Diffusive and Unimolecular Nonradiative Decay of Excited States in Doped Carbon Nanotubes

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Abstract

Doping can profoundly affect the electronic- and optical-structure of semiconductors. Here we address the effect of surplus charges on non-radiative (NR) exciton and trion decay in doped semiconducting single-wall carbon nanotubes. The dependence of exciton photoluminescence quantum yields and exciton decay on the doping level, with its characteristically stretched-exponential kinetics, is attributed to diffusion-limited NR decay at charged impurity sites. By contrast, trion decay is unimolecular with a rate constant of $2.0 \text{ ps}^{-1}$. Our experiments thus show that charged impurities not only trap trions and scavenge mobile excitons but that they also facilitate efficient NR energy dissipation for both.

Introduction

Doped and intrinsic semiconducting single-wall carbon nanotubes (s-SWNTs) are considered as promising materials for electronics, sensors, photonics, photovoltaic, and bioimaging-applications. Such broad interest can be attributed to favorable charge carrier transport properties, large exciton and trion (charged exciton) oscillator strengths and near infrared photoluminescence (PL).

However, optical applications generally suffer from small photoluminescence quantum yields (PLQYs) on the order of one percent as well as from short excited state lifetimes. Both of these reflect the efficiency of non-radiative (NR) decay. This represents a particular challenge for applications which utilize the conversion of excited state energy into photons or dissociated charges and motivates research into the origins and detailed mechanisms of NR decay.

Broadly speaking, the decay of excited states in extended systems can be classified as homogeneous, i.e. the same for all excited states or as inhomogeneous, i.e. dependent on the excited state localization and location. The latter is a reflection of imperfections in the real world and may become prevalent, for example when the lattice symmetry of periodic systems is broken by impurities or by interactions with an environment, as in the case of carbon nanotubes. Regardless, the NR decay of excitons and trions in carbon nanotubes has frequently been described by homogeneous models. These include couplings between bright excitons, dark excitons, trions and the ground state on the basis of unimolecular- or in the case of high excita-
Other studies have favored an inhomogeneous description, specifically regarding the mechanism of NR exciton decay. Such models were particularly successful in describing the dependence of fluorescence quantum yields in SWNTs on nanotube length, the effect of impurities on PL-imaging of SWNTs or the influence of diffusive exciton transport on NR decay observed in time-domain investigations of exciton dynamics. Moreover, localization of excess charge carriers has also been instrumental for the interpretation of Breit-Wigner-Fano resonances in the IR spectra of doped SWNTs.

Here, we present findings in favor of inhomogeneous NR decay of excitons and trions in doped s-SWNTs. The discussion thus evolves around the role of charged impurity sites for the dynamics of excitons and of trions. It a) provides evidence for excitons being scavenged by stationary impurities, b) allows to predict the dependence of the exciton PLQY on the doping level, c) shows that exciton scavenging, confinement, trion states and NR decay are associated with the same charged impurity sites and lastly d) reveals that trions are not exclusively populated by exciton scavenging but also by direct optical excitation of their manifold.

Discussion

Figure 1a) shows a waterfall plot of absorption spectra from a suspension of p-doped (6,5) s-SWNTs with doping levels increasing from top to bottom. The first subband $X_1$ exciton band at 1.239 eV looses practically all of its oscillator strength while becoming broader, more asymmetric and shifting to higher energies by about 70 meV before disappearing into a broad and featureless absorption background at the highest doping levels. Changes in the second subband range are considerably more subtle. The exciton $X_2$ at 2.158 eV appears to split into two features, one of which undergoes similar blue-shift as the $X_1$ band, while the other seems to acquire most of the oscillator strength and shifts to slightly lower energies.

Absorption spectra also feature a trion band $X_1^+$ at 1.058 eV emerging at intermediate doping levels. The latter is generally considered a hallmark for the presence of excess charge carriers in doped semiconductors as is the decrease of exciton oscillator strength.

The effect of doping on NR exciton and trion decay is most evident from the PL spectra of Figure 1b) with an expanded view of the first subband range from 0.9 to 1.4 eV. Here, PL spectra are normalized to the same overall PL intensity to facilitate a closer inspection of changes in the shape and relative intensity of emission bands. The dramatic decrease of photoluminescence with increasing doping level can be seen in Figure 1c) where we have plotted the normalized total PL signal as a function of gold(III) chloride dopant concentration (upper panel). The lower panel shows the relative contributions of the trion and exciton PL to the total PL signal.

In molecular systems, the simultaneous emission of light from a set of strongly coupled electronic states is excluded by Kasha’s rule. This is a reflection of the short time-scale for relaxation within such a set of excited states, if compared to the decay of the lowest optically allowed state. Here, this rule is not obeyed because of the very short lifetime of the trion state (see discussion further below) and also because of the diffusion-limited relaxation of the exciton state, which effectively results in slow population transfer between excited states. Thus, exciton- and trion bands may show up simultaneously in PL spectra as seen in Figure 1b).

Interestingly, the exciton emission band shows no significant blue shift in the doping range over which the absorption band is found to shift by 12 meV. This is difficult to reconcile with a homogeneously broadened exciton band and we take this as further evidence of inhomogeneous doping. This interpretation is based on the notion that excitons which are more strongly confined by closely spaced impurities are also more strongly blue shifted in absorption. At the same time these excitons also decay more rapidly due to their proximity to quenching impurities, thus becoming practically imperceptible in PL spectra. The result
is that PL spectra are dominated by emission from weakly confined excitons that are not blue-shifted, need more time to diffuse to a quenching site and thus have a higher probability for radiative decay.

This interpretation is in line with previous findings showing that the rate of NR exciton decay is determined by the rate at which excitons diffuse to the nearest, charged impurity site. According to this view, excitons between closely spaced impurities will thus experience a greater confinement-induced blue shift while at the same time being more strongly coupled to NR decay channels at the charged impurity sites.

The doping-induced changes of absorption and emission spectra are summarized in Figure 2. This includes normalized data sets for the change of absorbance at the energy of the second subband exciton, the change of first subband exciton and trion oscillator strengths, and the change of their PL signals. Noteworthy is the clear correlation of the decrease of the $X_1$ exciton oscillator strength $f(X_1)$ with the rise of trion oscillator strength $f(X_1^\uparrow)$ seen in Figure 2b) and d). Exciton oscillator strengths have in the past thus also been used as proxy for assessing doping levels.

The data of Figure 2 was used for calculation of the normalized exciton PLQY as well as of the relative PLQY of the trion shown in Figure 3. These yields are plotted as a function of gold(III) chloride concentration (top axis) and $X_1$ exciton oscillator strength (bottom axis). The steep initial decrease of the exciton PL in Figure 3a) with doping- or impurity-level concentration $n_i$ then allows to assign an experimental sensitivity of the exciton PL signal to the concentration of excess charge carriers of $\Phi(f_{X_1})/\Phi_0 \approx 10 n_i$ nm. Here, $\Phi(f_{X_1})/\Phi_0$ is the normalized change of exciton PLQY. A PL change of 1% thus corresponds to $n_i \approx 10^{-3}$ nm$^{-1}$.

Next, we investigate the decrease of the PL quantum yield with oscillator strength seen in Figure 3a). To this end, we again test whether the view of an inhomogeneously doped system, with impurity sites capturing charges in the low doping regime, can account for the observed ef-
fects. The dependence of PLQYs on doping levels would then have to be modeled by the rate at which excitons diffuse to charge impurities where NR decay is most likely to occur.\textsuperscript{15} Such diffusion-limited quenching of excitons has previously also been used to describe the dependence of PLQYs on nanotube length in intrinsic s-SWNT samples\textsuperscript{15,39} where nanotube ends are assumed to act as quenching impurities.

\[ \frac{\Phi(f_{X_1})}{\Phi_0} = \left[ 1 + \frac{d_0(1-f_{X_1})}{\Delta f_{X_1}} \right]^{-2} \]  

where \(d_0\) is the distance of quenching sites for intrinsic s-SWNTs and \(\Phi_0\) is the PLQY of the intrinsic nanotube. The square root dependence of diffusion length on diffusion time is here reflected by the squared term on the right hand side. If we account for the stochastic distribution of impurity spacings around a mean value \(\bar{d}_i = n_i^{-1}\) we obtain best agreement with experimental data for \(d_0/\Delta_i = 25 \pm 4\), see red curve in Figure 3. Using previously reported values of the impurity size \(\Delta_i \approx 4\) nm\textsuperscript{22} would yield an average impurity spacing in the intrinsic s-SWNTs of \(d_0 \approx 100\) nm, in good agreement with previous estimates\textsuperscript{15,40–43}. A simple fit of equation [1] to experimental data would yield an unlikely small value \(d_0/\Delta_i = 14 \pm 2\). This underscores the importance of accounting for the stochastic nature of the impurity site distribution when modelling diffusion limited NR decay.\textsuperscript{39} By contrast, PL from the trion state is considerably weaker than that of the \(X_1\) exciton, reaching only about 1/40 of the PL intensity from intrinsic nanotubes. This may be interpreted as an exceedingly small PLQY on the of \(10^{-4} - 10^{-3}\), reflecting the small fraction of photons emitted with respect to the number of photons absorbed. However, we caution that this may be misleading if considering the intrinsic PLQY of the charged impurity, because trions at impurity sites can possibly be excited indirectly through exciton scavenging as well as directly by light absorption. The above PLQY is thus only a global yield that may have limited value when trying to assess the likelihood of NR decay of a directly excited trion state.

Accordingly, changes of the global trion

![Figure 2](image-url)

**Figure 2: Overview of doping induced spectral changes.** Normalized a) absorbance at the peak of the second subband exciton, b) oscillator strength of the first subband exciton, c) PL signal intensity of the first subband exciton, d) oscillator strength of the first subband trion and e) PL signal intensity of the first subband trion. The doping level increases from weak on the left to degenerate doping levels on the very right.

Accordingly we here describe PLQYs in doped s-SWNTs using a similar model. The rate of NR decay is determined by the time required for excitons to diffuse to an impurity site. The distance between charged impurity sites is designated by \(d_i\). This can be related to the charge carrier concentration \(n_i\) by \(d_i = n_i^{-1}\). Moreover we assume that impurities reduce the nanotube exciton oscillator strength by an amount proportional to the impurity size \(\Delta_i\). We can then relate the oscillator strength \(f_{X_1}\) to impurity distances by \(f_{X_1} = d_i/(d_i + \Delta_i)\). The normalized changes of exciton PLQY can then be cast into the simple form
PLQY seen in Figure 3(b) may be affected by a number of processes such as the exciton scavenging efficiency, the competition among scavenging impurity sites, changes in the character of impurity sites with increasing doping levels, etc.

Figure 3: Dependence of exciton and trion PLQYs on dopant concentration and exciton bleach. a) Normalized change of the first subband exciton PLQY and b) relative change of the first subband trion PLQY for excitation at 568 nm. The blue line is a guide to the eye.

For additional insights into NR exciton and trion decay we thus turn to femtosecond time-resolved pump-probe experiments which provide more direct information on excited state dynamics. Figure 4(a) shows pump-probe traces from excitons in intrinsic and $p$-doped nanotubes as well as the trion decay in a moderately doped sample up to 100 ps time-delay. The data representation in this semi-log plot clearly reveals that exciton dynamics can not be described by a monoexponential decay, contrary to predictions from band-filling models of doped SWNTs.\textsuperscript{140-144} In contrast, the linear decay of pump-probe traces with $\exp(-\sqrt{t/\tau_D})$

Figure 4: Exciton and trion dynamics. a) Semi-log plot of the normalized exciton photo bleach in intrinsic (solid black markers) and doped samples (brown to orange) as well as of the trion state in a moderately doped sample (blue markers). The sample was excited at 576 nm. b) The same as in a) but without the trion signal and plotted as a function of $\sqrt{t}$. The linear decay in this representation here indicates that the kinetics are diffusion-limited with characteristic diffusion times of (20.4 ± 0.4), (14.1 ± 0.3), (5.5 ± 0.1), and (1.9±0.1) ps for the intrinsic and weakly doped samples respectively. c) Semi-log plot of the trion bleach for two excitation wavelengths, resonant with the exciton at 1000 nm (open markers) and with the trion band at 1170 nm (solid markers). The linear decay in the degenerate pump-probe scheme can be characterized by a decay time of 0.49 ps.
Exciton decay in the intrinsic sample (black markers) can be characterized by a diffusion time of $(20.4 \pm 0.4)$ ps. This corresponds to a diffusion length of about $150$ nm, roughly consistent with nanotube lengths or $d_0$ the intrinsic impurity spacing introduced above. Increasing slopes of pump-probe traces at higher doping levels clearly illustrate that the kinetics remain diffusive but accelerate, as spacings between quenching sites decrease accordingly.

As seen for resonant excitation of the trion state, the pump-probe trace in Figure 4c) follows unimolecular kinetics with a characteristic rate-constant of $2.0$ ps$^{-1}$ (solid circles). This is in good agreement with time-resolved experiments by Koyama et al., Nishihara et al. and Akizuki et al.\textsuperscript{19,21} For resonant excitation of the exciton, the trion still exhibits a unimolecular but somewhat slower decay. This illustrates two important effects: a) excitation at the exciton band energy leads to some indirect population of the trion state, possibly through the aforementioned exciton scavenging mechanism and b) the dynamics of the trion does not appear to be subject to a stretched recovery of the ground state, at least not to the extent that this affects the photo-bleach of the exciton band in Figure 4a). This has previously been interpreted in terms of a partially decoupled ground state of the trion state\textsuperscript{22} and is taken as further evidence of the localized nature of this manifold.

Next, we use changes of the exciton energy and characteristic diffusion times to calculate impurity concentrations within the confinement- and diffusion-limited quenching-models.\textsuperscript{22,35} The confinement model relates the exciton energy shift to its confinement length $d_c$ as described by Eckstein et al.\textsuperscript{35} The diffusion-limited quenching-model relates the NR exciton decay of Figure 4b) to diffusion lengths $d_q$\textsuperscript{22} using an averaged diffusion coefficient $D$ of $(9 \pm 2)$ cm$^2$ s$^{-1}$\textsuperscript{15,27}

The inverse of these length scales can be identified with the concentrations of additional confinement impurities $n_c$ and of additional quenching impurities $n_q$ introduced by doping. A plot of $n_q$ versus $n_c$, shown in Figure 5 reveals a good linear correlation of the two quantities up to impurity concentrations of about $0.015$ nm$^{-1}$. This suggests that both types of impurities, those that are associated with exciton confinement and those which are attributed to quenching sites are in fact identical. This is taken as further evidence for the co-localization of trion states in s-SWNTs with positively or negatively charged impurities. Such trion localization is consistent with the temperature-independence of trion PL as observed by Mouri et al.\textsuperscript{48} Deviations from the linear behavior in Figure 5 at higher carrier concentrations likely arise from interactions between impurity sites.
Conclusions

In conclusion, we found that the decay of excitons and trions in doped (6,5) carbon nanotubes is dominated by non-radiative quenching at charged impurity sites which appear to be co-localized with sites of trion state formation. Evidence for this is obtained from the dependence of exciton PLQYs and exciton confinement on the doping levels as well as from pump-probe spectroscopy of excited state dynamics.

The kinetics of exciton decay has been described as diffusion-limited, with the rate of diffusive transport of excitons to charged impurity sites governing the rate of energy dissipation. This is confirmed by both, the dependence of the exciton PLQY on impurity concentrations as well as by the stretched character of exciton pump-probe traces.

The experiments also indicate that trions may be populated both, directly by optical excitation as well as indirectly by exciton scavenging. The relative likelihood of these two processes remains to be discovered by future experiments and their quantification will greatly benefit from improved signal-to-noise ratios in NIR pump-probe data.

Methods

Nanotube samples were fabricated as described previously from organic (6,5) s-SWNT enriched suspensions of PFO-BPy polymer-stabilized (American Dye Source) CoMoCAT nanotubes (SWeNT SG 65, Southwest Nano Technologies Inc.). The s-SWNT thin-film samples used for the study of trion dynamics (Figure 4) were prepared by vacuum filtration from the same type of colloidal suspensions. Redox-chemical doping of s-SWNTs in suspension (5:1 toluene to acetonitrile solvent mixture) was achieved by titration of aliquots of gold(III) chloride (Sigma-Aldrich, ≥99.99%) solution using the same solvent mixture, whereas s-SWNT film samples were doped by immersion into AuCl₃ solutions for 10 min. The description of the optical setups used for stationary and time-resolved absorption spectroscopy as well as for photoluminescence measurements (PL) can be found elsewhere. The detector setups used for near infrared time-resolved spectroscopy of the trion band were described by Shi et al.

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