Nonlinear Photoluminescence Excitation Spectroscopy of Carbon Nanotubes: Exploring the Upper Density Limit of One-Dimensional Excitons

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We have observed that photoemission from single-walled carbon nanotubes saturates in intensity as the excitation intensity increases. Each emission peak arising from specific-chirality tubes exhibited a saturation value independent of the excitation wavelength, suggesting an upper limit on the exciton density for each nanotube species. We developed a model based on diffusion-limited exciton-exciton annihilation, which allowed us to estimate exciton densities in the saturation regime. The estimated densities were found to be still substantially smaller than the expected Mott density.

Optical processes in 1D semiconductors are affected by strong Coulomb interactions and have been the subject of many theoretical [1–4] and experimental [5–11] studies. Early studies of lasing in semiconductor quantum wires [5,6] stimulated much interest in the properties of high-density 1D excitons, or correlated electron-hole (e-h) pairs, especially in their stability against biexciton formation, band-gap renormalization, and dissociation. Although it has been established that excitons in quantum wires are stable up to very high densities (10⁵–10⁶ cm⁻¹), unanswered questions remain. An insulating exciton gas is expected to become unstable at high densities and eventually transform into a metallic e-h plasma at the Mott density, where the interexciton distance approaches the exciton size. At what density gain should appear and whether a clear Mott transition exists in 1D systems are open questions [2–4,7–11].

Single-walled carbon nanotubes (SWNTs) [12] have recently emerged as novel 1D solids. The exciton binding energies reported for semiconducting SWNTs are very large (~400 meV [13,14]) compared to typical GaAs quantum wires (~20 meV [2,6]). Despite much recent progress in understanding their basic optical properties, only a limited number of studies have been performed under the condition of high carrier or exciton densities [15–17]. In particular, there have been no reports quantifying exciton densities in relation to the Mott density.

Here we describe detailed characteristics of photoluminescence (PL) and photoluminescence excitation (PLE) spectra of SWNTs at high exciton densities. Although PL intensity rapidly saturated with increasing pump fluence, PL spectra were stable, indicating that there is no band-gap renormalization, screening, or dissociation into an e-h plasma. However, we observed broadening and eventual complete flattening of PLE spectra at high laser intensities. We show that this originates from strong exciton-exciton annihilation (EEA) that provides an upper limit for the exciton population in the lowest-energy (E₁₁) state. Our model, taking into account exciton diffusion in EEA, allowed us to estimate exciton densities from the saturation curves. The estimated densities for the highly saturated regime were on the order of 1 × 10⁵ cm⁻¹, which is more than 1 order of magnitude smaller than the expected Mott density and explains the observed stability of PL spectra in the saturation regime.

The sample was prepared by ultrasonicking CoMoCAT SWNTs in D₂O with 1 wt% sodium cholate for 1 h, followed by ultracentrifugation at 111 000 g for 4 h. Only the upper 50% of the supernatant was collected. Through this procedure, SWNT bundles were effectively removed. The solution was held in a 1-mm-thick quartz cuvette. The optical density in the E₂₂ region was below 0.2, which helped avoid inhomogeneous excitation and reabsorption of PL. Our tunable excitation source was a 1 kHz, ~250 fs optical parametric amplifier (OPA) pumped by a chirped pulse amplifier (Clark-MXR, CPA2010). The OPA beam was focused onto the sample with a spot size of 300–400 μm.

Figure 1(a) compares two PL spectra. The black solid curve was taken with the OPA tuned to 654 nm (or 1.90 eV) with pulse energy ~ 29 nJ, while the red dotted curve was obtained using a weak (100 μW) cw laser with a wavelength of 658 nm. It is seen that the relative intensities of different PL peaks [labeled by their chiral vectors (n, m)] are drastically different between the two curves. The inset confirms that the two spectra coincide accurately when the OPA pulse energy is kept low (300 pJ). Figure 1(b) shows PL spectra for pulse energies of 1 nJ (curves 1 and 7), 4 nJ (2 and 6), 10 nJ (3 and 5), and 30 nJ (4). The (7,5) peak is dominant at low fluences while the (6,5) peak becomes dominant at high fluences. It is important to note that the different curves were taken in the order of no. 1 to no. 7. The near coincidence of the pair of curves at 1, 4, and 10 nJ demonstrates that the observed changes are reproducible and are not caused by any laser-induced permanent change in the sample. We also reproduced a similar power dependence in a dried film, showing that the power dependent...
changes are not an artifact caused by the fluidic nature of the sample. Finally, note that the PL intensities tend to saturate at high laser fluences, while their peak positions do not change at all and linewidths increase only slightly (by ~15% from curve 1 to 4).

Figures 2(a)–2(c) plot integrated PL intensities for (6,5), (7,5), and (8,3) tubes, respectively, versus pump fluence with pump wavelengths of 570, 615, and 654 nm. The $E_{22}$-resonant wavelengths of these tube types are 570, 647, and 673 nm, respectively. The integrated PL intensities were obtained through spectral decomposition assuming 50% Lorentzian + 50% Gaussian, while keeping the peak positions fixed. Figure 2 indicates that saturation starts at a lower (higher) fluence when the sample is resonantly (nonresonantly) excited. The unexpectedly fast saturation of the (7,5) peak with 570 nm excitation (which is nonresonant) is likely due to its proximity to the phonon sideband at 585 nm [18]. The solid curves and the dashed curves are theoretical fits to the experimental curves based on our model to be discussed later.

Figures 3(a)–3(d) show PLE maps taken with various pump fluences. The step size for the pump photon energy was 20 meV. The lowest fluence data [Fig. 3(a)] is essentially the same as that taken with low-intensity cw light. However, as the fluence is increased [Figs. 3(b)–3(d)], the $E_{22}$ excitation peaks gradually broaden and eventually become completely flat at the highest fluence ($\sim 1.3 \times 10^{14}$ photons/cm$^2$); i.e., PL intensities become independent of the excitation wavelength. The corresponding PLE spectra are shown in Figs. 3(e)–3(h) for three PL wavelengths at 983, 1034, and 1125 nm.

To provide further insight into the nature of the observed broadening and flattening of PLE spectra, we performed absorption measurements in the $E_{22}$ region using OPA pulses. Figure 4 compares two transmission spectra measured with fluences of $1.0 \times 10^{12}$ photons/cm$^2$ (linear regime) and $1.0 \times 10^{14}$ photons/cm$^2$ (saturation regime), respectively, and a transmission spectrum taken with weak cw white light. It is clear from the figure that the $E_{22}$ absorption peaks do not exhibit any broadening and shifts even in the saturation regime, strongly suggesting that
these intensities are not high enough to cause light-induced nonlinear effects such as state (or phase-space) filling on states in the $E_{22}$ range.

We interpret these observations as results of very efficient EEA [17,19]. We assume that the formation of $E_{11}$ excitons occurs in a very short time scale (e.g., $\sim 40$ fs [20]), shorter than our pulse width ($\sim 250$ fs). Thus, they accumulate in $E_{11}$ during and right after photocreation of $e$-$h$ pairs. However, the number of excitons that can be accommodated within their lifetime. Therefore, we assume that $I_x$ is determined by the diffusion length and any two excitons formed within $I_x$ undergo EEA.

The essence of our model is described as follows (the complete details and validations are given in Ref. [24]): A 1D space of length $L$ is considered where $N$ segments of length $I_x$ have populated without overlapping each other (i.e., $NI_x < L$). The probability for a new segment of length $I_x$ entering the system not to overlap with any of the $N$ existing segments, $p(N)$, is given by

$$p(N) = \left(1 - \frac{NI_x}{L}\right)\left(1 - \frac{I_x}{L - NI_x}\right)^N. \quad (1)$$

We also assume that an exciton promoted to a higher energy level as a result of EEA returns to the $E_{11}$ level.
with 100% probability due to ultrafast and efficient $E_{22}$-to-$E_{11}$ relaxation; i.e., two excitons become one exciton through EEA. In this case, the expectation value of the increment of $N$ by the addition of the new segments, $\langle \Delta N \rangle_N$, is equal to $p(N)$ in Eq. (1). Therefore, in the instantaneous limit where the initial creation of excitons occurs within a very short time before EEA follows, the relationship between the number of initially created excitons $N_0$ and resultant $N$ is described by a differential equation of $dN_0/dN = 1/(\Delta N)_N = 1/p(N)$.

This differential equation, based on $N \approx I_{PL} \equiv c_1 \zeta$ and $N_0 \approx I_{pump} \equiv c_2 \psi$ ($c_1, c_2$, coefficients; $I_{PL}$, $I_{pump}$, PL and pump intensities), is expressed with $\zeta$ and $\psi$ as

$$\frac{d\psi}{d\zeta} = \frac{1}{(1 - \zeta)(1 - \frac{I_{PL}}{I_{pump}})} \frac{1}{(1 - \frac{I_{pump}}{I_{PL}})}.$$  \hspace{1cm} (2)

The Taylor expansion of the denominator of Eq. (2) and elimination of higher-order terms of $I_{PL}/I_{pump}$ result in a differential equation of only $\zeta$ and $\psi$. Finally, the integration yields the solution for the instantaneous limit as

$$\psi = \frac{1}{\epsilon} \left( \text{Ei} \left( \frac{1}{1 - \frac{I_{PL}}{I_{pump}}} \right) - \text{Ei}(1) \right).$$  \hspace{1cm} (3)

and similarly, the solution for the steady-state limit corresponding to cw excitation [24] is obtained as

$$\psi = \frac{\zeta}{1 - \zeta} \exp \left( \frac{\zeta}{1 - \frac{I_{PL}}{I_{pump}}} \right) \left[ \zeta = \frac{I_{PL}}{c_1}, \psi = \frac{I_{pump}}{c_2} \right].$$  \hspace{1cm} (4)

The actual experimental situation is somewhere between these two limits but closer to the former. Equations (3) and (4) are implicit equations relating $I_{PL}$ and $I_{pump}$ in terms of their respective dimensionless parameters, $\zeta$ and $\psi$. They contain no fitting parameters other than the two linear scaling factors $c_1$ and $c_2$ and simply become a linear relationship ($\psi = \zeta$) in the low density limit ($\zeta \to 0$).

The solid curves and the dashed curves in Fig. 2 are fits to the data by Eqs. (3) and (4), respectively, showing good agreement. The values of $\zeta$ were obtained through this analysis for respective data points shown in Fig. 2. Finally, the exciton density can be obtained through $n_s = \zeta/l_x$. Using $l_x = 45$ nm (one half of the excitation range defined in [23]), we estimated $n_s$ for (6,5) to be $1.7 \times 10^5$, $1.3 \times 10^5$, and $1.1 \times 10^5$ cm$^{-1}$ for excitation with 570, 615, and 654 nm, respectively, at a fluence of $1.02 \times 10^{14}$ photons/cm$^2$ in the instantaneous limit. These densities are still much smaller than the expected Mott density $n_s^* \approx 7 \times 10^6$ cm$^{-1}$, assuming exciton size $\sim 1.5$ nm [25]), which can explain the stability of PL (Fig. 1) in the saturated regime. On the other hand, the densities of as-created $e-h$ pairs before undergoing EEA are estimated to be $1-2 \times 10^6$ cm$^{-1}$ in the cases of resonant excitation, which is similar to $n_s^*_r$. These observations appear qualitatively different from GaAs quantum wires where PL saturation is not obvious until the formation of biexcitons and an $e-h$ plasma [11]. Highly efficient and rapid EEA in SWNTs, which is consistent with the reported absence of biexciton signatures [26], is probably the direct reason for such characteristic differences.

In summary, we have studied PL and PLE spectra of SWNTs at high exciton densities. Complete flattening of PLE spectra and clear PL saturation were observed, indicating the existence of an upper density limit. We developed a model that reproduced the observed saturation behavior and allowed us to estimate exciton densities, which remained more than 1 order of magnitude lower than the expected Mott density and explained the stability of PL spectra in the saturated regime.

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