Temperature effects on femtosecond transient absorption kinetics of semiconducting single-walled carbon nanotubes

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We report femtosecond transient absorption kinetics measured for selected semiconducting single-walled carbon nanotubes at different temperatures between 77 and 290 K. The nanotubes are embedded in a thin polymethylmethacrylate film, and the dominance of individual species enabled to probe selectively the kinetics associated with two desired tube types, the (6,5) and (7,5) tubes. A strikingly similar temperature dependence is found between the maximum change in the amplitude of transient absorption kinetics, the overall decay time and steady-state fluorescence emission intensity. The simplest explanation for our data is that the temperature dependence of the fluorescence intensity and the exciton decay kinetics are dominated by nonradiative decay and that the radiative decay rate is weakly temperature dependent.

1. Introduction

Discovery of the band-gap fluorescence emission from semiconducting single-walled carbon nanotubes (SWNTs) dispersed individually in sodium dodecyl sulfate micelles has stimulated extensive research interests in optical spectroscopy.1 Remarkable advances have been achieved recently, including establishment of the correlation between the nanotube structure and the specific electronic characteristics,2–4 unambiguous identification of the excitonic nature of the elementary excitations in semiconducting species,5–7 and experimental assessment of fundamental photophysics.8–12 These advances have provided important information for further exploring the fundamental physics in these quasi-1-D materials, and for realizing their novel applications.

The effect of temperature on the fundamental electronic properties of SWNTs has been addressed both theoretically and experimentally.13–20 Steady-state fluorescence emission and resonant Raman measurements on SWNTs suspended in air reveal a rather small downshift of optical transition energy of ca. 10 meV with increasing temperature over the range 20–300 K for fluorescence13 and 113–300 K for resonant Raman spectra,14 respectively. The magnitude of the observed shift is fully consistent with the results of theoretical calculations.20 A concomitant moderate decrease of the emission intensity by about a factor of two was also observed.13 In contrast, a much larger, chirality-dependent shift of the transition energy towards either high- or low-frequencies with a similar range of temperature variation was found for the SWNTs wrapped with surfactants and/or embedded in polymer matrices.14–16,18 This shift has been shown to arise from extrinsic strain resulting from contraction of the nanotube wrapping surfactants and/or embedding polymer matrix upon freezing.14–16,18,19 The large spectral shift observed is further accompanied by a significant decrease of the fluorescence emission intensity by 10 times or more. The physical origin of these differing temperature dependences of the fluorescence emission intensity is not known and can not be accessed from steady-state fluorescence measurement. Here, we address this question experimentally using femtosecond transient absorption (TA) spectroscopy at different temperatures between 77 and 290 K. The experiment was performed on a thin polymethylmethacrylate (PMMA) film containing predominantly individual nanotubes. We examined two types of semiconducting SWNTs, the (6,5) and (7,5) tubes (the notation for tube types is described in ref. 21), whose fluorescence emission spectra exhibit shifts towards opposite directions with decreasing temperature. Quantitative analysis of the experimental data enables us to reveal strikingly similar temperature dependence between the maximum change in the TA amplitude, the decay time of the TA kinetics, and the corresponding fluorescence emission intensity.

2. Experimental

The femtosecond TA setup employed here has been described extensively elsewhere.11,22,23 In short, the light source was an optical parametric amplifier pumped by a 250 kHz Ti:sapphire regenerative amplifier, which generates 50 fs pulses at 567 and 653 nm. These pump wavelengths were chosen in order to excite resonantly the second excitonic states (E22) of the (6,5) and (7,5) tubes, respectively. In order to minimize possible effects arising from nonlinear dynamical processes such as exciton-exciton annihilation,11,12,23,24 the pump intensity was kept at ~1.0 × 1014 photons cm−2 pulse−1. The
pump beam was focused to a spot size of \( \sim 150 \mu m \) at the sample. A single-filament white-light continuum served as the probe beam. Selection of the probe wavelength was realized using a single-grating monochromator with a typical band-width of 8 nm. The detection scheme consists of a Si photodiode and a lock-in amplifier. The intensity of the probe beam was monitored right after each TA kinetics measurement by placing a second chopper into the beam, and the measured intensity was used to correct the corresponding TA signal whenever a noticeable change was observed. The polarization of the pump beam was set to the magic angle (54.7°) with respect to the probe beam.

The sample was a \( \sim 100 \mu m \) thick film of SWNTs embedded in PMMA matrix. The film, which consists of predominantly individual nanotubes, was fabricated by drying PMMA solutions in toluene/xylene mixed with micelle-dispersed SWNTs. These organic solutions were prepared by carefully transferring SWNTs suspended in detergent–water media to the PMMA solution using ultrasound and thermal treatments.\(^ {18} \) The water-based SWNT suspension was prepared using high-pressure CO-SWNT material according to the procedure described previously.\(^ {1} \) The film was placed in the sample chamber of an Oxford Instruments liquid-N\(_2\) cryostat, which allows continuously varying temperatures between 77 and 300 K. Experiments on different spatial regions of the sample produced identical results, although scattering did vary within the film.

3. Results and discussion

As demonstrated recently,\(^ {11,22} \) spectrally selective detection of desired semiconducting tube types from a micelle-dispersed aqueous solution that contains various metallic and semiconducting nanotubes is attainable in femtosecond TA experiments. This is accomplished by carefully setting the pump and probe wavelengths to ensure electronically resonant excitation and detection. While the nanotubes in the sample used for this work are embedded in solid polymer films, the dominance of individual tubes retains this spectral selectivity. This can be seen from the well-separated fluorescence emission/excitation spectra associated with structurally distinct semiconducting nanotubes, which has been observed using this or similar films.\(^ {15,16,18} \) To selectively detect the TA kinetics associated with the (6,5) and (7,5) tubes in this work, we pumped their \(E_{11}\) states and probed the corresponding \(E_{11}\) states, i.e. the energetically lowest transition-allowed exciton states. The resulting TA signal, as observed previously for the aqueous samples,\(^ {11,22,25} \) is characterized by an induced transmission owing to the dominant contributions from ground state bleaching and stimulated emission of the respective \(E_{11}\) state.

Because the \(E_{11}\) transition energy depends on temperature, the corresponding wavelengths at chosen temperatures must be known in advance in order to correctly set the probe wavelength, and thus to ensure detection of the same tube type. We set our probe wavelengths at different temperatures according to the steady-state fluorescence measurements on a similar SWNT/PMMA film.\(^ {18} \) As also observed by others,\(^ {15,16} \) a decrease of temperature from 300 to 77 K leads to a remarkable shift of the \(E_{11}\) transition wavelength towards longer- and shorter-wavelength for the (6,5) and (7,5) tubes, respectively. While the corresponding \(E_{22}\) transition wavelengths vary as well, ranging from 563 to 567 nm and from 657 to 650 nm, respectively, these changes are 3 and 5 times smaller than those of their respective \(E_{11}\) transitions. These smaller shifts of the \(E_{22}\) transition wavelengths, in particular their narrow band widths [with a typical full width at half maximum (FWHM) of \(\sim 35\) meV at room temperature]\(^ {26} \) in comparison to the widths of the pump pulse spectra (\(\sim 55\) meV, FWHM), justify the use of a fixed pump wavelength for each tube type to collect data at different temperatures.

Representative TA kinetic profiles obtained at different temperatures are shown in Fig. 1. For ease of comparison, we normalized the kinetics data to have their maximum changes of the TA signal amplitudes (\(\Delta OD_{\text{max}}\)) equal to \(-1.0\). As is evident from Fig. 1, the variation of temperature substantially affects the TA kinetic decays. An increase of temperature generally results in a faster decay for both (6,5) and (7,5) tubes. This temperature effect further appears to be

\[ \text{Fig. 1 } \text{The TA kinetics probed for the (7,5) tube (upper panel) at 77, 190 and 220 K and the (6,5) tube at 77 and 290 K (lower panel). The thick solid lines represent the fits according to a stretched exponential function. All kinetics are normalized at the maximum changes of the TA signals. The detection wavelength was 1002 nm (77 K), 1014 nm (190 K) and 1018 nm (220 K) for the (7,5) tube and 1008 nm (77 K) and 994 nm (290 K) for the (6,5) tube.} \]
chirality dependent: a much more pronounced effect was observed for the (7,5) tube than for the (6,5) tube type. Upon closer inspection of the data collected for the (7,5) tube, we also found that the kinetics measured at 250 and 293 K shows noticeably slower decays than the one obtained at 220 K. It is noteworthy that the temperature corresponding to this change of the decay behavior coincides with a phase transition temperature of PMMA, and thus the observed slower decays at 250 and 293 K may be related to an external effect.

The kinetics recorded at different temperatures clearly exhibit non-exponential decays, and satisfactory fits of the data generally require a model function consisting of three exponential components. This multi-exponential decay behavior has been observed in previous time-resolved measurements on the micelle-dispersed aqueous solution samples with either femtosecond or picosecond time resolution. To extract a unique set of fitting parameters (lifetimes and relative amplitudes) from such an analysis is not trivial, and the resulting large number of parameters further complicates characterization of the temperature dependence. In order to simplify the data analysis and, most importantly, to quantify unambiguously the overall temperature dependence, we employed a model function consisting of a stretched exponential function and a small constant offset in this work, which can be written as

\[ f(t) = a_0 e^{-(kt)^b} + a_1. \]

We find that this model function provides satisfactory description of all the kinetics, and representative fits are provided in Fig. 1 (thick solid lines). The resulting rate constant \( k \) and the stretching parameter \( b \) are plotted as a function of temperature in Fig. 2. For the (7,5) tube, both the \( k \) and \( b \) values increase exponentially with temperature up to 220 K, whereas for the (6,5) tube they change linearly with temperature over the entire range of temperature. As evident from Fig. 2, the pronounced temperature effect on the kinetics of the (7,5) tube corresponds to a concomitant increase of both \( k \) and \( b \), while the weak effect observed for the (6,5) tube is manifested by an increase of both \( k \) and \( b \) values. Moreover, for both tube types a maximum \( a_1 \) value is obtained from the kinetic data measured at 77 K, which is about 10% of the corresponding \( a_0 \) value. It should be noted that the offset represented by \( a_1 \) actually accounts for a long-lived decay component of the kinetics, which appears as a constant in the time range of our detection (\( \sim 100 \) ps).

We also attempted to fit the kinetics to other functional forms that describe specific physical mechanisms of exciton relaxation. The first function we employed is of a hyperbolic-like form, with an additional constant offset to account for the long-lived decay component. As demonstrated previously, such a hyperbolic-like function provides a satisfactory description of time-resolved fluorescence decay kinetics probed for semiconducting SWNTs under high excitation intensities, where nonlinear exciton–exciton annihilation dominates the exciton relaxation. Using this form, fits of the same quality as reported by Russo et al., which describes an exciton population relaxation via 1-D diffusion-limited two-body recombination. However, the fits obtained for both tube types are clearly unsatisfactory (results not shown). The clear difference in the decay behavior of kinetics observed by us and Russo et al. may be at least partially due to use of 30 times lower excitation intensity in our experiment, plus possible effects arising from the use of different surfactants in individualizing the nanotubes.

Besides the substantial effects on the kinetics as shown in Fig. 1 and 2, the change of temperature further affects strongly the \( \Delta OD_{\text{max}} \) values measured for the (6,5) and (7,5) tubes (Fig. 3, squares). For both tube types, we find that an increase of temperature results in a monotonic decrease of the \( \Delta OD_{\text{max}} \) up to 220 K. Upon further increasing the temperature, the \( \Delta OD_{\text{max}} \) values either show a slower decrease [for the (6,5) tube] or become a sharp increase [for the (7,5) tube]. It is noteworthy that the temperature corresponding to this turnover point coincides again with the phase transition temperature of PMMA.

A more surprising observation is that a strikingly similar temperature dependence to that observed for the \( \Delta OD_{\text{max}} \) values is found for the decay time of the kinetics \( \tau_f \), the inverse of the decay rate \( k \), and the fluorescence emission
This means that the TA kinetic decays observed are notubes.8,9 This implies that the radiative lifetime estimated for semiconducting nanotubes.8,9 Thus, it is noteworthy to mention that a fairly similar temperature dependence is also found for the (6,5) tube. As a final remark, we now briefly discuss the temperature dependence of the PL decay time (τ) and intensity reported by Hagen et al. based on single tube spectroscopy.39 The authors found a pronounced increase of τ with decreasing temperature, which is qualitatively similar to our data shown in Fig. 3. However, the concomitant decrease of PL intensity appears unusual, as it is in contrast to all results of previous PL measurements on both ensembles and individual tubes.13e16,18 The reason for this discrepancy is currently unclear.
In conclusion, our femtosecond TA measurements on two structurally distinct semiconducting nanotube types reveal strong temperature dependence. This dependence appears chirality dependent with a much more pronounced effect observed for the (7,5) tube than the (6,5) tube. An increase of temperature from 77 to 290 K results in a general decease of the maximum change of the signal amplitude, $\Delta OD_{max}$, and an enhancement of the overall decay rate $k$. A striking similarity is found between the temperature dependences of the nonradiative rate. The reason for the similar temperature dependence of the radiative decay rate is weakly dependent on temperature in the range from 77 to 290 K and that what is being observed is the temperature dependence of the nonradiative rate. The reason for the similar temperature dependence of the $\Delta OD_{max}$ values awaits further theoretical and experimental studies, although contribution from some extrinsic effects can not be ruled out.

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