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Enhanced photocurrent in single-walled carbon nanotubes by exciton interactions

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We theoretically investigate the photocurrent generation efficiency of single-walled carbon nanotubes by considering the interplay between exciton many-body effects. We calculate the photocurrent by solving rate equations that incorporate the influences of the two competing processes, multiple exciton generation (MEG) and the Auger recombination (AR) processes. We find that MEG substantially enhances photocurrent generation in spite of the competing AR process. Our calculation shows that the generation efficiency is up to 150% higher than that without MEG. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4798274]

The increasing global population and burgeoning economic activity require huge amounts of electrical power. Solar energy is the most promising renewable and sustainable energy source. Although much experimental and theoretical effort has been devoted to developing and designing photovoltaic devices with high power conversion efficiencies, the conversion efficiency of conventional solar cells is fundamentally limited by the Shockley–Queisser (SQ) limit.1 Therefore, novel device structures and new materials that can overcome the SQ limit are required to substantially increase the power conversion efficiency of solar cells.

Multiple exciton generation (MEG) is a promising process for exceeding the SQ limit. In low-dimensional materials, a single photon can create an exciton (a bound electron–hole pair) that has a sufficiently high energy that it can generate other excitons by transferring its energy via the strong Coulomb interaction.2–6 This contrasts with the process observed in bulk semiconductors for low exciton densities for which a single photon can create only a single exciton since any excess energy of the photon above the band gap energy is released as heat through exciton–phonon interactions. Carbon nanotubes (CNTs) are ideal materials for realizing MEG since their quasi-one-dimensional structure enhances the Coulomb interaction.7–12 Indeed, MEG has recently been experimentally observed in semiconducting single-walled carbon nanotubes (SWCNTs)13–16 and has been theoretically studied.17–19

Auger recombination (AR) is another important process for photoexcited states of SWCNTs. In AR, an exciton recombinates by transferring its energy to another exciton through exciton–exciton scattering. This is one of the most dominant processes in nonradiative relaxation of excitons in SWCNTs under high-intensity photon irradiation.20–25 AR simultaneously generates free carriers from strongly bound excitons when scattering excitons have sufficiently high energies to ionize other excitons.26,27 In SWCNTs and other low-dimensional materials that have strong Coulomb interaction, the interaction between these two processes results in the highly diverse physics associated with excitons. In particular, photoconductivity in CNTs is determined by competition between these two processes. Although several theoretical studies have investigated photoconductivity in CNTs,26,28–30 a unified understanding of photocurrent generation has yet to be attained.

In this letter, we investigate the efficiency of photoelectric conversion in SWCNTs by accounting for possible competition between MEG and AR processes. Our calculations reveal that photocarriers are generated from both single excitons and multiple excitons generated by MEG, despite AR causing recombinaction of the generated multiple excitons. The results indicate that MEG significantly enhances the photocurrent and is a major pathway for carrier generation in SWCNTs.

Here, we consider the dynamics of carriers and excitons including MEG and AR by solving rate equations that describe the exciton and electron (hole) dynamics

$$\frac{d n_{ex}}{d t} = G - \frac{n_{ex}}{\tau_{ex}} - \Gamma_A L n_{ex}^2 - \Gamma_{eh} n_{eh}, \quad (1)$$

$$\frac{d n}{d t} = \Gamma_A L n_{ex}^2 + \Gamma_{eh} n_{eh} - \frac{n^2}{\tau_{eh}}, \quad (2)$$

where $n_{ex}$ and $n$ are the exciton and electron (or hole) densities, respectively. Here, we assumed the electron and hole densities are equal to each other. The generation rate $G$ in Eq. (1) is the sum of the single-exciton generation rate and the MEG rate given by Eq. (5). The light polarization is assumed to be parallel to the SWCNT axis. In the present study, we consider only multiple exciton states consisting of two excitons. We phenomenologically include phase relaxation of a single exciton such as induced by the exciton–phonon interaction31 as a spectral width of 40 meV in $G$. The radiative lifetimes $\tau_{ex}$ and $\tau_{eh}$ are calculated as the spontaneous emission lifetime.32 The third and last terms on the right-hand side of Eq. (1) represent the AR process for excitons and exciton dissociation by an external electric field, respectively. Both AR and field dissociation cause free carrier generation in Eq. (2). We solve Eqs. (1) and (2) for the isolated SWCNT with the length of $L = 1 \mu m$ to obtain the carrier density $n$ under

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stationary conditions. The carrier density can be used to calculate the steady photocurrent using

$$I = 2e\mu F n,$$

(3)

where $F$ is the bias field and the mobility $\mu$ is calculated as in Ref. 33.

Exciton states with an amplitude $Z_{k \alpha}$ and an energy $E^n$ are obtained by solving the Bethe–Salpeter equation\textsuperscript{7,8,34,35} for exciton states and resonant with the final states, a single exciton with zero momentum through the Coulomb interaction $V$ act with each other. The MEG process is described by the following equations:

$$\left( \epsilon^0_k - \epsilon^0_v \right) Z^n_{k,q} + \sum_{k'} K_{k,k'} Z^n_{k',q} = E^n_Z Z^n_{k,q},$$

(4)

where $K_{k,k'}$ is the Coulomb interaction kernel that consists of bare-exchange and screened-direct terms. The quasiparticle excitations of the electron and hole, the wavy lines indicate the Coulomb interaction, and the squares indicate the exciton states.

From Eq. (5), we obtain the threshold energy for MEG occurring at $\hbar \omega = E^1_q + E^{1\ast}_{-q}$. We phenomenologically consider dephasing processes for the intermediate states by incorporating the dephasing rate of $\gamma = 20 \text{ meV}$ in the denominator of Eq. (5).

The AR rate for two-exciton scattering is given by\textsuperscript{20,26}

$$\Gamma_A = \frac{2\pi}{\hbar} \sum_{q_k} |M|^2 (1 - n^e_k)(1 - n^h_{-q})$$

$$\times \delta(E^1_q + E^{1\ast}_{-q} - \epsilon^0_k - \epsilon^0_v).$$

(6)

Figure 1(b) diagrammatically depicts the matrix element $M$ of the Auger process. This diagram represents the interaction between the two initial $E_{11}$-excitons that results in the formation of a free e–h pair as the final state. The population factors $(1 - n^e_k)$ and $(1 - n^h_{-q})$ for available scattering states of an electron and a hole are taken to be unity because the thermal populations of these states have negligible thermal populations. The AR rate is calculated to be 0.2 ps\textsuperscript{−1} for a length of $1 \mu$m.\textsuperscript{20,26}

Field dissociation of excitons, represented by $\Gamma_F$ in Eqs. (1) and (2), is calculated using the Fowler–Nordheim equation, which is given by\textsuperscript{37}

$$\Gamma_F(F) = \frac{E_b}{\hbar} \exp \left( -\frac{E^{3/2}_b m^{1/2}}{eF \hbar} \right).$$

(7)

where $F$ is the dissociation field that is the same as the bias field in Eq. (3), $E_b$ is the exciton binding energy, and $m$ is the effective exciton mass.

Figure 2 shows photocurrent spectra for various field strengths. In this calculation, the laser intensity was fixed at 0.1 W/m\textsuperscript{2}. At an electric field strength of 1 V/µm, exciton states do not contribute to the photocurrents. The photocurrent spectrum has a one-dimensional asymmetric structure, which reflects the absorption spectrum of free electrons and holes in the one-dimensional structure. Under these conditions, carriers are generated from continuum states above the energy band gap.

In contrast, for electric field strengths of 6 V/µm and higher, we find two new peaks associated with excitons at energies of about 0.7 and 1.5 eV. The lower peak is attributed to an $E_{11}$ exciton, while the higher asymmetric peak originates from excitons with a momentum of zero through the Coulomb interaction $V$. From Eq. (5), we obtain the threshold energy for MEG occurring at $\hbar \omega = E^1_q + E^{1\ast}_{-q}$. We phenomenologically consider dephasing processes for the intermediate states by incorporating the dephasing rate of $\gamma = 20 \text{ meV}$ in the denominator of Eq. (5).

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In contrast, for electric field strengths of 6 V/µm and higher, we find two new peaks associated with excitons at energies of about 0.7 and 1.5 eV. The lower peak is attributed to an $E_{11}$ exciton, while the higher asymmetric peak originates

![FIG. 1. Exciton scattering processes included in the calculations: Feynman diagrams for (a) MEG and (b) AR. The solid lines indicate the Green’s functions of the electron and hole, the wavy lines indicate the Coulomb interaction, and the squares indicate the exciton states.](image1)

![FIG. 2. Electric field dependence of photocurrents as a function of excitation energy.](image2)
from the two-exciton state formed by MEG. The energy of the two-exciton state is twice that of the $E_{11}$ exciton. MEG increases the photocurrents relative to those from continuum states so that they exceed the threshold energy although the increases the photocurrents relative to those from continuum MEG increases the total photocurrent. This result directly demonstrates that AR does not play any role due to the rapid dissociation of the exciton into free carriers. Our calculation unravels the effects of the two competing processes, AR and MEG, on photocurrent generation and shows that these processes are crucial for determining the efficiency of photocurrent generation in SWCNTs. We found that MEG can compete with AR, which increases the photocurrent. SWCNTs are thus promising materials for high-efficient photovoltaic devices.

In summary, we have calculated the photocurrent in SWCNT by accounting for the effects of exciton interactions. Our calculation unravels the effects of the two competing processes, AR and MEG, on photocurrent generation and shows that these processes are crucial for determining the efficiency of photocurrent generation in SWCNTs. We found that MEG can compete with AR, which increases the photocurrent. SWCNTs are thus promising materials for high-efficient photovoltaic devices.

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