Bimolecular recombination coefficient as a sensitive testing parameter for low-mobility solar-cell materials

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Abstract
Bimolecular charge carrier recombination has been clarified in bulk-heterojunction solar cells based on a blend of regioregular poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene using the time-of-flight method. We show how bimolecular recombination influences the charge carrier transport, how it limits the efficiency of low-mobility solar cells, and how to estimate the bimolecular recombination coefficient. We found that bimolecular recombination in these efficient photovoltaic materials is orders of magnitude slower as compared to Langevin recombination expected for low-mobility materials. This effect is inherent to the nanomorphology of the bicontinuous interpenetrating network creating separate pathways for electrons and holes, and paves the way for the fabrication of bulk-heterojunction solar cells where bimolecular recombination is not the limiting factor.

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Bimolecular Recombination Coefficient as a Sensitive Testing Parameter for Low-Mobility Solar-Cell Materials

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Bimolecular charge carrier recombination has been clarified in bulk-heterojunction solar cells based on a blend of regioregular poly(3-hexylthiophene) and 1-(3-methoxy carbonyl)propyl-1-phenyl-[6,6]-methanofullerene using the time-of-flight method. We show how bimolecular recombination influences the charge carrier transport, how it limits the efficiency of low-mobility solar cells, and how to estimate the bimolecular recombination coefficient. We found that bimolecular recombination in these efficient photovoltaic materials is orders of magnitude slower as compared to Langevin recombination expected for low-mobility materials. This effect is inherent to the nanomorphology of the bicontinuous interpenetrating network creating separate pathways for electrons and holes, and paves the way for the fabrication of bulk-heterojunction solar cells where bimolecular recombination is not the limiting factor.

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The discovery of ultrafast photoinduced charge transfer between the photoexcited state of a nondegenerate semiconductor π-conjugated polymer (PCP) and 1-(3-methoxy carbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) facilitated intensive research towards the development of large area, low cost photovoltaic devices and photodetectors manufactured from these materials, the so-called bulk-heterojunction solar cells [1,2]. In general, PCPs are considered to be disordered systems. One of the drawbacks in disordered materials is the significantly lower carrier mobility, compared to crystalline semiconductors. The low mobility is caused by the hopping distance, which is shorter than the Coulomb radius \( r_c = \varepsilon^2/4\pi\varepsilon_0\varepsilon_r kT \), where \( \varepsilon \) is the electron charge, \( \varepsilon_0 \) the relative (absolute) dielectric permittivity, \( k \) the Boltzmann constant, and \( T \) the temperature, and consequently the probability for escaping recombination will be lowered. This causes low photogeneration efficiency and diffusion controlled charge carrier recombination of Langevin-type determined by the probability for photogenerated electrons and holes to meet in coordinate space [3,4]. The magnitude of the recombination rate is then described by the Langevin recombination coefficient \( \beta_L = \varepsilon (\mu_p + \mu_n)/\varepsilon_0 \), where \( \mu_p \) (\( \mu_n \)) is the electron (hole) mobility [5].

To achieve current densities of the same order as in crystalline solar cells, the concentration of photogenerated charge carriers \( n_{ph} \) must be much higher for low-mobility materials used in solar cells. High carrier concentration causes a small lifetime of the charge carriers \( \tau(t) = [\beta n_{ph}(t)]^{-1} \), where \( \beta \) is the bimolecular recombination coefficient, and, consequently, short diffusion and drift distances. The necessary condition for a high energy conversion coefficient of a solar cell is that the lifetime of the charge carriers must be higher than their transit time in the intrinsic electric field \( t_g \), i.e., \( \tau > t_g \). Thus, \( n_{ph} < \mu U_{bi}/\beta d^2 \), where \( U_{bi} \) is the built-in electric field.

In order to reach a conversion efficiency of \( \geq 5\% \) for solar cells with a thickness of \( d = 300 \text{ nm} \) and open circuit voltage of \( V_{oc} \approx 0.5 \text{ V} \), a photocurrent density of \( \geq 15 \text{ mA/cm}^2 \) is required, leading to a necessary condition that \( \mu \beta_1/\beta > 5 \times 10^{-3} \text{ cm}^2/\text{V s} \). This criterion clearly shows that the bimolecular recombination coefficient is an important testing and characterization parameter to evaluate the suitability of low-mobility materials to be used in efficient solar cells.

The charge carrier generation and recombination in bulk-heterojunction solar cells has been widely studied using optical techniques such as photoinduced absorption or light induced electron spin resonance on films with no electrodes attached [6–11]. Recombination losses in devices also have been studied electrically by correlating the short circuit current of the solar cell to the excitation light intensity at different temperatures [12,13]. Usually a linear dependence of the short circuit current on the excitation light intensity at room temperature is found, leading to the conclusion that bimolecular recombination is not important in bulk-heterojunction solar cells. We want to emphasize that, to the best of our knowledge, none of the studies directly address the issue of bimolecular recombination in an operating device.

In this Letter, we show the importance of the bimolecular recombination coefficient as a sensitive testing parameter for low-mobility materials for solar cells. We show how bimolecular recombination affects the charge transport and causes an upper limit on the charge that can be extracted. Furthermore, we have experimentally clari-
fied the bimolecular recombination in bulk-heterojunction solar cells using well established time-of-flight (TOF) techniques. We also would like to point out that this technique is useful for thin films. We show that the recombination in bulk-heterojunction solar cells based on a blend of regioregular poly(3-hexylthiophene) (RRPHT) and PCBM is greatly reduced, which is in agreement with previous studies [12]. We propose that the slower recombination is inherent to the nanomorphology of the inter-penetrating network of these photovoltaic materials.

At high light intensities, the photogenerated charge carriers creates a reservoir where the electric field is immediately screened. The extraction of charge carriers from the reservoir causes a decrease of the reservoir width, while the field will remain zero in the reservoir. We can therefore neglect the influence of carrier extraction on the recombination and simplify the decay kinetics in the reservoir as

$$\frac{dn_{ph}}{dt} = -\beta n_{ph}^2, \quad (1)$$

with the solution

$$n_{ph}(x, t) = \left( \frac{1}{\alpha L \exp(-\alpha x)} + \beta t \right)^{-1}, \quad (2)$$

where \( \alpha \) is the absorption coefficient and \( L \) is the intensity of the laser pulse given in photons per unit square. The decay of the photogenerated charge carrier concentration is governed by carrier recombination and extraction from the sample in the electric field, and we can write the equation

$$N(t) = \int_0^d n_{ph}(x, t) dx - \frac{1}{e} \int_0^t j(t) dt$$

\[= \frac{1}{\alpha \beta t} \ln \frac{1 + \beta \alpha L t}{1 + \beta \alpha L t \exp(-\alpha d)} - \frac{1}{e} \int_0^t j(t) dt, \quad (3)\]

where \( N(t) \) is the amount of charge carriers per unit square at the moment \( t \). The complete extraction of photogenerated charge carriers is obtained at the charge carrier reservoir extraction time \( t_e \) such that \( N(t_e) = 0 \).

With increasing light intensity, the extraction current will become space charge limited under surface generation (\( \alpha d \gg 1 \)) or limited by the circuit resistance when \( \alpha d \approx 1 \) (bulk generation). For high light intensities (\( L \to \infty \)) and thin films (\( \alpha d \approx 1 \)), the extracted charge will saturate and become independent on light intensity due to bimolecular recombination and we get an expression for the extracted charge \( Q_e \) by simplifying Eq. (3):

$$Q_e = \int_0^\infty j_e dt = \frac{edS}{\beta t_e}, \quad (4)$$

where \( S \) is the electrode area. Equation (4) can be rewritten as

$$\frac{\beta}{\beta_L} = \frac{CU_0}{t_e}, \quad \frac{Q_e}{t_e} = \frac{Q_e}{t_e}, \quad (5)$$

where \( C \) is the geometrical capacitance of the sample, \( U_0 \) is the applied voltage on the sample, and \( t_e \) is the transit time of the photogenerated charge carriers. We note that if only monomolecular recombination is present, \( t_e \) does not saturate as a function of light intensity, but has a logarithmic intensity dependence \( t_e \propto \ln L \) [14].

We have numerically calculated current transients by solving the set of Poisson, current, and kinetic equations neglecting thermally generated charge carriers, monomolecular recombination, and trapping [14,15] using values typically observed in bulk-heterojunction solar cells [2]. In Fig. 1 the results of the numerically calculated current transients, normalized to the space charge limited current value \( j_{SCLC} = 9e0\mu U_0^2/8d^3 \), as a function of light intensity normalized to the charge that can be stored on the electrodes \( L' = L eS/CU_0 \) are shown for \( RC/t_\tau = 10 \), and in (a) \( \beta/\beta_L = 1 \) and in (b) \( \beta/\beta_L = 0.01 \).

![FIG 1](color online). Numerically calculated TOF transients normalized to the space charge limited current value \( j_{SCLC} = 9e0\mu U_0^2/8d^3 \), as a function of normalized light intensities \( L' = eLS/CU_0 \). The parameters used in the calculations are typical of a bulk-heterojunction solar cell, namely, \( RC/t_\tau = 10, \alpha d = 4, \) and (a) \( \beta/\beta_L = 1 \) and (b) \( \beta/\beta_L = 0.01 \). The reservoir extraction time \( t_e \) is determined as the difference between the half time of the extraction current at high and low light intensities, respectively.
From Fig. 1 the amount of extracted charge $Q_e$ and the extraction half time $t_{1/2}$ as a function of light intensity were estimated and shown for various $\beta/\beta_L$ ratios in Fig. 2. It is clearly seen that the extraction half time starts to increase when the extracted charge equals the charge stored on the contacts.

To experimentally clarify the bimolecular recombination in bulk-heterojunction solar cells, we used a 3 ns Nd:YAG laser operating in the second harmonic (532 nm) with the energy of 0.3 mJ per pulse. The sandwich-type samples were made by spin coating a 0.7 μm thick film from a blend of RRHPHT and PCBM in the ratio 1:2 on top of an indium tin oxide (ITO) glass substrate covered by a 80–100 nm poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) film [16]. The absorption coefficient of the blend is $\alpha = 6.3 \times 10^4$ cm$^{-1}$ ($\lambda = 532$ nm), giving $\alpha d = 4.4$. We use integral mode TOF ($Q$-TOF), where $\tau_{RC} \gg \tau_{tr}$ in the experiment. To get highest possible charge carrier densities, the samples were illuminated through the ITO. To experimentally determine $\tau_e$, we use the difference of the time at high and low light intensities when the TOF transients have decreased to half their initial value, i.e., $\tau_e = t_{1/2}(L) - t_{1/2}(L_0)$, as suggested by Juška et al. [14] [see Fig. 1(b)].

The experimentally measured $Q$-TOF transients are shown in Fig. 3(a). There is a striking similarity between the experimentally measured and numerically calculated curves both in magnitude and shape. At high light intensities the current transients saturate due to bimolecular recombination as predicted by Eq. (3). The extracted charge $Q_e/CU_0$ and the extraction half time $t_{1/2}$ as a function of light intensity were estimated and shown in Fig. 3(b). It is clearly seen that the extraction half time starts to increase when $Q_e/CU_0$, as is also seen in the calculated curves in Fig. 2. Both $Q_e/CU_0$ and $t_{1/2}$ clearly saturates on increasing light intensity, and from the saturation value we estimate the bimolecular recombination coefficient using Eq. (4) as $\beta = 2 \times 10^{-13}$ cm$^3$/s. We were also able to measure the mobility of the fastest carriers using current mode TOF in the same solar cell and found that $\mu = 4 \times 10^{-3}$ cm$^2$/Vs independent of time and of electric field [17]. We can therefore calculate
the Langevin recombination coefficient as \( \beta_L = 2 \times 10^{-9} \text{cm}^3/\text{s} \), allowing us to estimate \( \beta / \beta_L = 10^{-4} \). From our measured values of \( Q_e \) and \( I_e \) as a function of light intensity and applied voltage, we find that the estimated values of \( \beta \) are all within the error limit of the experiments. The temperature dependence of \( \beta / \beta_L \) was measured and we found a small activation energy of approximately 30 meV. The weak temperature dependence of \( \beta / \beta_L \) indicates that the probability for an electron and a hole to meet is determined by tunneling. If the lower recombination were caused by thermal activation over a barrier, then an energy barrier of approximately 0.5 eV would be required, which is clearly not the case.

In low-mobility materials such as amorphous selenium [3] and PCPs [4,18] \( \beta = \beta_L \), causing an upper limit on the current density while reduced bimolecular recombination is necessary for efficient solar-cell operation. In bulk-heterojunction solar cells, i.e., PCPs mixed with PCBM, the photogeneration efficiency is close to unity [1,2] and independent of electric field. The immediate creation of a separated electron-hole pair together with the fact that the recombination is greatly reduced suggests that the nanomorphology of the bicontinuous interpenetrating network creates separate pathways for electrons and holes [19]. The nanomorphology of the bulk-heterojunction solar cell which both enables efficient charge generation and enhances transport of holes and electrons via separate pathways to the contacts therefore seems to be important for high power conversion efficiency solar cells [20]. This effect is analogous to the random potential in \( \mu\text{-Si}:\text{H} \), which decreases the probability for the holes and electrons to meet and recombine [21,22].

In conclusion, we have shown how to determine bimolecular recombination losses in low-mobility materials suitable for solar cells using TOF. We found that the bimolecular recombination coefficient is greatly reduced in a model system of bulk-heterojunction solar cells so that \( \beta / \beta_L = 10^{-4} \). The reduced recombination allows charge carriers to escape recombination and reach high enough densities so that energy conversion efficiencies of the bulk-heterojunction solar cells is not limited by bimolecular recombination. The nanomorphology of the bicontinuous interpenetrating network is the key for both the efficient generation as well as for reduced recombination.

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