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Initial transient photocurrent as a result of polarization of geminate pairs in organics with donor-acceptor bulk heterojunction

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ABSTRACT

The effect of geminate recombination on the photocurrent kinetics is modeled by Monte-Carlo numerical simulation in organic bulk heterojunction. Non-correlated Gaussian distribution of hopping centers is considered. Non-stationary polarization of geminate pairs by external electric field has a considerable influence on transient photocurrent at the time scale of the order of 0.1 μs after generation pulse, and even inversion of the photocurrent sign is possible. Increase of an energetic barrier at donor-acceptor interface weakens this effect and increases a characteristic time.

1. Introduction

The kinetics of photoconductivity and relaxation of excited states in organic semiconductors investigated in recent years in connection with the use of materials in photo-electronic devices such as photovoltaic cells [1–6]. However, in a number of cases it remains unclear the question of the dominant mechanism of recombination of charge carriers (e.g., geminate or bimolecular) [1–3]. Geminate recombination is the recombination of an electron-hole pair, formed by dissociation of an exciton (a molecular excited state) and bounded by Coulomb interaction, although these carriers moving in a non-correlated manner (a geminate pair), while bimolecular recombination results from a meeting of an electron and a hole, produced previously by dissociation of different geminate pairs. In this regard, an important source of information are the transient photoconductivity measurements [2,3]. These measurements may also provide an answer to the question, what is the primary mechanism of loss of charge carriers – recombination or exit from the sample [3]. Elucidation of these circumstances is important to find ways to optimize organic photovoltaics.

Donor-acceptor bulk heterojunctions are widely used in organic photovoltaic devices [7]. Bulk heterojunction is a contact between two chemically different semiconductors with different types of conductivity, for example, P3HT polymer (donor of electrons) and C_{60} fullerene or its derivative (acceptor). Bound states of electrons and holes (excitons) are formed by absorption of light in organic semiconductors. Exciton should separate into free charges. The generation of free charges in organic heterojunction structures occurs as follows (Fig. 1). Exciton migrates to the border of the heterojunction. Typically, only those excitons, which were generated not further than the diffusion length (characteristic distance traveled by exciton during its life, usually about 10 nm) from the heterojunction, reach the donor-acceptor contact. Boundaries of the donor and acceptor phases are distributed throughout the volume so, that the exciton, being generated anywhere, may reach the border and dissociate into free charges. Further, an electron (hole) moves to the respective electrode via the acceptor (donor) molecules. Probability of reaching is maximal in the case of ordered heterojunction (Fig. 2a), whereas in the disordered heterojunction (Fig. 2b) the some fraction of charges can be isolated from the respective electrodes.

If the energy difference between the lowest unoccupied molecular orbitals (LUMOs) of the donor and acceptor exceeds the binding energy of an exciton (0.2–1 eV), electron moves to the LUMO of the acceptor on the donor-acceptor boundary. The electron and the hole, which are located on different molecules (a distance of about 1 nm), linked by the Coulomb interaction, form a geminate pair [8]. Subsequently, these charges can recombine (geminate recombination, GR), or separate, to form a pair of free charges.

It is usually assumed that the photoconductivity formed entirely by free charges and the effect of geminate recombination is reduced only to the temperature and field dependence of the separation probability [9]. However, geminate pairs can contribute to the transient photocurrent even prior to their separation. Indeed, one can express the projection of the current density on the x-axis (providing that uniform electric field is directed in parallel to this axis) as $j_x = en_0\langle v_{hx} - v_{ex}\rangle = n_0 dP_x/dt$, where e is the elementary charge, n_0 is the initial concentration of geminate pairs, $P_x = e\langle x_h - x_e\rangle$ is the ensemble-averaged x-projection of the dipole

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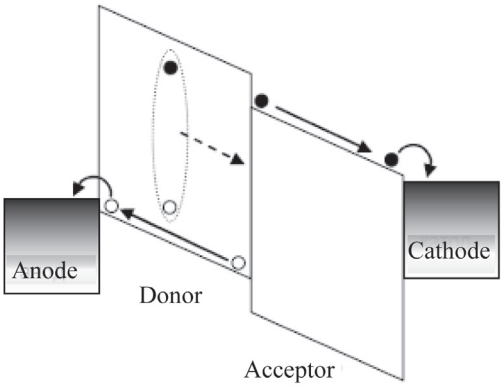

Fig. 1. Schematic of the generation of free charges.

moment of a geminate pair, v_{hx}, v_{ex}, and x_h, x_e are the x-projections of velocities and coordinates of holes and electrons, respectively. The averaged dipole moment P_x and it's time derivative are non-zero, even if $P_x = P_y = P_z = 0$ at $t = 0$ (obviously, $j_y = j_z \equiv 0$ in this case), as it is assumed below, due to the time-dependent polarization of the geminate pairs by the uniform electric field [10–12]. Ensemble averaging accounts for the decrease of survival probability of a geminate pair along with time (recombined pairs does not contribute to P_x). We will refer below the current, described above, as the polarization current. One can observe this effect prior to separation or recombination of majority of geminate pairs (worth noting, the above description provides the asymptotic transition to the current of free carriers, when the pair is separated), if the duration of the laser pulse and the RC time of the circuit is much smaller than the characteristic time of the GR.

In the previous papers [11,12], the Monte-Carlo (MC) modeling of polarization current of geminate pairs in a homogeneous medium has been carried out. It was shown, in qualitative agreement with previous analytic results, that the kinetics of photoconductivity can be non-trivial: the time dependence of the current is non-monotonous, if the initial distance between charges, r_0, is small enough. The purpose of this work is to elucidate the effect of GR on the photocurrent kinetics in the presence of bulk heterojunction.

2. The model and method of simulations

As a result of an exciton dissociation, an electron is located in the acceptor area at a distance r from the fixed hole (which is in the donor area, next to the planar boundary) at the initial time, $t = 0$. The electron's position is given randomly, ensuring a uniform angular distribution in a semi-sphere. Two cases are considered: a fixed distance $r = r_0 = 2$ nm and the distribution of r, in accordance with the function

$$G(r) = Ar^2 \exp[-r^2/2r_0^2] \quad (1)$$

(in a cubic lattice), where $r_0 = 2$ nm [13]. A normalization factor, A, is calculated from the condition that the total probability of finding the electron at a distance from the hole, not exceeding $r_{max} = 12$ nm, is equal to unity.

Providing a disordered bulk heterojunction, see the Fig. 2a, three positions of the donor-acceptor boundary has been modeled, assuming that the uniform external electric field is directed to the right: 1) donor media is to the left, field is perpendicular to the boundary; 2) acceptor media is to the left, the field direction is the same; 3) acceptor media is on the top, and field is parallel to the planar boundary.

According to the well-known Gaussian disorder model [14], the electron undergoes a random walk over the sites of the cubic lattice, energies E are uncorrelated and distributed according to a Gaussian function of the variance σ,

$$g(E) = (1/\sqrt{2\pi\sigma^2})\exp[-(E-\Delta)^2/2\sigma^2] \quad (2)$$

where Δ is the mean position of LUMO energy in the donor or acceptor media. In the acceptor media $\Delta = 0$, while in the donor's region the value of Δ varieties from zero to 0.7 eV. Thus, the energy position of hopping sites in donor's region shifted upward in energy relative to the acceptor's region, see the Fig. 1, by the value Δ. Recombination occurs at a donor molecule, hence an electron should overcome this additional barrier prior to recombination, resulting in the kinetic delay. The case $\Delta = 0$ (no barrier) is also considered for the reference.

Calculations are terminated after the carriers recombine or separate to a distance of more than $8r_c$, afterwards the probability of geminate recombination is negligible [12]. The MC algorithm of simulations of random walks is described in the work [12]. In each test, random energies of hopping centers generated again, according to a Gaussian distribution (2). For each mutual position of the acceptor and donor the polarization current is calculated averaged over the tests. To calculate the polarization current in the external

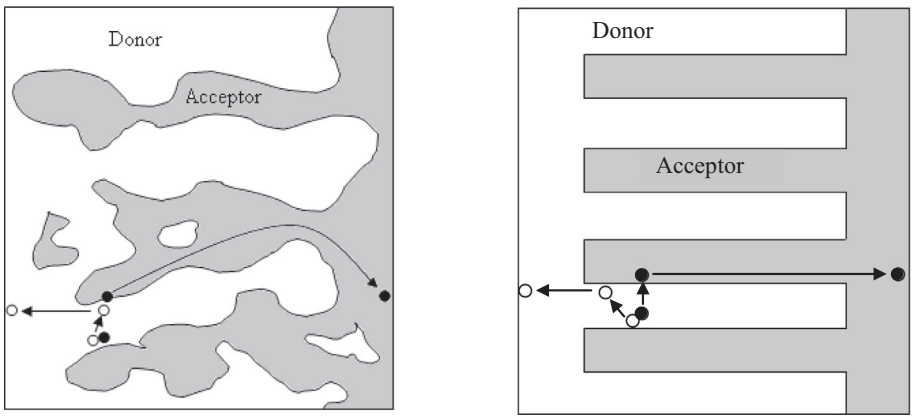

Fig. 2. a) A disordered bulk heterojunction. b) An ordered bulk heterojunction.