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Device simulation of low-band gap polymer solar cells: Influence of electron-hole pair dissociation and decay rates on open-circuit voltage

Yuan Shang,[1] Qikai Li,[1] Lingyi Meng,[1] Dong Wang,[2] and Zhigang Shuai[1,2,a)]
[1]*Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Science (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, 100190 Beijing, People's Republic of China*
[2]*Department of Chemistry, MOE Key Laboratory of Organic Opto-Electronics and Molecular Engineering, Tsinghua University, 100084 Beijing, People's Republic of China*

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We simulated the performance of recently developed highly efficient bulk heterojunction photovoltaic cells with poly [N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] as the donor and [6,6]-phenyl C_{70}-butyric acid methyl ester as the acceptor, using a device model. The simulated current-voltage curve is in excellent agreement with the experiment. This enables us to analyze how microscopic processes of excitons and charges govern the device performance. The influence of dissociation rate and decay rate of photoinduced electron-hole pairs on the open-circuit voltage V_{OC} is investigated. It is shown that a high dissociation rate relative to decay rate will lead to enhanced V_{OC}. © *2010 American Institute of Physics*. [doi:10.1063/1.3494527]

Polymer solar cells have attracted tremendous attention for their potential in low-cost fabrication as well as applications in flexible, lightweight, and large-area devices. Since the proposal of bulk heterojunction (BHJ) structure consisting of electron donating and accepting moieties,[1] there has been a dramatic improvement in the efficiency of polymer solar cells. Very recently, power conversion efficiencies above 6% under air mass 1.5 global (AM 1.5 G) illumination were reported.[2,3] In these devices, low band gap polymers with deeper highest occupied molecular orbital (HOMO) energies were fabricated, leading to a high short-circuit current density J_{SC} and an increased open-circuit voltage V_{OC}.

V_{OC} is one of the key parameters in solar cell devices. In order to optimize the performance of organic solar cells, it is essential to understand the fundamental processes of excitons and carriers governing photovoltaic conversion.[4–6] In a polymer/fullerene solar cell, the photogenerated excitons result in bound electron-hole pairs via an ultrafast electron transfer[5] from the donor to the acceptor.[6] The bound electron-hole pairs either decay to the ground state with a decay rate k_f or dissociate into free carriers with a rate k_d.[4] In this work, we show that both dissociation rate and decay rate are of vital importance to the performance of solar cells, especially to V_{OC}.

In order to disentangle the effect of k_d and k_f on V_{OC}, we performed device simulations of BHJ solar cells based on poly [N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl C_{70}-butyric acid methyl ester ($PC_{70}BM$), using a numerical model first developed by Koster *et al.*[7] incorporating exciton diffusion, bimolecular recombination (the Langevin type, governed by the slowest charge carrier[8]), space-charge effect, and charge dissociation or decay of bound electron-hole pairs.[4] The net generation of free charge carriers depends on exciton generation and its subsequent dissociation as well as nongeminate recombination. The net generation rate U is then written as $U=PG-(1-P)R$, where G is the exciton generation rate, R is the recombination rate and $P=k_d/(k_d+k_f)$.

The space-dependent U is related to the gradient of current density $J_{n(p)}$ through the continuity equations

$$\frac{\partial}{\partial x}J_n(x)=qU(x) \quad \text{and} \quad \frac{\partial}{\partial x}J_p(x)=-qU(x), \tag{1}$$

with q the elementary charge. The current density has two contributions: the drift current due to the electrostatic potential gradient and the diffusion current due to the charge density gradient

$$J_n=-qn\mu_n\frac{\partial}{\partial x}\psi+qD_n\frac{\partial}{\partial x}n$$

$$\text{and} \quad J_p=-qp\mu_p\frac{\partial}{\partial x}\psi-qD_p\frac{\partial}{\partial x}p, \tag{2}$$

where $D_{n(p)}=\mu_{n(p)}k_BT/q$ is the carrier diffusion coefficient and $\mu_{n(p)}$ is the carrier mobility. The electrostatic potential and the charge density satisfy the Poisson equation

$$\frac{\partial^2}{\partial x^2}\psi(x)=\frac{q}{\varepsilon}[n(x)-p(x)], \tag{3}$$

where ε is the dielectric constant. With appropriate boundary conditions, the Poisson and continuity equations can be solved iteratively based on the scheme of Gummel.[9] Finally, the current-voltage curve and carrier densities can be obtained. The device structure and the flow chart of the simulation program are depicted in Fig. 1.

We choose physical parameters based on the BHJ solar cells consisting of PCDTBT as the hole conductor and the fullerene derivative $PC_{70}BM$ as the electron conductor.[3] The PCDTBT/$PC_{70}BM$ solar cells exhibit one of the best performance of polymer solar cells studied to date, with $J_{SC}=10.6$ mA cm^{-2}, $V_{OC}=0.88$ V, $FF=0.66$, and $\eta_e=6.1\%$. The thickness of the active layer is 80 nm.

a)Author to whom correspondence should be addressed. Electronic mail: zgshuai@tsinghua.edu.cn.

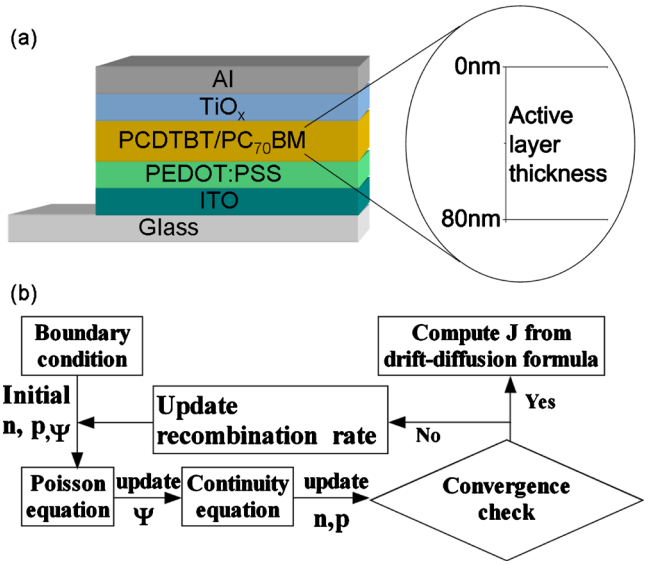

FIG. 1. (Color online) (a) Device structure of the BHJ solar cell. (b) Flow chart of the simulation process. It starts with an initial guess for the potential and carrier densities. The steady state is obtained by solving the Poisson and continuity equations iteratively with a convergence criterion of 10^{-7}.

First, the exciton generation rate G under AM 1.5 G irradiation is calculated[10] by the experimental optical absorption spectrum for the blend[3] and the AM 1.5 G solar spectrum through the following equation:

$$G = \int_0^{800\ nm} \{N_i(\lambda) \times [1 - 10^{-A(\lambda)\times L}]\} d\lambda / L, \tag{4}$$

where A is the normalized absorption coefficient, λ is the photon wavelength, N_i is the incident photon number per unit area, and L is the thickness of the active layer of the solar cell.

In the above, the exciton generation is assumed to be uniform, nonspace-dependent. This is a reasonable assumption since the active layer of the device is very thin (80 nm). Previous studies also show that it does not give rise to serious inconsistencies.[7,11] Through Eq. (4), we obtain the rate as $G=1\times10^{28}$ m^{-3} s^{-1} under AM 1.5 G irradiation. The charge carrier mobilities are taken from the experimental measurements as $\mu_n=3.5\times10^{-3}$ cm^2 V^{-1} s^{-1} (Ref. 12) and $\mu_p=1.0\times10^{-3}$ cm^2 V^{-1} s^{-1}.[13] The dielectric constant ε for conjugated polymers is typically between 3 and 4, here we set it to be 3.5. The effective density of states for electrons and holes at respective electrode is chosen to be 2.5×10^{25} m^{-3}, which gives the boundary condition for carrier densities.[7] The energy gap E_{gap} between the lowest unoccupied molecular orbital (LUMO) of the $PC_{70}BM$ and the HOMO of the PCDTBT is 1.3 eV,[14,15] which sets the boundary condition for solving the Poisson equation as

$$\psi(0) - \psi(L) = 1.3 - V_a, \tag{5}$$

where $L=80$ nm is the position of anode and V_a is the applied external voltage.

Our particular interest in this work is to investigate the influence of the electron-hole pair dissociation rate k_d and decay rate k_f on V_{OC}. It has been shown that k_d depends on the electron-hole pair separation distance a as well as the built-in field and temperature as[4,7]

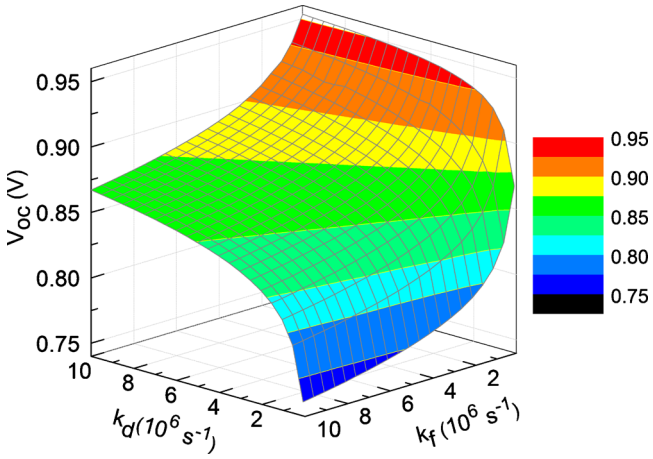

FIG. 2. (Color online) Influence of the dissociate rate k_d and the decay rate k_f on the open-circuit voltage V_{OC} of the $PCDTBT/PC_{70}BM$ solar cells.

$$k_d = \frac{3R}{4\pi a^3} e^{-E_b/kT}\left(1 + b + \frac{b^2}{3}\right), \tag{6}$$

where R is the Langevin bimolecular recombination rate, E_B is the electron-hole pair binding energy $q^2/(4\pi\varepsilon a)$, and $b=q^3F/(8\pi\varepsilon k_B^2T^2)$ where F is the field strength.

Here, we vary the electron-hole pair distance a from 1 to 2.2 nm, which results in a range of k_d from 10^5 to 10^7 s^{-1}. The decay rate k_f is varied accordingly from 10^5 to 10^7 s^{-1} as a parameter. These values cover the practically accessible organic materials useful in photovoltaic cell applications.[16–18] The simulated V_{OC} versus k_d and k_f is shown in Fig. 2. For $V_{OC}>0.9$ V, which corresponds to the regime of $k_d>4k_f$, 79% of the bound electron-hole pairs dissociate into free charge carriers without significant decay to the ground state. In this case, a large number of free charge carriers can participate in the transport and reach the electrodes. We show in Fig. 3 the electron and hole density distributions for various k_d at fixed $k_f=5\times10^5$ s^{-1}. It can be seen that the amount of electron-hole pairs which decay in the bulk reduces dramatically as k_d increases.

In BHJ organic solar cells, V_{OC} is equal to the splitting of quasi-Fermi levels between the contacts. Based on the concept of zero gradient of the electrochemical potential, V_{OC} can be defined from the quasi-Fermi level splitting as[19]

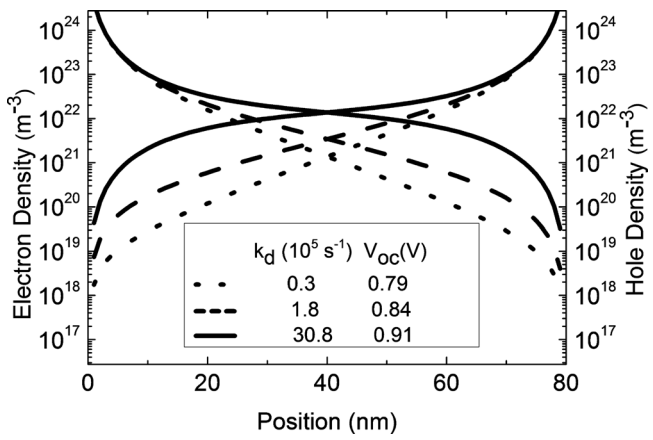

FIG. 3. Electron and hole density distributions for various dissociation rate k_d at fixed $k_f=5\times10^5$ s^{-1} under open-circuit condition.

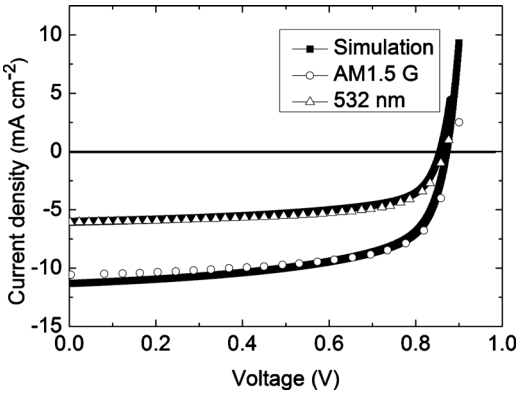

FIG. 4. Comparison between the simulated and experimental *J-V* curves for the PCDTBT/$PC_{70}BM$ device. Two types of illumination condition are considered, AM 1.5 G and monochrome at 532 nm. Both manifest very nice fit with a single set of parameters.

$$eV_{OC} = E_{\text{gap}} - \underbrace{k_B T \ln\left(\frac{N_L N_H}{np}\right)}_{>0} \tag{7}$$

where N_L and N_H are the densities of states in the LUMO of the acceptor and HOMO of the donor, respectively,[20] that cannot be exceeded by n and p. The high k_d and low k_f values will lead to high values of n and p, and as a result increased V_{OC} according to Eq. (7). This is fully in line with the simulation results shown in Fig. 3.

In another extreme case, for $k_d < 0.071 k_f$, Fig. 2 shows that $V_{OC} < 0.8$ V. Under such situation, only 6.6% of electron-hole pairs dissociate into free charge carriers, most of them decay to the ground state. This means that the electron (hole) density within the device is low. The open-circuit voltage is consequently low according to Eq. (7).

The experimental and simulated *J-V* curves under the illumination of both monochromatic green light (532 nm) and AM 1.5 G irradiation are shown in Fig. 4 for comparison. The best fit is obtained by choosing $k_f = 1.5 \times 10^6$ s^{-1} and $k_d = 1.8 \times 10^6$ s^{-1} (the value given is for the open-circuit condition because k_d is field dependent). The good agreement between the experiment and the simulation justifies the model adopted in our investigation.

To conclude, we have investigated the influence of dissociation rate and decay rate on the open-circuit voltage by a numerical simulation model. We demonstrated that to achieve a high open-circuit voltage, the photogenerated electron-hole pairs must dissociate with a rate much faster than their decay rate. The experimental current-voltage curve for the BHJ PCDTBT/$PC_{70}BM$ device can be perfectly reproduced by a set of reasonable parameters, either predetermined by measurements or by fit.

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