Impact Excitation by Hot Carriers in Carbon Nanotubes

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We investigate theoretically the efficiency of intra-molecular hot carrier induced impact ionization and excitation processes in carbon nanotubes. The electron confinement and reduced screening lead to drastically enhanced excitation efficiencies over those in bulk materials. Strong excitonic coupling favors neutral excitations over ionization, while the impact mechanism populates a different set of states than that produced by photoexcitation. The excitation rate is strongly affected by optical phonon excitation and a simple scaling of the rate with the field strength and optical phonon temperature is obtained.

The excellent electrical properties and direct gap of carbon nanotubes (CNTs) offer the possibility of a unified electronic and optoelectronic technology based on this material [1]. The electroluminescence (EL) in CNTs field effect transistors has already been demonstrated, where electrons and holes were independently injected in an ambipolar device [2, 3, 4]. Recently, light emission has been observed under unipolar transport conditions in the suspended tubes [5] and from the CNT-metal contacts [4, 5]. In the suspended sample the light intensity is stronger by a factor of about 1000 compared to ambipolar devices. The mechanism of this enhanced EL was proposed to involve an unusually efficient intra-nanotube impact excitation process involving the hot carriers in CNTs, generated by the high local fields at the interface between the suspended and nonsuspended parts of the tube and the metal-nanotube contact. By utilizing such impact excitation process in quasi one-dimensional confined structures, high exciton densities can be achieved for probing the interactions of such boson systems and for generating ultra bright nanoscale light sources used in nanophotonics.

Here, we provide detailed theoretical study of the impact excitation in semiconducting CNTs. In low dimensional materials, the Coulomb interactions are weakly screened, and large exciton binding energies in CNTs have been predicted theoretically [6, 7, 8] and verified experimentally [9, 10, 11]. This presents an additional challenge for the computation of impact excitation rates in CNTs. We find that the impact scattering rate is very fast, up to five orders of magnitude larger than those in bulk semiconductors [12]. This can be easily rationalized since the same Coulomb interactions responsible for the large exciton binding are also responsible for the impact excitation scattering. The electron-hole correlations in the final state make the impact excitation process, on the average, twice more efficient than the impact ionization, where the created electron hole pairs are treated as independent particles. Impact excitation generates a different initial distribution of excited states than that produced by photon excitation due to the different selection rules and momentum conservation requirements. It has recently been shown that under high bias the energetic carriers in nanotubes excite optical and zone-boundary phonons [14, 15, 16, 17] and generate a nonequilibrium phonon distribution [18, 19], particularly when energy dissipation to the substrate is suppressed as in suspended CNTs [19]. We have calculated the effect of optical phonon excitation and found that the exciton production rate depends exponentially both on the electronic temperature and on the electric field, and the effect can be described by a simple scaling relation.

As a result, optical phonon excitation significantly increases the EL intensity under unipolar transport conditions. The energy spectra of the excitons generated consist of several peaks corresponding to excitons with different angular momenta L: \( E_{11}^L, E_{22}^L, \) and \( E_{22}^{L+2} \), where \( E_{21}^L \) stands for exciton with electron and hole primarily from bands i and j. The relative intensities and the overall excitation efficiencies are functions of the electric field, the optical phonon temperature, and the CNT chirality.

The impact ionization scattering rate of an electron with momentum and energy \((k_1, \epsilon_{k_1}^v)\) scattered to state \((k_1 - q, \epsilon_{k_1 - q}^c)\) plus an e-h pair with a hole \((-k_2, -\epsilon_{k_2}^c)\) and an electron \((k_2 + q, \epsilon_{k_2 + q}^c)\) is given by

\[
W_{k_1,k_1 - q} = \frac{2\pi}{\hbar} \sum_{k_2} |M_{\nu\nu'}|^2 |\delta(\epsilon_{k_1}^c - \epsilon_{k_2}^c - \epsilon_{k_1 - q}^c - \epsilon_{k_2 + q}^c)|
\]

(1)

where \( \nu = k_1 k_2 q, M_{\nu\nu'} = J(k_1 k_2, k_2 + q k_1 - q) \) and \( M_{\nu}^c = J(k_1 k_2, k_1 - q k_2 + q) \) are the direct and the exchange integrals:

\[
J(k_1 k_2, k_1 - q k_2 + q) = \int d\vec{r}_1 d\vec{r}_2 \Psi^*_{ck_1}(\vec{r}_1) \Psi^*_{ck_2}(\vec{r}_2) \Psi_{ck_1}(\vec{r}_1) \Psi_{ck_2+q}(\vec{r}_2) V(\vec{r}_1, \vec{r}_2)
\]

\[
(2)
\]

\( V(\vec{r}_1, \vec{r}_2) \) is the Coulomb potential screened by the dielectric environment of the nanotube [3] and \( \Psi^*_c(\vec{r}) \) and \( \Psi^*_e(\vec{r}) \) are the electron and the hole wavefunctions, given by a \( \pi \)-orbital tight-binding model with hopping matrix element \( t = 3.0 \) eV. In Eq. (1) we neglect e-h pair occupation in the initial state and, hence, processes where electron can absorb an e-h pair.

To include the effect of e-h correlation in the final state we follow [21] and show that the impact excita-
tion scattering rates due to the production of singlet (S) and triplet (T) excitons are given by:

\[ W_{k_1 k_2 \rightarrow q}^{[S]} = \frac{\hbar}{\epsilon} \sum_{\mu} |\tilde{M}_{k_1 q \mu}^{[S]}|^2 \delta (\varepsilon_{k_1}^e - \varepsilon_{k_2}^e - E_{q \mu}^S) \]

\[ W_{k_1 k_2 \rightarrow q}^{[T]} = \frac{\hbar}{\epsilon} \sum_{\mu} |\tilde{M}_{k_1 q \mu}^{[T]}|^2 \delta (\varepsilon_{k_1}^e - \varepsilon_{k_2}^e - E_{q \mu}^T) \]

\[ |\tilde{M}_{k_1 q \mu}^{[S]}|^2 = M_{k_1 q \mu}^{d} M_{k_2 q \mu}^{d} + 2 M_{k_1 q \mu}^{d} \]

\[ |\tilde{M}_{k_1 q \mu}^{[T]}|^2 = M_{k_1 q \mu}^{d} M_{k_2 q \mu}^{d} + 2 M_{k_1 q \mu}^{d} \]

where \( E_{q \mu}^{S,T} \) and \( E_{q \mu}^{T} \) are the singlet and triplet exciton transition energies, \( A_{\mu}^{n} \) is the solution of the Bethe-Salpeter equation for the exciton two-particle wavefunction:

\[ \Phi_{q}^{n}(\vec{r}_1, \vec{r}_2) = \sum_{k} A_{k q}^{n} \psi_{ck+q}(\vec{r}_1) \psi_{ck}(\vec{r}_2). \]

We model the screening of the Coulomb interaction by the dielectric constant of the medium embedding the nanotube, both for the Bethe-Salpeter equation kernel and the impact ionization Coulomb potential Eq. 23. The CNT diameter dependence of exciton binding energies obtained by two-photon florescence excitation spectroscopy agree very well with our model calculations by choosing \( \epsilon = 3.3 \), a value which we use in the rest of the paper.

The impact ionization and impact excitation scattering rates for a tube of diameter \( d = 2 \) nm are shown in Fig. 1a and 1b respectively. This is a typical diameter of tubes used in opto-electronic applications and grown by chemical vapor deposition. The impact excitation rates in CNTs are roughly twice as large as the impact ionization rates due to the e-h confinement in the final state. To understand the structure of the impact ionization scattering rates in Fig. 1a, we need to consider the implications of energy and momentum conservation. The momentum has two components: a discrete angular momentum, which labels the bands, and a linear momentum along the tube axis. The CNT bands are non-parabolic and an angular momentum conservation law plays a crucial role in determining the threshold energy of the impact excitation. As seen from Fig. 1a, angular momentum conservation allows electrons in the third, \( \epsilon_3 \), and the forth, \( \epsilon_4 \), bands to undergo impact ionization scattering by creating electron hole pairs in the first and the second bands respectively: \( \epsilon_1^e = \epsilon_1^h + h_1^3 \) and \( \epsilon_2^e = \epsilon_2^h + e_2^h + h_2^3 + h_2^4 \), where the upper subscript \( L_i \) is the angular momentum in units of \( 2/3d \). In addition, angular momentum determines the band edge energy \( \Delta_i \). In the large \( d \) limit, \( \Delta_i = \hbar v_F L_i \), where \( v_F \) is the Fermi velocity of graphene. Therefore, in this limit, the energy and momentum conservations are simultaneously satisfied for the electrons at the bottom of the third and the fourth bands. However, for finite diameter tubes: \( \Delta_3 < \Delta_2 + 2\Delta_1 \) in \( \text{mod}(n - m, 3) = 1 \) chirality and \( \Delta_4 < \Delta_1 + 2\Delta_2 \) in \( \text{mod}(n - m, 3) = -1 \) chirality. This pushes the lowest impact ionization threshold energy \( E_{ih3} \) of a (25,0) CNT in the third band at energies higher than its bottom \( \Delta_3 \), i.e. \( E_{ih3} > \Delta_3 \), and a power law dependence is obtained \( \Gamma_{ih3} \propto (E - E_{ih3})^\alpha \) with \( \alpha \approx 2 \). Whereas at the bottom of the fourth band \( \Delta_4 \), energy and momentum conservation laws are simultaneously satisfied such that the threshold energy \( E_{ih4} \) coincides with the bottom of the band \( \Delta_4 \), i.e. \( E_{ih4} = \Delta_4 \). The energy dependence of the scattering rate at the onset in the fourth band is similar to that of a step function \( \Gamma_{ih4} \propto \Theta(E - E_{ih4}) \). In a (25,0) tube the impact ionization threshold in the third band coincides with \( \Delta_3 \), i.e. \( E_{ih3} = \Delta_3 \), and it is higher than \( \Delta_4 \) in the fourth band, i.e. \( E_{ih4} > \Delta_4 \). For impact ionization to take place in the first (second) band via the decay channel \( \epsilon_1^e = \epsilon_1^h + h_1^3 \) and \( \epsilon_2^e = \epsilon_2^h + e_2^h + h_2^3 + h_2^4 \), the threshold energy should be at least \( E_{ih1} \geq 3\Delta_1 \) \( (E_{ih2} \geq 2\Delta_2) \) and momentum conservation along the 1D wavevector in non-parabolic bands brings the threshold for the first (second) bands to energies beyond the scale of Fig. 1a.
applied electric field of (a)

FIG. 2: Electron distribution function in a (25,0) nanotube at applied electric field of (a) \( F = 0.1 \) MV/cm and (b) \( F = 0.05 \) MV/cm as a function of energy in the first six conduction bands shown in red, blue, green, cyan, magenta, and light red, respectively. Black curves are the total distributions. In (a) solid curves use impact excitation and dotted curves impact ionization values \([24]\). At the onset of impact conduction bands (Fig. 1b) are significantly reduced from the non-equilibrium phonon effect on the carrier distribution, as in Fig. 2, and the impact excitation scattering rate, as in Fig. 1b, and it is shown in Fig. 2. The higher threshold for impact ionization results in a “hotter” carrier distribution than in the case of impact excitation (Fig. 2).

The non-equilibrium phonon effect on the carrier distribution is shown in Fig. 2. Although at optical phonon temperature \( T_{op} = 1500 \) K the phonon scattering rate is a factor 1.7 larger than at room temperature, the slope of \( \ln (g(E)) \) versus \( E \), as in Fig. 2. The higher threshold for impact ionization results in a “hotter” carrier distribution than in the case of impact excitation (Fig. 2).

The exciton production rate itself is given by the product of the carrier distribution, as in Fig. 2 and the impact excitation scattering rate, as in Fig. 1b, and it is shown in Fig. 4. We find that the rate \( P \) can be well fitted by the following equation:

\[
P = P_0 \exp \left( \frac{E_t}{\sqrt{(k_B T_{op})^2 + (eF\lambda_{op})^2}} \right),
\]

where \( E_t \) is the impact excitation threshold energy and \( P_0 \) is a constant. The form of Eq. 4, resembles the Boltzmann distribution with an effective temperature in the
presence of the field. The inset of Fig. 3 shows an excellent scaling of the exciton production rate with the effective temperature. The diameter dependence of the distribution of the exciton production rate with the electric field. The inset of Fig. 3 shows an excellent scaling of the exciton production rate with the electric field.

Excitons in nanotubes can be created either by optical pumping as in photoluminescence experiments, or by electrical excitation as in electroluminescence. In the photoluminescence case, the energy of the created excitons follows the photon energy of the excitation light, and the angular momentum distribution is determined by the dipole selection rules. Whereas in the electrical excitation process, the energy distribution of the generated excitons depends on the applied bias and it is not subject to the same selection rules. In Fig. 4 we plot the distribution function of the initially created excitons at different fields. The distribution has several distinct peaks, which we identify by analyzing the contributions from excitons with different angular momenta. At the onset of impact excitation, the third and the fourth band electrons generate the low energy excitons with finite angular momenta: $E_{11}^2$, $E_{12}^3$, $E_{12}^4$, whereas at higher bias electrons in the first band produce unbound excitons of zero angular momentum, which contribute significantly to a broad continuum at energy of about 0.9 eV in Fig. 4.

We conclude that CNTs and other 1D systems are characterized by unusually high impact excitation rates and can be used as efficient exciton sources to be employed in fundamental studies of interacting boson systems at high densities and in opto-electronic device applications.

![FIG. 4: Energy distribution $I_0$ of excitons produced in the impact excitation process in (a) a (25,0) tube and (b) a (26,0) tube with phonons at $T = 300$ K and different applied electric fields $F$ in MV/cm: 0.03 - red, 0.06 - blue, 0.09 - green, 0.12 - cyan, 0.15 - magenta, and normalized to the total production rate $P = \int I_0 d\omega$.](image-url)
For two parabolic valence and conduction bands the onset of the impact excitation has the usual power law dependence \[ \Gamma \propto (E - E_{th})^\alpha \] with \( \alpha \approx 2 \) and \( E_{th} \approx 1.5E_g \), where \( E_g \) is the bandgap. Due to the non-parabolicity of the CNT bands, in (25,0) tube: \( E_{th1} = \Delta_1 + 2.6 \text{ eV} \), \( E_{th2} = \Delta_1 + 4.6 \text{ eV} \) or \( E_{th} \approx 6.5E_g \).

[24] V. Perebeinos, J. Tersoff, Ph. Avouris, Nano Lett. 5, 2495 (2005).