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Bimolecular recombination in polymer/fullerene bulk heterojunction solar cells

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Bimolecular recombination in organic semiconductors is known to follow the Langevin expression, i.e., the rate of recombination depends on the sum of the mobilities of both carriers. We show that this does not hold for polymer/fullerene bulk heterojunction solar cells. The voltage dependence of the photocurrent reveals that the recombination rate in these blends is determined by the slowest charge carrier only, as a consequence of the confinement of both types of carriers to two different phases. © 2006 American Institute of Physics. [DOI: 10.1063/1.2170424]

Organic solar cells are a promising alternative to conventional inorganic solar cells because of their low-cost fabrication of large areas and the possibility to use flexible substrates. Recently, attention has mainly been focused on solar cells consisting of a mixture of poly(3-hexylthiophene) (P3HT) and 6,6-phenyl C₆₁-butyric acid methyl ester (PCBM).^{1–4} Power conversion efficiencies exceeding 4% under AM 1.5 illumination have been reported.⁵ In these bulk heterojunction solar cells, light absorption leads to the production of excitons that subsequently dissociate at the internal interface by an ultrafast electron transfer process⁶ due to an energy offset between the lowest unoccupied molecular orbitals of the donor (P3HT) and acceptor (PCBM). After dissociation a geminate pair of a hole on the donor and an electron on the acceptor is formed, strongly bound by Coulomb interaction.⁷ To generate a photocurrent, these geminate pairs have to be dissociated and the resulting free charge carriers have to move to the electrodes.

An important loss mechanism in these devices is bimolecular recombination of free charge carriers, its rate R is given by

$$R = \gamma(np - n_{\text{int}}p_{\text{int}}), \quad (1)$$

where $n(p)$ is the free electron (hole) density, $n_{\text{int}}(p_{\text{int}})$ is the intrinsic electron (hole) density and γ is the Langevin recombination constant. For pristine materials γ is given by⁸

$$\gamma = \frac{q}{\epsilon}(\mu_e + \mu_h), \quad (2)$$

where q is the elementary charge, ϵ is the dielectric constant, and $\mu_{e(h)}$ is the electron (hole) mobility. The sum of the mobilities of both carriers appears in Eq. (2) since both carriers are free to move toward each other. Thus, if one of the carriers is much faster than the other, e.g., $\mu_e \gg \mu_h$, it is the fastest carrier that determines the recombination rate, as schematically indicated in Fig. 1(a). The validity of the Langevin theory to organic semiconductors was confirmed by investigations of the electron-hole recombination in anthracene by Karl and Sommer in 1971.⁹ Furthermore, it was demonstrated that the bimolecular recombination processes in conjugated polymers is correctly described by the Langevin expression.¹⁰

However, the major difference between a pristine semiconductor and a blend is that in the latter the electrons and holes are confined to different phases, and the recombination of free electrons and holes now mainly occurs across the interface of the materials, as schematically indicated in Fig. 1(b). As a first approach, it was proposed by Braun¹¹ that the recombination constant γ has to be adapted to

$$\gamma = \frac{q}{\epsilon} \langle \mu_e + \mu_h \rangle, \quad (3)$$

where $\langle \rangle$ denotes the spatial average. The idea of using a spatial average value is to compensate for eventual mobility differences between electrons and holes in the components of the blend. However, consider the situation as depicted in Fig. 1(b), where the electron is at distance r_e from the interface, while the hole is at a distance r_h . Depending on the initial values of r_e and r_h , the carriers have to travel a certain distance and, subsequently, are stuck at the interface due to the energy offsets between the energy levels of the donor and acceptor. When $\mu_e \gg \mu_h$ the electron reaches the interface much faster than the hole and the total time needed for both carriers to reach the interface is dominated by the hole. Thus, in contrast to a pristine material [Fig. 1(a)], the bimolecular recombination in a blend is now governed by the slowest charge carrier. Therefore, it is expected that for bulk heterojunction solar cells the recombination constant should not depend on $\mu_e + \mu_h$, as in Eq. (2), but will be close to

$$\gamma = \frac{q}{\epsilon} \min(\mu_e, \mu_h), \quad (4)$$

i.e., the recombination constant is dominated by the *slowest* carrier, in contrast to the original Langevin result Eqs. (2) and (3).

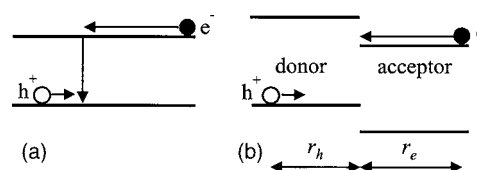


FIG. 1. Schematic semiconductor energy diagram showing bimolecular recombination in pristine semiconductors (a) and in bulk heterojunction solar cells (b). Due to the energy barrier at the donor/acceptor interface, the charge carriers are confined to two different materials.

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TABLE I. Overview of experimentally determined mobilities, parameters used in the fits to the data of Fig. 3, and corresponding FFs.

Parameter	Unit	Annealed at 52 °C	Annealed at 70 °C
μ_e (exp.)	m^2/Vs	2.5×10^{-8}	1.1×10^{-7}
μ_h (exp.)	m^2/Vs	3×10^{-12}	1.1×10^{-10}
μ_e	m^2/Vs	2×10^{-8}	1×10^{-7}
μ_h	m^2/Vs	8×10^{-12}	2×10^{-10}
a	nm	1.8	1.8
k_f (slow)	s^{-1}	1.0×10^4	1.2×10^4
k_f (spat. av.)	s^{-1}	1.1×10^7	2.5×10^6
FF (exp.)	%	40	61
FF (slow)	%	39	60
FF (spat. av.)	%	32	48

A major experimental difficulty to investigate bimolecular recombination in donor/acceptor blends is that the (photo)luminescence, which can serve as a fingerprint of free electron and hole recombination, is completely quenched due to the ultrafast electron transfer. In this study we will make use of the fact that the voltage dependence of the photocurrent, which in solar cells is characterized by the so-called fill factor, is also strongly dependent on the bimolecular recombination strength. In order to discriminate between the spatially averaged Langevin or slowest-only Langevin recombination a large difference between the mobilities of electrons and holes is required. Only in that case the predicted recombination constants are clearly different. The hole mobility in the P3HT phase may be varied over several orders of magnitude by annealing the film, at the same time slightly changing the electron mobility in the PCBM phase,¹² see Table I.

Recently, we have developed a numerical model that consistently describes the photocurrent-voltage characteristics of polymer/fullerene solar cells.^{7,13} In this model, drift and diffusion of charge carriers, bimolecular recombination, and the effect of field- and temperature dependent generation of free charge carriers is included. The steady-state continuity equation for electrons is given by

$$\frac{1}{q} \frac{\partial}{\partial x} J_n(x) = PG - (1 - P)R, \quad (5)$$

where J_n is the electron current density, G is the generation rate of bound electron-hole pairs, and P is the probability for dissociation of a bound electron-hole pair. The dissociation probability is dependent on the initial electron-hole separation distance (a) and the decay rate of the bound pair (k_f).⁷ The factor $1 - P$ appears in Eq. (5) since the recombination of electrons and holes in a blend system does not directly lead to loss of charge carriers. Instead, a bound electron-hole pair is created, analogous to the creation of a bound pair after electron transfer across the materials interface, effectively lowering the recombination constant to $(1 - P)\gamma$.

Solar cells are usually characterized by three parameters: the current density under short-circuit conditions (J_{sc}), the open-circuit voltage (V_{oc}), defined as the voltage for which the current in the external circuit equals zero, and the fill factor (FF), defined as

$$\text{FF} = \frac{J_{mpp} V_{mpp}}{J_{sc} V_{oc}}, \quad (6)$$

where J_{mpp} and V_{mpp} are the current density and voltage corresponding to the maximum output power of the device. The

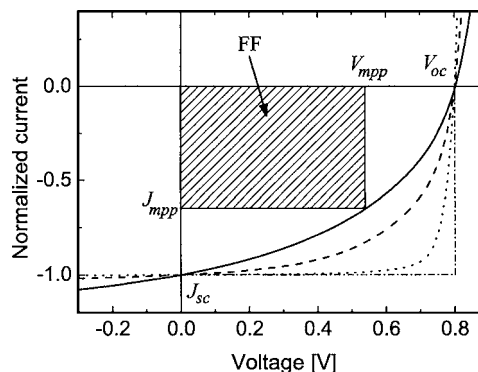


FIG. 2. Simulated current-voltage characteristics of a bulk heterojunction photovoltaic device. The solid line corresponds to the recombination constant of Eq. (3), while the dashed line denotes the result for Eq. (4), i.e., taking only the slowest charge carrier into account. The maximum obtainable FF would be 84%, corresponding to no recombination (dotted line). The FF corresponds to the ratio of the area of the shaded rectangle (maximum power) to the area of the outer rectangle defined by J_{sc} and V_{oc} .

FF is, therefore, a measure of the shape of the current-voltage characteristic of a photovoltaic device. Of these parameters, the FF has the most marked dependence on recombination strength. Figure 2 shows simulated current-voltage characteristics for various recombination strengths and a two orders of magnitude difference between electron and hole mobility ($\mu_e = 3 \times 10^{-7} \text{ m}^2/\text{Vs}$ and $\mu_h = 3 \times 10^{-9} \text{ m}^2/\text{Vs}$). Without bimolecular recombination the fill factor is 84% (Fig. 2, dotted line), but the FF drops from 57% to 44% when increasing γ from taking only the slowest carrier [Eq. (4)] to the spatial average result [Eq. (3)]. This sensitivity of the FF on the recombination strength allows us to determine whether the slowest carrier determines the Langevin rate instead of the spatial average of the mobilities.

Apart from bimolecular recombination, there are two other processes known that influence the FF of this type of solar cell: Buildup of space-charge and a large series resistance due to the electrodes or substrate. The series resistance of our devices typically amounts to 30–40 Ohm, and due to the relatively low currents of polymer/fullerene devices this effect does not play a role. The occurrence of space-charge-limited photocurrents is known to reduce the fill factor to about 42%.¹⁴ Space charge in bulk heterojunction solar cells is caused by either a large difference in mobilities combined with a high illumination intensity, or a substantial amount of traps. Since the transport characteristics of electrons and holes in P3HT/PCBM blends bear all the characteristics of trap-free conduction,¹² space charge due to charge trapping does not occur. Figure 3 shows current-voltage measurements performed on P3HT/PCBM devices, for two different annealing temperatures and, hence, mobility ratios. The mobility difference ranges from two (70 °C) to more than three orders of magnitude for the device annealed at 52 °C. To avoid space-charge-limited photocurrents due to the large difference in mobilities,¹⁴ the measurements were performed at low intensity (approximately 8 W/m²). The currents in Fig. 3 have been normalized to the short-circuit current in order to make the comparison between the two different recombination mechanisms easier: When the recombination strength is increased, the current will drop slightly because of higher recombination losses. The lines in Fig. 3 denote simulation results for both recombination mechanisms. The values of the parameters used in our simulations and result-

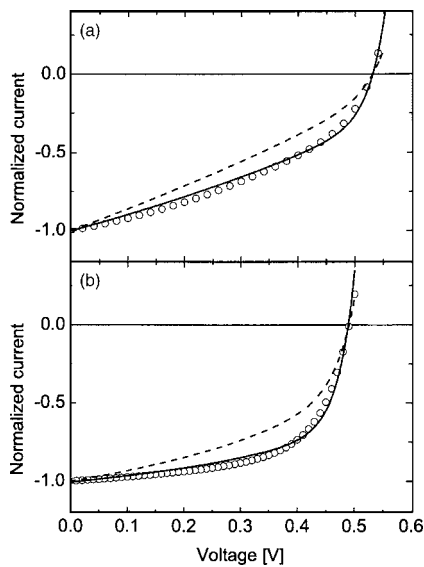


FIG. 3. Current-voltage characteristics normalized to the short-circuit current (symbols) of two P3HT/PCBM solar cells annealed at 52 °C (a) and 70 °C (b). The solid lines denote simulations using Eq. (4), while the dashed lines correspond to simulations using Eq. (3).

ing FFs are listed in Table I. The parameters a and k_f are determined separately from the field dependence of the dissociation probability P .¹² From Fig. 3 and the calculated FF it is obvious that the recombination strength taking only the slowest carrier into account reproduces the experimental data very well, in contrast to the (spatially averaged) Langevin rate. Furthermore, the model calculations confirm that at the low light intensities used here space-charge-limited photocurrents are absent. It should be noted that due to the absence of free parameters it is impossible to obtain a good fit with the spatially averaged Langevin recombination rate. The spatially averaged recombination leads in all cases to too low values for the FF. This observation clearly supports the slowest-only dominated recombination rate. As the difference in electron and hole mobility becomes smaller, the spatially averaged Langevin rate approaches the slowest-only dominated model, eventually leading to identical results when the electron and hole mobilities are equal. Figure 4 shows the experimental FF (symbols) as a function of μ_h/μ_e , as well as the result for both recombination models. As already demonstrated, the difference in the FF is large when $\mu_h \ll \mu_e$, but when the difference in mobility is in the order of a factor of ten or less, it is hard to distinguish between both models. Consequently, in previous work¹³ on the simulation of solar cells with only a factor of 10 mobility difference, the spatially averaged Langevin rate was used, the slowest-only model giving approximately the same result.

Further direct proof of the slowest-only dominated bimolecular recombination comes from recent experiments in which the recombination constant has been measured directly in a polymer/fullerene blend. In blends of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) with PCBM Mozer *et al.*¹⁵ found $6 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ for the recombination constant in this material system. Using $\mu_h = 2 \times 10^{-8} \text{ m}^2/\text{Vs}$ (Ref. 16) and $P=0.52$ (Ref. 13), we obtain in case of slowest-only dominated recombination $(1-P)\gamma = 5.8 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$, in excellent agreement with the experimental result by Mozer *et al.* The recombination constant

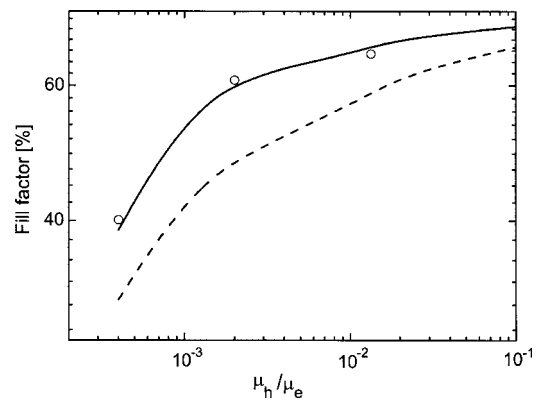


FIG. 4. The experimental FF (symbols) as a function of the mobility ratio. The solid line denotes simulations using Eq. (4), while the dashed line corresponds to simulations using Eq. (3).

based on the spatial average amounts to $(1-P)\gamma = 4.4 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$, which clearly exceeds the measured value by almost an order of magnitude.

In conclusion, we have shown that the Langevin recombination constant for recombination in polymer/fullerene solar cells is not dominated by the fastest charge carrier but by the slowest one, as a consequence of the confinement of the respective carriers to different materials. The sensitivity of the FF of the current-voltage characteristics of solar cells and the infeasibility to obtain a good fit with the original (spatially averaged) Langevin rate allow us to discriminate between the original (spatially averaged) Langevin rate and the rate dominated only by the slowest charge carrier. Moreover, recent measurements of the recombination rate in a conjugated polymer/PCBM blend quantitatively confirm this reduction of the Langevin recombination constant.

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