based on energetic disorder that can successfully describe the hole transport in P3HT, the electron transport in PCBM, and the charge transport in P3HT:PCBM blends. This suggests that the improved mobility model can be used for both positive and negative charge carriers in organic materials, leading to simplified modeling of the charge transport. Moreover, we find that the width of the Gaussian DOS and zero-field mobility of holes and electrons in P3HT:PCBM blends are the function of annealing temperature. The hole and electron mobilities gradually increase with increasing annealing temperature, while the value of the width of the Gaussian DOS gradually decreases with increasing annealing temperature, indicating the mobility in organic materials is closely related to the energetic disorder. This further suggests that the amount of energetic disorder in disordered organic semiconductors appears to govern the charge transport. These results provide information about the energetic disorder and a simplified modeling of the charge transport in disordered organic semiconductors.

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