Ultrafast Exciton Dephasing in Semiconducting Single-Walled Carbon Nanotubes

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Femtosecond two-pulse degenerate four-wave mixing spectroscopy was applied to study the exciton dephasing in a broad range of excitation intensities and lattice temperatures. We find that both exciton-exciton and exciton-phonon scattering have profound effects on the dephasing process. The dominant phonon mode involved in the dephasing is identified as the out-of-plane, transverse optical mode with a frequency of 847 cm$^{-1}$. The extracted homogeneous linewidths at all measured temperatures are in excellent agreement with the results of a single-tube photoluminescence experiment.

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The excitons created in semiconductors with an ultra-short laser pulse initially possess a definite phase relationship between themselves and the electromagnetic radiation creating them [1]. Subsequent scattering among themselves and with charged carriers, phonons, impurities, and defects will lead to dephasing, and eventually population relaxation. Investigations of exciton dynamics in this coherent regime employing coherent transient spectroscopy [1] have provided insight into fundamental assets of a variety of systems, including many quantum-confined materials such as quantum wells [2–4], wires [5,6], and dots [7,8]. The determination of the time scales of various dephasing processes has further provided a wealth of information about the intrinsic homogenous linewidths of specific exciton transitions directly through an ensemble measurement [3,5,6].

The optical properties of semiconducting single-walled carbon nanotubes (SWNTs) are governed by excitons with anomalously large binding energies [9,10]. Although the ultrafast dynamics of these excitons has attracted considerable interest [11], their coherent behavior remains unexplored experimentally. Of particular interest is understanding the complex interactions among various quasiparticles and examination of the intrinsic linewidths. Interpretation of linear spectra is hampered by substantial sample heterogeneity, and currently very limited and highly variable results from single-tube spectroscopy [12–14]. Here, we present an experimental study of ultrafast exciton dephasing in semiconducting SWNTs utilizing a femtosecond four-wave mixing (FWM) technique. Our measurements for a broad range of excitation intensities and lattice temperatures enable us to separate the effects of exciton-exciton and exciton-phonon scattering on exciton dephasing, to identify the dominant phonon mode, and to quantify the dephasing time scales and the corresponding homogeneous linewidths.

The sample used in this study is highly enriched in a single-tube type, the (6, 5) nanotube, which was isolated through density-gradient ultracentrifugation [15]. An aqueous solution was mixed with water soluble polyvinylpyrrolidone (PVP) polymer to fabricate a thin composite film abundant in individualized nanotubes. Use of this solid sample greatly suppresses the light scattering arising from motion of nanotubes in the solution.

We studied the coherent exciton dynamics using femtosecond two-pulse degenerate FWM spectroscopy. The light source was an optical parametric amplifier pumped by a 250 kHz Ti:Sapphire regenerative amplifier [16], which was tuned to a central wavelength of 990 nm in order to resonantly excite the lowest excitonic transition ($E_{11}$) of the (6, 5) tube (see Fig. 1). In this experiment, two nearly equal intensity laser pulses of 45 fs duration with a variable delay $t_{12}$ are focused to the sample. The first pulse with wave vector $k_1$ generates a coherent macroscopic polarization of the exciton ensemble, and when the second pulse with wave vector $k_2$ arrives before the dephasing of the induced polarization an interference grating is produced. This transient grating diffracts photons into the background-free, phase-matching direction $2k_2 - k_1$. A schematic of the FWM geometry is shown in Fig. 2(a). As the time delay $t_{12}$ increases, the amplitude of the grating decays and the diffracted signal decreases. Measurement of the diffracted signal as a function of $t_{12}$ yields a time scale that is directly proportional to the dephasing time $T_2$ (see following discussion). The diffracted signal was detected in a time-integrated manner with an InGaAs photodiode and a lock-in amplifier.

We performed measurements at seven lattice temperatures ranging from 77 to 292 K, and at each temperature several different excitation intensities between 1.70 and 12.30 $\mu$J/cm$^2$ were employed. Figure 2(b) shows the data collected at 100 K for five different excitation intensities.
Here, the intensity of the FWM signal is plotted as a function of the time delay $t_{12}$. The decay of the diffracted signal depends strongly on the intensity, manifesting a significantly faster decay with increasing intensity. Quantitative analysis employing a least square deconvolution fitting algorithm with explicit consideration of the finite temporal response shows that the decay time ($\tau_{\text{decay}}$) decreases from 71 fs at 1.69 $\mu$J/cm$^2$ to 36 fs at 12.33 $\mu$J/cm$^2$. Such a trend of the decay time change with excitation intensity is also observed at other lattice temperatures measured (77, 130, 200, 250, and 292 K). Furthermore, a comparison of the data collected at $1.70 \mu$J/cm$^2$, the lowest intensity used in this work, demonstrates a clear temperature effect [see Fig. 2(c)]. The decay time extracted from the data decreases from 77 fs at 77 K to 35 fs at 292 K. The observed strong dependence on temperature and excitation intensity provides the direct evidence for the involvement of both excitons and phonons in the exciton dephasing process.

The markedly enhanced contribution of phonons to the exciton dephasing with increasing temperature results in strikingly distinct excitation intensity effects on the FWM decays at different temperatures. For the given sevenfold increase of excitation intensity, we find that the reduction of $\tau_{\text{decay}}$ at 292 K (from 22 to 35 fs) is 3 times smaller than that observed at 77 K (from 35 to 26 fs). This temperature-dependent phonon contribution further leads to a prominent difference in the intensity dependence of the corresponding dephasing rate, $1/T_2$, or equivalently the homogeneous linewidths [full width at half maximum (FWHM)] $\Gamma_h$ of the $E_{11}$ transition, at different lattice temperature. Here, the dephasing time $T_2$ is calculated from the $\tau_{\text{decay}}$ by assuming $T_2 = 4\tau_{\text{decay}}$, which is strictly valid for a strongly inhomogeneously broadened, independent two-level system [17]. The corresponding $\Gamma_h$ value is then obtained from $\Gamma_h = 2\hbar/T_2$, and is indicated by the label on the right side of Fig. 3. As shown in Fig. 3, the dephasing rate (or the homogeneous width) at 77, 100, and 130 K increases linearly with intensity. Such linear dependence has been observed in quantum wells [3,4] and wires [5,6]. However, at higher temperatures, the dependence
found for the same intensity change deviates clearly from linearity. This obvious deviation strongly suggests a pronounced phonon contribution at high temperature.

The linear intensity dependence of $1/T_2$ (or $\Gamma_h$) observed at 77, 100, and 130 K represents a typical characteristic of dominant exciton-exciton collision broadening. The linear dependence can be described by $1/T_2(N_x) = 1/T_2(0) + \beta N_x$, with $N_x$ the exciton density, $\beta$ the exciton-exciton scattering parameter, and $1/T_2(0)$ the temperature-dependent zero-density dephasing rate. $N_x$ is estimated from an absorption cross section ($5.2 \times 10^{-14}$ cm$^2$ per tube), a mean tube length of 600 nm, the measured $1/e^2$ beam diameter (148 $\mu$m) and the excitation intensity, and is depicted by the labels of the top axes of Fig. 3. The linear fits shown in Fig. 3(a) give a $\beta$ value of 0.84, 0.85, and 0.78 ps$^{-1}$ $\mu$m at 77, 100, and 130 K, respectively. The corresponding $1/T_2(0)$ values are 2.84, 3.01, and 3.67 ps$^{-1}$. As the absorption cross section employed in the calculation represents a lower limit of the actual value, the resulting $N_x$ must be underestimated. Consequently, this suggests that the $\beta$ values are an upper limit. Note that these $\beta$ values are several times smaller than those determined from one-dimensional quantum wires [5,18], suggesting a reduced exciton-exciton scattering in semiconducting SWNTs.

By extrapolating the decay times determined at different intensities to the limit of zero intensity for each temperature, we can examine the contribution of the phonons to the dephasing without other effects. This extrapolation involves a nonlinear regression using an empirical function $\tau_{\text{decay}} = c_1 \exp(-I/I_0) + c_2$ ($I$ is the intensity, $c_1$, $c_2$, and $I_0$ are the variables). Similar results were also obtained using a hyperbolic function $\tau_{\text{decay}} = 1/(c_1 + c_2 I)$ for the data measured at 77, 100, and 130 K. The dephasing rate $1/T_2$ and the corresponding homogeneous width $\Gamma_h$ are plotted in Fig. 4 as a function of temperature. The resulting temperature dependence can be best described by the function $\Gamma_h = a + b \exp(-\Delta E/k_BT)$, where $T$ is the lattice temperature and $\Delta E$ denotes an energy scale. The solid line in Fig. 4 is obtained with $a = 4.2$ meV, $b = 254$ meV, and $\Delta E = 847$ cm$^{-1}$. Note that the second term in the fitting function is equivalent to the thermal occupation function of optical phonons after neglecting the constant term of 1 in the denominator [1,4], which is negligible for the given $\Delta E$ value and the temperature range. Thus from the fitting result we deduce a frequency of 847 cm$^{-1}$ for the phonon mode involved in the dephasing. This frequency matches well with the frequency of the out-of-plane, transverse optical (TO) phonon mode found in the Raman spectra of both SWNT bundles and single tubes as a broad and weak feature [19,20]. We therefore conclude that this TO phonon mode plays a dominant role in the exciton dephasing process. As this TO mode has an atomic displacement along the tube axis [21], it may effectively modulate both the exciton binding energy and $E_{11}$ energy, and thus induce dephasing. We found no evidence for a contribution from the much stronger G-band mode (~1590 cm$^{-1}$), which was predicted to dominate the exciton dephasing in recent calculations [22].

It is interesting to note that the homogeneous widths determined in the zero-intensity limit are in excellent agreement with the results of a single-tube photoluminescence (PL) measurement at all lattice temperatures we studied [23]. This agreement justifies the applicability of the simple relation $T_2 = 4\tau_{\text{decay}}$. We therefore can confidently deduce in the zero-intensity limit an exciton dephasing time of 380 and 162 fs at 77 and 292 K, respectively. The dephasing time obtained at 77 K is very close to the

![FIG. 3 (color online). Dependence of the dephasing rates and the corresponding homogeneous linewidths on excitation intensity at different lattice temperatures. (a) 77, 100, and 130 K, (b) 160, 200, 250, and 292 K. The solid lines in (a) are the linear fits to the data obtained at 77, 100, and 130 K. The dashed lines in (b) are drawn to guide the eye. The corresponding exciton densities estimated from the absorption cross section, mean tube length, laser beam size at the focus, and the excitation intensities are depicted by the scales on the top of the plots.](image-url)
Arity is observed at higher temperatures. Our analysis in the dependence is linear, whereas a clear deviation from line-
lattice temperature. At 77, 100, and 130 K, the intensity but the precise intensity dependences vary markedly with
homogeneous linewidths increase with excitation intensity,
SWNTs. Both the dephasing rates and the corresponding
effect on exciton dephasing in semiconducting
exciton and exciton-phonon scattering processes have pro-
widths of 6.1.

This gives a ratio of inhomogeneous to homogeneous
gies, we estimate an inhomogeneous width of 49.7 meV .

In summary, we have demonstrated that both exciton-
result (350 fs) of a recent frequency domain, single-tube
PL experiment at 90 K [24]. Literature values for the homogeneous width vary substantially [12–14]. However,
the experiments reported in Refs. [23,24] were performed
on as-grown, air-suspended nanotubes. In comparison to
those experiments employing the tubes subjected to rigor-
ous post-growth processing, these results should be least
affected by environment [11,25], defects [12], and uninten-
tional doping [14], and therefore we expect them to more
closely reflect the intrinsic spectral properties of individual
tubes. Moreover, the homogeneous width appears much
narrower than the FWHM width of the linear absorption
spectrum, with room temperature FWHM widths of 8.1 and
50.3 meV, respectively. Clearly, the absorption spectrum
shown in Fig. 1 is dominated by inhomogeneous broad-
ening. Assuming a Gaussian distribution of the $E_{11}$ ener-
gies, we estimate an inhomogeneous width of 49.7 meV.
This gives a ratio of inhomogeneous to homogeneous
widths of 6.1.

In summary, we have demonstrated that both exciton-
exciton-phonon scattering processes have pro-
ponents on exciton dephasing in semiconducting
SWNTs. Both the dephasing rates and the corresponding
homogeneous linewidths increase with excitation intensity,
but the precise intensity dependences vary markedly with
lattice temperature. At 77, 100, and 130 K, the intensity
dependence is linear, whereas a clear deviation from line-
arity is observed at higher temperatures. Our analysis in the
zero-intensity limit further identifies the dominant phonon
mode as the out-of-plane TO mode with a frequency of
847 cm$^{-1}$. Moreover, the room temperature absorption
spectrum is strongly inhomogeneously broadened, with a
large ratio of the inhomogeneous to homogeneous widths
of 6.1. The observed long dephasing times will enable the
study of many-body coherent effects in real time, along
with the resulting dynamical and spectroscopic signatures.

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Nanotubes: Basic Concepts and Physical Properties


