Photoluminescence saturation independent of excitation pathway in air-suspended single-walled carbon nanotubes

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Photoluminescence (PL) spectroscopy is a useful probe of excitonic interactions in optically excited nanostructures. Under intense optical excitation, the diffusion-annihilation of excitons in single-walled carbon nanotubes (SWCNTs) results in strong nonlinear PL. This behavior has been observed in a number of samples and has, until recently, been believed to be independent of excitation pathway. Contrary to this assumption, recent studies show that nonlinear PL in encapsulated SWCNTs, excited resonant to E_{22}, is not dominated by diffusion-annihilation but instead by laser induced quenching sites. In this paper, we show that, unlike encapsulated SWCNTs, air-suspended SWCNT PL saturation is independent of excitation pathway, validating the use of a diffusion model for excitons generated via E_{22} excitation. In addition, we show that the diffusion of excitons in air-suspended SWCNTs is independent of atmospheric adsorbates, strengthening the assertion that in this system exciton diffusion is intrinsic and not disorder limited.

I. INTRODUCTION

A semiconducting single-walled carbon nanotube (SWCNT) is an ideal system to study the photophysics of strongly bound electron-hole pairs (i.e., excitons) in a one-dimensional semiconductor. There are currently two main sample preparation methods that yield high quality individual SWCNTs: isolation by surfactant wrapping (processed) [1] and growing suspended over patterned substrates (unprocessed) [2]. When a SWCNT is optically excited, an exciton population is generated that can relax through photon emission [photoluminescence (PL)]. Measurements of PL thus provide noncontact access to exciton population, interactions and relaxation mechanisms. Even when carefully prepared, the optical properties of luminescent SWCNTs (e.g., exciton energy) are still sensitive to their surroundings [3,4].

The nanotube environment does not simply shift the band energies through dielectric screening; it also creates electrostatic potential fluctuations, which give rise to an entirely new species of excitations (e.g., trions [5,6]), which have never been observed in undoped air-suspended SWCNTs. While air-suspended SWCNTs have greatly reduced environmental perturbations, they are never completely free of adsorbates. An air-suspended SWCNT which has undergone heat treatment exhibits a significant band-gap transition, indicative of nonnegligible environmental screening [4]. Since environmental perturbations can play such a significant role in the physical properties [7–10], relaxation dynamics [7,11–18], and even excitation species [5,6,19] of photoexcited SWCNTs, it is important to show that for air-suspended SWCNTs, perturbations due to adsorbates do not significantly affect exciton dynamics. By comparing the relaxation dynamics of excitons in an air-suspended SWCNT in an adsorbed and desorbed state, we are able to provide evidence that airborne particulates do not create electrostatic inhomogeneities deep enough to change the exciton diffusion from intrinsic to disorder limited [20].

This is further evidenced by the extracted diffusion constants from air-suspended SWCNTs [21], which are in line with the expected values for intrinsic diffusion [20].

Another important assumption for many SWCNT studies is the independence of excitation pathway on the E_{11} exciton dynamics, for example, diffusion limited PL saturation [21–24]. This assumption was shown to not be of general validity when studies of "pristine" SWCNTs dispersed in deoxycholate solutions revealed a strong role of the excitation pathway on the interpretation of PL saturation [5]. It was concluded that, in contrast to phonon-sideband excitation where PL saturation is dominated by exciton-exciton annihilation (EEA) [12], E_{22} excitation results in PL saturation dominated by laser-induced quenching sites. If this result applies to other SWCNT samples, it discredits studies which rely on a diffusion limited saturation model for excitons generated through E_{22} excitation [21–24]. In this work, we validate the use of a diffusion limited EEA model for E_{22} excitation in air-suspended SWCNTs [21] by showing that, unlike processed samples [5], the observed PL saturation of air-suspended SWCNTs is independent of the excitation pathway.

In addition, studies of air-suspended SWCNTs [22,25,26], often assume that the underlying substrate does not play a role even under high excitation fluence. Since the excitation light is strongly absorbed by the substrate, thermal expansion or local transient electric fields could perturb the exciton dynamics [27,28] or induce PL quenching [29]. By comparing a SWCNT suspended over a SiO_2 trench to one suspended across a metal grid, we show that the observed PL saturation is not substrate dependent, and thus the substrate plays a negligible role in exciton population dynamics.

II. EXPERIMENTAL

Two different sample platforms are used in this study, suspended over Si/SiO_2 and suspended over air. The Si/SiO_2 sample is 500-μm thick, coated by evaporation with a thin layer of cobalt at a low density that serves as the catalyst for SWCNT growth [4]. The substrate is then patterned into

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trenches ($\sim$0.4 μm in depth) by photolithography of variable width [30,31]. Suspended SWCNTs are grown by chemical vapor deposition on a Si/SiO$_2$ substrate. The other sample platform that consists of SWCNTs suspended over air is obtained by contacting a metal grid substrate to SWCNTs grown on a Si/SiO$_2$ substrate [32]. During experimentation, nanotube samples are kept in vacuum or in dry nitrogen purged environment to allow reproducible results.

The optical excitation of a single SWCNT is achieved using a Ti:Sapphire laser operating either on continuous wave (CW) or pulse mode ($\sim$150 fs duration; 76-MHz repetition rate). Individual SWCNTs are located by scanning a sample with laser excitation (CW) resonant at E$_{22}$ and detecting PL resonant at E$_{11}$. High-quality SWCNTs are selected by their bright and spatially uniform PL and narrow PL spectral widths. The laser polarization matches a SWCNT's axis, maximizing the SWCNT absorption. A small beam diameter ($\sim$2 μm) is used to two-dimensionally map the PL and to measure the SWCNT's length and orientation. During experimentation, a large-diameter beam (typically 25–40 μm in diameter) is used to quasiuniformly excite a SWCNT. Quasiuniform excitation simplifies the modeling of PL dependence on excitation fluence [25,33]. The spatial profile of exciton generation in a SWCNT must be taken into account in the case of nonuniform optical excitation (e.g., in Moritsubo *et al.* [22]).

Under quasiuniform excitation, two experimental methods are used to explore the optical behavior of SWCNTs. The first is PL dependence on excitation fluence (i.e., power-resolved PL) and the second is time-resolved PL using femtosecond excitation correlation (FEC) [8,25,33–35]. In a typical SWCNT power-resolved PL study, PL increases linearly under low excitation fluence and nonlinearly at higher fluence. The extreme nonlinear behavior has been attributed to both nonlinear exciton-exciton annihilation [12] and laser-induced quenching sites [5]. In the case of exciton-exciton annihilation, power-resolved PL studies have been used to study the range of this mechanism [25,36,37]. Additionally, since the emission of most air-suspended SWCNTs is extremely low and beyond the silicon cutoff, it is challenging to measure exciton ultrafast relaxation dynamics using conventional methods, such as optical Kerr gating [11,12] or time-correlated single photon counting [7,38,39]. Instead, exciton effective lifetime is extracted using FEC [18,21,25,33].

In the first case, to verify that PL saturation (from the E$_{11}$ transition) at low fluences is not related to laser induced quenching sites (like in processed SWCNTs), a second excitation channel is utilized (an E$_{11}$ excited state [40]). Due to the strong Coulomb electron-hole interactions, optical transitions are dominated by the bright exciton states, typically 0.5–1 eV below the continuum (free career energy state) [41,42]. Relatively weak, excited states of each bright exciton are calculated and observed above the bright but below the continuum state using PL excitation spectroscopy [4,40]. The strongest excited state observed is hundreds of meV above the bright state depending on SWCNT diameter. We have observed this excited state in a SWCNT and use it as an alternative excitation pathway to increase our understanding of the nature of PL saturation at low excitation fluences.

In the second case, literature has shown that SWCNTs suspended in air are coated with atmospheric adsorbates [4].

These adsorbates generally reduce the band gaps of pristine SWCNTs [4] but it is not clear how these adsorbates change the exciton interaction efficiency and relaxation lifetime. To test if atmospheric adsorbates perturb exciton dynamics, we compare PL characteristics for SWCNTs with different levels of surface contamination using a band-gap shift transition (BST). Upon heating at temperature above 450 °C in a dry nitrogen purged environment, a SWCNT undergoes a BST of 20–30 meV possibly by detaching the adsorbates. This "desorbed state" is metastable and only lasts for several hours in air ambient and several days in dry nitrogen. We measure PL and compare results from the same SWCNT on its desorbed state (right after the heating process) and followed by its stable adsorbed state after three days kept in dry nitrogen. Comparison on the same SWCNT in these two distinct states help to clarify if these adsorbates affect exciton behavior. All optical measurements are completed at room temperature.

III. RESULTS AND DISCUSSION

A. Pathway independent PL saturation

An estimation of the photoexcited exciton density at a given excitation fluence is essential to develop a model for exciton interaction and relaxation mechanisms. Since the absorption and emission efficiencies are coupled, the estimation is often indirect. Studies of E$_{11}$ exciton relaxation by direct excitation at E$_{11}$ are desired but very challenging using PL spectroscopy. Very weak PL emission limited by efficient exciton-exciton annihilation from a single SWCNT is overwhelmed by much stronger scattering light at the excitation photon energy. Alternatively, PL measurement at E$_{11}$ upon excitation at at E$_{22}$ often assumes an ultrafast depopulation from E$_{22}$ to E$_{11}$ excitons and no laser induced damage. Although this depopulation rate was experimentally measured in processed SWCNT ensembles [43,44], the fast relaxation from E$_{22}$ to E$_{11}$ in single unprocessed SWCNT has not yet been experimentally measured. Previous analysis of PL saturation assumed that the results were independent of the specific exciton injection pathway, and the nonlinearity occurred through interactions of E$_{11}$ excitons. To verify this, we inject excitons through a different pathway, independent of E$_{22}$.

Figure 1(a) shows a photoluminescence excitation (PLE) spectrum of a single (9,7) SWCNT. The strongest peak is at E$_{22}$ resonance, 1.57 eV. A secondary peak is a E$_{11}$ excited state, E$_{11}^*$, resonant at 1.38 eV [4]. Additional peaks on either side of the E$_{22}$ resonance are attributed to phonon sidebands. Excitation through either E$_{22}$ or E$_{11}^*$ channels yields similar normalized PL spectra (Fig. 1, inset). Since the PLE spectrum is obtained at low fluences (CW), the measured PL at E$_{11}$ is proportional to the PL action cross section at a given excitation energy:

$$PL(E_{22}) \propto \sigma(E_{22})\,\eta(2 \to 1)\,\eta, \tag{1}$$

$$PL(E_{11}^*) \propto \sigma(E_{11}^*)\,\eta(1^* \to 1)\,\eta. \tag{2}$$

$\sigma(E_{22})$ and $\sigma(E_{11}^*)$ are the absorption cross sections. $\eta(2 \to 1)$ and $\eta(1^* \to 1)$ are the population transfer efficiencies from upper state to E$_{11}$. η is the effective quantum efficiency of
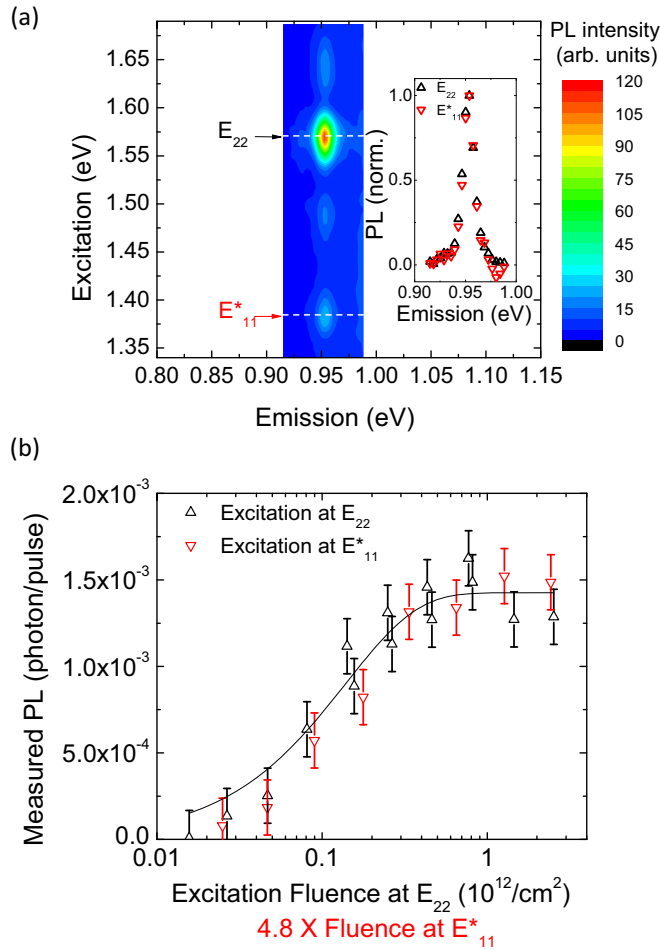
FIG. 1. (Color online) (a) PLE spectroscopy of a (9,7) SWCNT. (Inset) PL spectra excited at E_{22} and E_{11}^*. (b) Power-resolved PL excited at E_{22} ($\triangle$) and E_{11}^* ($\triangledown$). The excitation fluence at E_{11}^* is scaled by a factor of 4.8 according to the ratio of PL action cross sections (see text for details). Simple model (black curve, explained in text) fits to PL data resulting from E_{22} excitation.

E_{11}. Measured PL excited at E_{11}^* shows approximately a factor of 4.8 times smaller than that at E_{22} for identical incident fluences. Recent literature reports a considerable fraction of injected excitons spontaneously dissociate into free electron-hole pair at nonzero bias [26] [i.e., $\eta(2 \to 1) < 1$]. However, the individual absolute values for the absorption cross sections, population transfer efficiencies, and E_{11} quantum efficiency are not relevant for the present analysis. Theoretical calculation shows that the lowest bright exciton state carries the most weight on a SWCNT absorption spectra with rather weak absorption strengths for the excited states [45]. Thus, the factor of 4.8 may be dominated by the relative absorption strength. Nonetheless, it is important to compare nonlinearity for similar initial E_{11} exciton populations. This can be done by scaling the fluences of E_{11}^* excitation by a factor of 4.8 so that PL from the two excitation pathways overlaps in the linear regime. Unlike processed SWCNTs, the measured PL beyond the linear regime does not depend on excitation pathway, as shown in Fig. 1(b). This is consistent with the assumption made in the previous work that the source of nonlinearity (e.g.,

exciton-exciton annihilation) is due to E_{11} exciton interactions and not due laser induced defects.

To quantify this comparison, we calculate chi-square probability (i.e., P value) and determine if differences between the two data sets are statistically significant [46]. To assist the calculation of chi-square (χ^2), power-resolved PL excited at E_{22} is fit by a simple model: $\mathrm{PL}(X) \propto 1 - e^{-X/X_{SAT}}$, where X and X_{SAT} represent *Fluence* and a constant defining the saturation point respectively. The best fitting curve is shown by the solid line in Fig. 1(b). PL measured from E_{11}^* excitation is compared to the curve by calculating chi-square and P value. The resulting P value is calculated to be 0.99 ($\gg 0.05$), suggesting that the difference in the results from both excitation pathways is statistically insignificant. We thus conclude that E_{11} population rates and transfer efficiencies are indistinguishable from the two upper states. Exciton-exciton annihilation likely occurs at E_{11}, and annihilation rates are similarly fast and efficient through both excitation pathways.

B. Adsorbate independent linewidth and lifetime

Previous work has shown that a SWCNT's dielectric screening changes the strengths of electron-electron and electron-hole Coulomb interactions. The change in strengths leads to energy shifts of the exciton states [4]. In particular, an abrupt band-gap shift transition (BST) is observed in unprocessed suspended SWCNTs under heating above 450 °C. BST is attributed to detachment of adsorbate molecules which results in a lower dielectric constant surrounding the SWCNTs. For our unprocessed SWCNTs, we have observed similar BST including three different chiralities: (9,7), (9,8), and (10,8). Their E_{11} and E_{22} exciton energies and the energy shifts with respect to those in ambient (i.e., in "adsorbed" state) are listed in Table I.

The "desorbed" state of a SWCNT after BST does not last long. A SWCNT returns to its adsorbed state after several hours if it is in ambient air and after several days if it is in a dry nitrogen purged environment. Adsorbates, including water molecules, adhere to the suspended SWCNTs over time and increase the surrounding dielectric constant of these SWCNTs. Though the adsorbates shift the SWCNT's excitonic energies, it is not clear if they also change exciton interaction and relaxation mechanisms. If they introduce local trapping sites, PL linewidth and lifetime may change.

Figure 2(a) shows the PL spectra of a single (10,8) SWCNT in its desorbed state and in its adsorbed state after three days kept in dry nitrogen purged environment. Though the PL center energies shift, the PL linewidths and line shapes are similar in these two different states. Fitting to a Lorentzian function yields PL linewidths of 7.9 ± 0.5 meV in the desorbed state and 8.3 ± 0.5 meV in the adsorbed state. Similar PL linewidths

TABLE I. Resonances in adsorbed state and BST energy shifts.

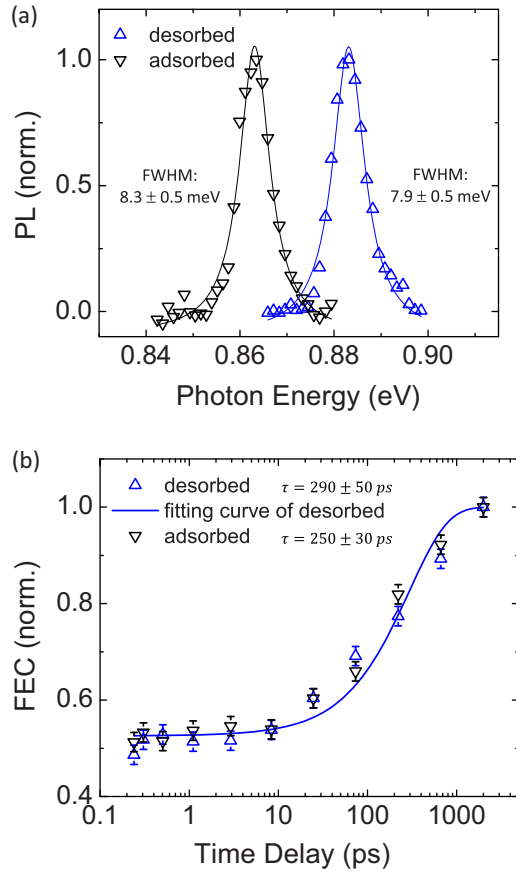| Chirality	E_{11} (eV)	E_{22} (eV)	BST ΔE_{11} (meV)	BST ΔE_{22} (meV)
(9,7)	0.98	1.61	30	41
(9,8)	0.92	1.57	24	20
(10,8)	0.88	1.47	21	31

FIG. 2. (Color online) Normalized PL spectra (a) and normalized FEC (b) of the same (10,8) SWCNT in its desorbed ($\triangle$) and adsorbed ($\triangledown$) states. Fits are explained in the text.

FIG. 3. (Color online) Power-resolved PL from SWCNTs suspended on two different substrates: Si/SiO$_2$ ($\square$) and metal grid ($\bigcirc$). PL normalization and the curve fit to the Si/SiO$_2$ results are explained in the text. Error bars represent the standard deviations.

suggest adsorbates do not significantly alter exciton-phonon dephasing processes [47,48].

Similar to Fig. 1(b), power-resolved PL are compared in these two states and the extracted X_{SAT} overlap within uncertainties. We further measured PL lifetimes using FEC and compared the results in these two states. The normalized FEC are shown in Fig. 2(b). Time-resolved FEC over three decades are similar for the two states. Fitting to a monoexponential function yields 290 ± 50 ps in desorbed state and 250 ± 30 ps in adsorbed state respectively. The P-value calculated from the FEC data is 0.19 suggesting the difference in E$_{11}$ exciton relaxation dynamics is statistically insignificant. We thus conclude that these adsorbates do not introduce significant trapping sites and alter the effective exciton lifetime. These results are collected at room temperature, in contrast to recent low temperature work where trapped excitons have been observed to have nanosecond lifetimes [49,50].

C. Substrate independent PL saturation

Si/SiO$_2$ is a common substrate for air-suspended SWCNTs. Typically, the E$_{22}$ excitation is at frequencies corresponding to the generation of excited carriers in this substrate. These carriers may result in changes to the local electric field experienced by the SWCNT, which may have an effect on
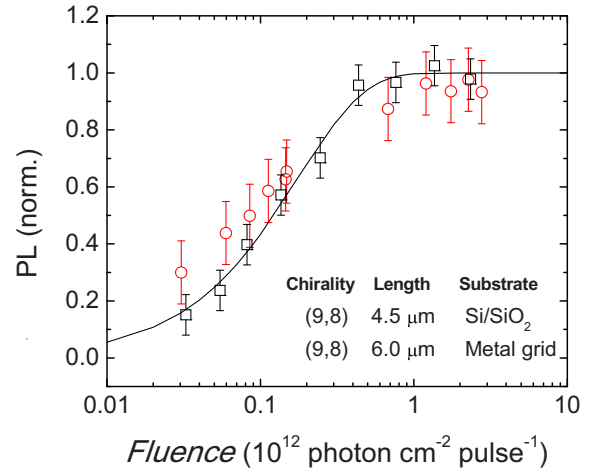
exciton dynamics [28], as well as be responsible for local heating.

In contrast to Si/SiO$_2$ supported SWCNTs, there is no substrate underneath the SWCNTs suspended on a metal grid. To explore possible substrate effects, experiments were conducted on two similar (9,8) SWCNTs each on a different substrate. In the literature, optical properties of SWCNTs on Si/SiO$_2$ substrate are compared with and without contacting the substrate [51]. Our approach takes one step further to examine the possible influence of the Si/SiO$_2$ substrate on the exciton behavior for the suspended segment of an unprocessed SWCNT.

Figure 3 shows the power-resolved PL from two single (9,8) SWCNTs, one with and one without the Si/SiO$_2$ substrate. Reflection from the substrate is considered in the incident fluence as explained in Ref. [25]. Since the absolute PL from a SWCNT is determined by sample-dependent collection efficiency, the effective quantum efficiency, and the nanotube length, we need to scale PL for comparison purposes. PL dependence on fluence largely overlaps within uncertainties between these two different sample substrates.

To quantify this comparison, power-resolved PL from the SWCNT on the Si/SiO$_2$ substrate is fit, as in Sec. III A (curve in Fig. 3). Measured PL from the SWCNT on the metal grid substrate is then scaled by a constant to achieve minimum χ^2 compared to the curve. $P = 0.83$ shows that the difference between the two sets of experimental results is statistically insignificant, which implies that the substrate plays no role in exciton dynamics.

IV. SUMMARY

We have demonstrated that, unlike processed SWCNTs, the measured power-resolved and time-resolved PL from selected unprocessed suspended SWCNTs is independent of the excitation pathway. This implies a lack of laser induced damage and justifies the use of a diffusion limited EEA model for air-suspended SWCNTs. In addition, similar PL

nonlinearity and lifetime of adsorbed and desorbed SWCNTs suggest that exciton interaction and relaxation mechanisms are negligibly affected by these adsorbates, strengthening the assertion that diffusion is intrinsic and not disorder limited. Lastly, through comparison to substrate-free samples, we provide strong evidence to support the standard assumption that the commonly used Si/SiO_2 substrate has a negligible effect on exciton interaction even under high excitation fluences.

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