Exciton dynamics in a film of carbon nanotubes for photovoltaic applications

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The quasi-1D structure of carbon nanotubes (CNTs) has led to a very unique set of optical, electronic, and mechanical properties. The strong optical absorptivity, tunable near-infrared bandgaps, ultrafast exciton and charge transport, excellent chemical stability, and economical solution-processability of semiconducting CNTs (s-CNTs) have made their application as the light absorbing material in photovoltaics the subject of much research effort in the past few years [1].

Bilayer donor/acceptor heterojuction photovoltaic devices based on s-CNT as the light absorber have been shown to have excellent efficiency in the exciton dissociation step at the heterojunction (Fig. 1). However, the overall efficiency of such s-CNT based photovoltaics needs to be improved further more before they become mainstream. The bottleneck in improving the efficiency of these photovoltaics lies in the process of exciton migration to the heterojunction. It has been shown that exciton diffusion length along the axis of CNT is on the order of 100 nm [2] due to the relatively fast intratube exciton transport. However, the intertube exciton transport is a much slower process yielding to much smaller diffusion lengths in the cross-sectional plane. There have been a number of studies using *ab initio* methods to explain the photophysics of CNTs with focus on the light absorption process and less emphasis on the effect of s-CNTs chirality, orientation, and surrounding environment in the exciton diffusion.

The intertube and intratube exciton dynamics in s-CNT composites is the focus of this study. The exciton transport process in a film of s-CNT happens through two different mechanisms: wave-like (intratube) and hopping (intertube) transport. Figure 2 shows an example of the wavefunctions in the case of two parallel tubes. Due to the dissimilarity between the tubes, the wavefunctions are localized in one of the tubes. An exciton, with a wavefunction localized in one tube, propagates along that tube (wave-like transport) and we do not observe any transport in the cross-sectional direction. However, if the exciton scatters from a state localized in one tube to a state localized in another tube the exciton is transported in the cross-sectional plane (hopping transport). The intertube scattering rates depend strongly on the respective orientation of the tubes, their chirality, and the surrounding environment.

The excitonic problem is a many-body effect which needs to be handled in the light of quantum field theory. We use the tight binding method and the first order perturbation theory to calculate the quasi-particle wavefunctions and energies. We solve the Bethe-Salpeter equation in a matrix form in the basis of quasi-particle wavefunctions to calculate the two-body wavefunction of the exciton [3]

$$(E_c - E_v)A^S_{vc} + \sum_{v'c'} \mathcal{K}_{vc,v'c'}(\Omega_S)A^S_{v'c'} = \Omega_S A^S_{vc}, \tag{1}$$

where Ω_S is the energy of the excited state S. A^S_{vc} is the expansion coefficient of the excitonic state in terms of the quasi-particle states from the conduction and valence band

$$|S\rangle = \sum_{vc} A^S_{vc}|\phi_v\rangle|\phi_c\rangle. \tag{2}$$

$\mathcal{K}_{vc,v'c'}$ is a matrix element of the interaction kernel between the valence band states v and v' and conduction band states c and c'. This kernel accounts for the electron-hole interaction. We use the GW approximation for the calculation of the self-energy term in the kernel and the relaxation phase approximation for the calculation of screened Coulomb interaction.

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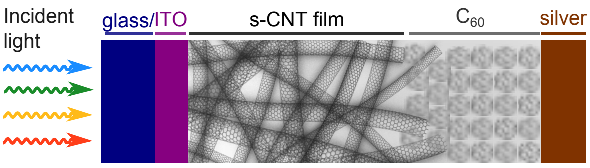

Fig. 1. Structure of a bilayer donor/acceptor heterojuction photovoltaic device based on s-CNT light absorber.

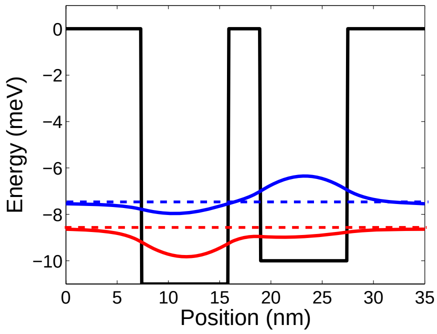

Fig. 2. Localized states in a coupled two-well system.

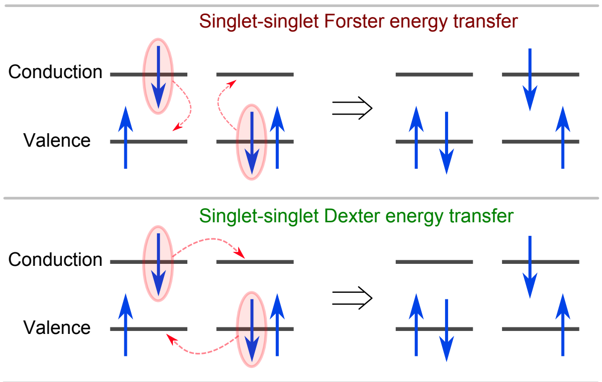

Fig. 3. Direct (Förster) and exchange (Dexter) Coulomb scattering processes.

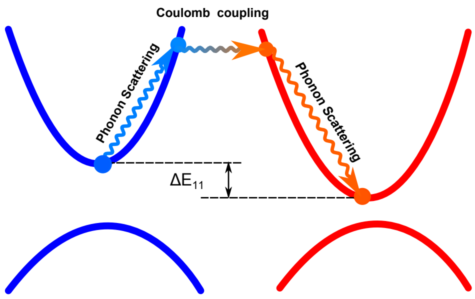

Fig. 4. Role of exciton-phonon interaction and Coulombic coupling in intratube and intertube exciton transport.

We consider two types of scattering sources for excitons: Coulomb interaction and exciton-phonon interaction. Scattering events through the Coulomb force are elastic and can be divided into two types: direct (Förster) and exchange (Dexter) scattering processes (Fig. 3). We show that only Coulomb interaction can result in intertube scattering (intertube transport). On the other hand, the exciton-phonon scattering is an inelastic scattering process and we show that it can only cause intratube scattering. Exciton-phonon scattering plays a direct role in the intratube exciton diffusion, however it also plays a significant indirect role in the intertube exciton transport. As we can see in Fig. 4, exciton-phonon interaction is crucial in energy conservation in the intertube hopping process between states with different energies. We further discuss the effect of CNT chirality, orientation, and the surrounding environment in the hopping process.

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