Ultrafast exciton dynamics in semiconducting single-walled carbon nanotubes

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Ultrafast exciton dynamics in semiconducting single-walled carbon nanotubes

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To define the origin of the electronic excited states of single-walled carbon nanotubes, femtosecond fluorescence up-conversion and frequency-resolved transient absorption measurements were used for selective excitation/probing of particular nanotubes in a micelle-dispersed preparation enriched with individual nanotubes. Analysis of the temporal and intensity profiles of the transient signals enable one to unambiguously identify the excitonic nature of elementary excitations in semiconducting nanotubes, and the predominant dynamical process as a remarkable manifestation of exciton–exciton annihilation. These studies convincingly support the conclusion that the longest wavelength electronic excitations are of excitonic origin. In addition, evidence is shown for bi-exciton formation in single walled nanotubes.

1. Introduction

A single-walled carbon nanotube (SWNT) can be considered as a rolled-up 2D graphene sheet whose structure is uniquely determined by a pair of indices \((n, m)\) that define its diameter and chirality [1]. Depending on its structure, a SWNT can exhibit either metallic or semiconducting characteristics with structure-specific transition energies between electronic states [1, 2]. These unique electronic properties, in combination with other remarkable physical properties, make SWNTs an ideal choice for a wide range of applications, such as nanometre-sized conducting wires, field effect transistors, and molecular electronics [3].

Recent advances in optical spectroscopy of SWNTs have enabled the connection between the nanotube structure and specific transition energies to be established [4–6]. These advances allow tube species in an unknown sample to be readily identified, and quantitative assessment of the change of electronic transition energies caused by extrinsic factors, such as wrapping medium [7, 8], temperature [9], etc. The wide range of ratios between the energies of the second \((E_2)\) and the first \((E_1)\) electronic transitions for different semiconducting nanotubes [4, 5], in contrast to the constant value predicted by conventional one-electron tight-binding calculations [1], has raised questions about the physical nature of the elementary excitations. This ‘ratio problem’ has stimulated detailed theoretical studies, and it has been concluded that the spatial confinement causes a dramatic enhancement of many-electron correlation effects, and results in an excitonic origin of the optical spectra [10–15].

Ultrafast spectroscopic studies of carbon nanotubes has been reported by several groups [16–21], and were interpreted by assuming either charge carriers (electrons and holes) or excitons, i.e., the Coulombically bound electrons and holes, as the elementary excitations. Distinct kinetics and their excitation dependence were found for each nanotube species [18]. Remarkable changes of kinetics were also noticed for data collected using micelle-dispersed, individual tube enriched aqueous samples and solid films of SWNT bundles/ropes [20]. In the latter case, the inter-tube interactions cause a loss of the spectroscopic characteristics of individual nanotubes [22, 23], making access to individual SWNT types impossible. To resolve the...
inconsistency of the reported results and to assess experimentally the physical nature of the elementary excitations and the associated ultrafast relaxation dynamics, it is crucial to selectively monitor desired nanotube species.

In this work, we employed an individual nanotube enriched SWNT preparation suspended in aqueous solution of sodium dodecyl sulfate micelles, in which the spectroscopic transitions associated with the specific semiconducting nanotube structures can be clearly resolved [4, 24, 25], allowing us to access independently specific nanotube types. We demonstrate that the selection of individual nanotube species from a mixture of ~50 types is attainable by tuning the excitation and detection wavelengths to be resonant with either one or two electronic transitions of a desired nanotube. We then focus on the ultrafast dynamics of several tube species and the analyses of the experimental data enable us to identify the excitonic nature of elementary excitations in semiconducting SWNT. We further show that exciton–exciton annihilation dominates the dynamics for the level of excitation intensity commonly used in femtosecond time-resolved experiments. Finally, we describe some evidence for the formation of biexcitons in SWNT.

2. Experimental methods

2.1. Femtosecond fluorescence upconversion

Fluorescence upconversion experiments were performed using a setup described previously [18]. Briefly, the light source was a commercial regenerative Ti:sapphire amplifier with a repetition rate of 250 kHz, generating ~50 fs (FWHM) pulses centred at 800 nm. The major portion (70%) of the amplifier output was used to pump an optical parametric amplifier (OPA) to produce pulses centered at 567 and 660 nm, respectively. A dual prism compressor consisting of two SF10 prisms was employed to compensate for group velocity dispersion, producing nearly transform-limited pulse of ~30 fs FWHM. The excitation beam was then focused to a spot size of 30 µm using a lens with f = 5 cm. The minor part of the amplifier output (30%) served as gate pulses, and was temporally delayed using a step-motor driven optical delay stage. A sample cell of 1.0 mm pathlength was placed at one focus of an ellipsoidal reflector, which collected the spontaneous emission from the sample and focused it into the upconversion crystal (0.5 mm BBO) positioned at the other focus. The residual pump beam, after passing through the sample cell, was blocked with a small metal rod at a point between the reflector and crystal allowing the majority of the collected fluorescence to pass. The upconverted fluorescence was collected with a lens and focused, after spatial filtering, into the entrance slit of a double grating monochromator. Finally, the upconverted light was detected with a photomultiplier tube connected with a gated photon counter (Stanford Research Systems SR400). To eliminate the background signal resulting from stray light from the excitation beam, the second harmonic of the gate beam and dim room light, the photon counter was operated in the gated mode using the output of a photodiode in the amplifier as a trigger source. The polarization of the excitation beam was set at the magic angle (54.7°) with respect to the gate beam using an achromatic λ/2 plate.

The instrument response function (IRF) was recorded using two different methods: by directly measuring the cross-correlation between the excitation and gate beams, and by upconverting the instantaneous water Raman scattering of the excitation light. In both cases, we flowed pure water through the sample cell to maintain similar dispersion of the excitation pulses for the sample. The FWHM of the IRF determined from the cross-correlation measurements were 80 and 105 fs for excitation at 567 and 660 nm, and the corresponding upconverted water Raman signal had FWHM of 98 and 120 fs, respectively. We further found that the latter gives a better fit of the leading edge of the fluorescence kinetics in the deconvolution analysis, and thus this IRF is used for all data analysis.

2.2. Femtosecond frequency-resolved transient absorption

The same laser system was used in the frequency-resolved transient absorption experiments. The visible and near-infrared (NIR) pump pulses were obtained from the signal and idler outputs of the OPA. The pump beam was focused to a spot size of ~300 µm at the sample position. To monitor the pump-induced change of absorbance, we employed a single-filament white light continuum generated in a sapphire plate of 2 mm thickness using the minor portion of the amplifier output. The remaining fundamental in the continuum was spectrally filtered using either a short- or a long-wavelength cut-off filter (CVI, SP750/LP850). The continuum was then split into two separate beams, a probe and a reference, which were focused to a spot of ~200 µm with two spherical mirrors with f = 20 cm. The probe and reference beams were vertically displaced on the sample cell by ~4 mm and only the probe beam was spatially overlapped with the pump beam. After passing through the sample, the probe and reference were focused onto the entrance slits of a spectrograph (SpectroPro 300i) equipped with a Peltier cooled CCD
on its exit port. The change of absorbance, $\Delta OD$, was calculated according to the following equation:

$$-\Delta OD = \log \frac{I_{pr}(\lambda)}{I_{ref}(\lambda)}_{ON} - \log \frac{I_{pr}(\lambda)}{I_{ref}(\lambda)}_{OFF}$$

where $I_{pr}(\lambda)$ and $I_{ref}(\lambda)$ are the intensities of the probe and reference beams at a given wavelength $\lambda$, and ‘ON’ and ‘OFF’ stand for the presence and absence of the pump pulse, respectively. The transient absorption spectra were recorded at a series of time delays between the pump and probe pulses, and the raw data obtained at each delay time were binned to a spectral resolution of 2.15 nm to enhance signal-to-noise. Correction is also made for the group velocity dispersion of the probing continuum. Frequency-integrated kinetics at selected probe wavelengths were recorded with a detection bandwidth of 4 nm by a photodiode connected to a lock-in amplifier. The polarization of the pump beam was set to the magic angle ($54.7^\circ$) with respect to the probe beam. A typical cross-correlation between pump and probe pulses had a temporal width of about 100 fs.

2.3. Sample preparation

The SWNT material was produced by a HiPco-type generator, and the same procedure as described previously was used to prepare a sample rich in individual nanotubes in a surfactant–water system (SDS in H$_2$O) [24]. The typical sample OD was about 0.2 per mm. During data acquisition, the samples were circulated slowly using a peristaltic pump in the fluorescence experiment, while in the transient absorption experiment a sample cell with 1 mm pathlength was continuously translated vertically. The stability of the sample was checked by recording the absorption spectra before and after the time-resolved measurements, which showed no observable change.

3. Results and discussion

3.1. Spectral selectivity to a single nanotube species

The coexistence of a large number of tube types in the sample makes it non-trivial to selectively detect the spectroscopic response and dynamics associated with a single desired tube species. This selection becomes even more difficult for a femtosecond time-resolved experiment because the broad pulse spectrum is likely to excite multiple tube types simultaneously. The general strategy that we used is to select tubes resonant with the excitation and detection wavelengths selected. In fluorescence upconversion experiment, this strategy is accomplished by varying both the excitation and detection wavelengths according to [4] to ensure electronic resonance with the $E_2$ and $E_1$ transitions of a given nanotube. Even though an excitation pulse may be resonant with a few types of nanotubes, emission from a single type can still be selected as long as it is spectrally well separated from the emission bands of the other tube types. When all the emission bands from these simultaneously excited nanotube species are separate from each other, tube-type selective detection becomes simplified and can be realized by changing only the detection wavelength. For instance, use of an excitation pulse centred at 660 nm allows us to excite four distinct tube structures with emission peaking at 952, 1024, 1119 and 1244 nm, corresponding to tube structures (8, 3), (7, 5), (7, 6) and (9, 5) [18]. The simultaneous excitation of multiple tube structures can be easily understood by studying the 2D steady-state fluorescence excitation-emission plot [4].

Because of the large background underlying the structured bands in the linear absorption spectrum, selective detection of any SWNT type is questionable for absorptive experiments. To find out whether selectivity is possible, we performed a frequency-resolved transient absorption measurement by pumping either the $E_1$ or $E_2$ transitions of selected tube types. The NIR spectra obtained show distinct bands peaked at wavelength(s) corresponding to the $E_1$ transitions. As an example, figure 1 shows the transient absorption spectra recorded

![Figure 1. Transient absorption spectra measured in the NIR region at a delay time of 50 fs for excitation at 660 (a) and 567 nm (b). The spectra are vertically offset for clarity, and the thin dashed lines are the baselines ($\Delta OD = 0$). The induced transmission bands observed in (a) and (b) show a good match with the bands in the linear absorption spectrum (c) as indicated by the vertical dotted lines.](image-url)
in the NIR region upon excitation at 660 and 567 nm. Excitation at 567 nm results in a dominant induced transmission band peaked at 975 nm, whereas excitation at 660 nm gives rise to two distinct bands with approximately equal amplitude, at 954 and 1026 nm. These induced transmission bands match the peaks in the linear absorption spectrum, and can be assigned to the (6, 5), (8, 3) and (7, 5) nanotubes [4, 5], respectively. Observation of these well-resolved spectral bands suggests that it is possible to selectively detect a desired SWNT type. We examined this selectivity by comparing the kinetics probed at 975 nm (figure 2) with pump pulses centred at 567 and 953 nm. The former is electronically resonant with the pulses centred at 567 and 953 nm. The former is electronically resonant with the (6, 5) nanotube type, whereas the latter causes simultaneous excitation of the \( E_1 \) transitions of both (8, 3) and (6, 5) tubes due to the broad spectrum of pump pulse. In addition, these pump wavelengths also excite the species responsible for the background absorption. Since this background absorption varies with wavelength, its contribution to the transient absorption spectra, if present, would change with excitation wavelength. The identical kinetics shown in figure 2 indicates that the contribution from this background is negligible. Further confirmation of the selectivity is obtained from the similarity between these two transient absorption kinetics and the fluorescence kinetics measured at 975 nm upon excitation at 567 nm, which originates exclusively from the (6, 5) nanotube type [4]. Based on the example shown in figures 1 and 2, we conclude that spectral selectivity of different tube structures is attainable at least for those semiconducting SWNTs with substantial concentration in the sample.

3.2. Dependence of time-resolved fluorescence decays on excitation intensity

In our time-resolved fluorescence experiments, we monitored selected tubes via the following combinations of excitation/emission wavelengths: 567/975, 660/950, 660/1119 and 660/1244 nm. These combinations select the four tube structures (6, 5), (8, 3), (7, 6) and (9, 5) [4]. Figure 3(a) shows the transient fluorescence intensity at 1244 nm for five different excitation densities. The fluorescence decays show strong intensity dependence, namely a faster decay with an increase of excitation intensity. In addition, the overall amplitude of the fluorescence kinetics clearly shows a nonlinear dependence on the excitation intensity (figure 3b). The amplitude, however, scales linearly with the square root of the excitation intensity (see figure 3(b), insert). For the tube structures (8, 3), (6, 5) and (7, 6), exhibiting fluorescence at 950, 975 and 1119 nm, similar behavior is observed (data not shown). This intensity dependence implies the existence of nonlinear relaxation, for example exciton–exciton annihilation for exciton states [26]. Following [26], the population relaxation kinetics of excitons under sufficiently high pump intensity satisfies the following equation:

\[
\frac{dn_{E_1}(t)}{dt} = -\frac{1}{2} \gamma n_{E_1}(t),
\]

where \( n_{E_1}(t) \) is the populations of \( E_1 \) excitons, and \( \gamma \) determines the exciton–exciton annihilation rate. An analytical solution of equation (2) is readily obtained,

\[
n_{E_1}(t) = \frac{n_{E_1}(0)}{1 + n_{E_1}(0)\gamma t}
\]

where \( n_{E_1}(0) \) is the initial population of excitons. As the fluorescence intensity, \( I(t) \), is proportional to \( n_{E_1}(t) \), equation (3) can be used directly to analyse the fluorescence decays obtained at different excitation intensities.

The analyses were performed concurrently for all the fluorescence kinetics measured for each tube structure, where \( \gamma \) and \( n_{E_1}(0) \) were taken as global and local fitting parameters, respectively. As shown in figure 3(a), the various fluorescence kinetics can be well described by this equation and only a minor deviation is seen in the kinetics detected at higher excitation intensity at a delay.
time of ~5 ps. This global analysis gives $\gamma = 0.19$ ps$^{-1}$ and $n_{E_1}(0) = 4.2, 8.1, 11.5, 21.5$ and 37.2 for the five excitation intensities used. In addition, the values of $n_{E_1}(0)$ obtained are plotted in figure 3(b) versus excitation intensity, which shows a nearly identical dependence to that of the maximum fluorescence intensity $I_m$ and the fitted parameter $n_{E_1}(0)$ versus the excitation intensities. The dotted line is drawn to guide the eye. The insert shows the same data plotted versus the square root of the excitation intensity, and the solid line represents the linear fit.

By rewriting equation (3), a linear dependence of the inverse of the normalized fluorescence intensity, $I(t)/I_m$, on delay time is obtained:

$$\left(\frac{I(t)}{I_m}\right)^{-1} \sim \left(\frac{n_{E_1}(t)}{n_{E_1}(0)}\right)^{-1} = \gamma n_{E_1}(0) \cdot t + 1 \quad (4)$$

where $I(t)$ is the fluorescence intensity at time $t$ and $I_m$ the maximum fluorescence intensity. As an example, figure 4 shows the data measured for (9, 5) tubes plotted as the inverse of the normalized fluorescence kinetics over time. The resulting linear behaviour for delay times up to several picoseconds suggests that exciton–exciton annihilation dominates the dynamics in this time range for all the excitation intensities used.

Since our fluorescence data are measured by exciting the $E_2$ transition and monitoring the emission from the $E_1$ state, analysis of the kinetics on the initial delay time may enable us to determine the time scale for the population of the $E_1$ excitons created in a given tube type at different excitation intensities. This determination requires an accurate absorption cross-section per tube and the branching ratio (to form the $E_1$ exciton and uncorrelated electron-hole pairs) following $E_2 \rightarrow E_1$ relaxation. Both the cross-section and branching ratio are currently unavailable. Nevertheless, the similar dependence of $n_{E_1}(0)$ and $I_m$ on excitation intensity (figure 3b) shows the self-consistency of our analysis.
$E_2 \rightarrow E_1$ relaxation. However, the very rapid decay observed at high excitation intensities such as $1.9 \times 10^{16}$ photons \cdot pulse$^{-1}$ \cdot cm$^{-2}$ competes with the $E_2 \rightarrow E_1$ relaxation process, and thus making it difficult to resolve the rise. Due to this reason, we choose the data recorded at an excitation intensity that is low enough to minimize the effect induced by this competitive decay, but still allows detection of transient signals with reasonable signal-to-noise ratio to distinguish the quality of the fits. Figure 5 shows the results of deconvolution fitting for the kinetics measured at an excitation intensity of $9.3 \times 10^{14}$ photons \cdot pulse$^{-1}$ \cdot cm$^{-2}$. A sum of exponential components is used as the model function, and inclusion of an additional exponential rise component with a time constant of $\sim 60$ fs gives a better fit as shown in figure 5(b). Based on this analysis, we conclude that the $E_2 \rightarrow E_1$ relaxation occurs in $<100$ fs.

### 3.3. Evidence for the exciton nature of elementary excitations in semiconducting nanotubes

While the dependence of the fluorescence kinetics on excitation intensity and the bimolecular decay behavior are consistent with exciton–exciton annihilation, further evidence is needed for identifying the excitonic nature of elementary excitations in semiconducting SWNT. This identification is of central importance for understanding the fundamental physics of these quasi-1D materials.

Depending on the magnitude of exciton binding energy, the elementary excitation in a semiconductor material can be either a neutral exciton, or a pair of uncorrelated charged carriers (electron and hole) [27]. Assuming that the elementary excitations in semiconducting SWNTs are uncorrelated charged carriers, the dependence of fluorescence kinetics on the excitation intensity (figure 3(a)) should accordingly be attributed to the so-called Auger recombination processes, a nonlinear process involving three quasiparticles [28–30]:

$$\frac{dn_{e,h}}{dt} = -\frac{1}{3} \gamma_A n_{e,h}^3,$$

(5)

where $n_{e,h}$ is the population of the free charge carries (electrons and holes), $\gamma_A$ is the rate of the three-particle Auger recombination. The population kinetics determined by equation (5) gives the following relationship: $\left[\frac{n_{e,h}(0)}{n_{e,h}(t)}\right]^3 - 1 = \gamma_A n_{e,h}(0) t$, where $n_{e,h}(0)$ is the initial population of charge carriers. Since the fluorescence emission results from the electron–hole recombination, its intensity $I(t)$ at a given delay time $t$ is proportional to $n_{e,h}(t)$ [31] and therefore the inverse of fluorescence intensity, $1/I(t)$, will scale linearly with $t$. Because the same linear dependence is also predicted from the exciton–exciton annihilation (equation (4)), we conclude that, from the temporal behaviour of the excitation-intensity-dependent fluorescence data, one cannot distinguish the nature of elementary excitations in semiconducting SWNT.

In contrast, the bi-molecular exciton–exciton annihilation and the Auger recombination involving three quasiparticles predict strikingly distinct time dependence for the kinetics recorded with transient absorption spectroscopy. In this case, the amplitude of the bleaching signal $|\Delta A(t)|$ is always proportional to the population of the elementary excitations regardless

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**Figure 5.** Comparison of the deconvolution fits of the fluorescence data obtained without (a) and with (b) an exponential rise component of 60 fs in the model function. The experimental data were collected for (9,5) tube structure at an excitation intensity of $9.3 \times 10^{14}$ photons \cdot pulse$^{-1}$ \cdot cm$^{-2}$. The thick solid lines are the fits and the dotted lines are the instrument response function. The residuals of the corresponding fits are shown on the bottom of the plots.
of their physical nature [31]. According to equation (4) and the solution of equation (5), a linear time dependence is expected for $1/\Delta A(t)$ when exciton–exciton annihilation dominates the kinetics, or for $1/\Delta A^2(t)$ when the Auger recombination of charged carriers is responsible for the observed kinetics. Figure 6(a) shows the data obtained for (8,3) tube structure by resonantly exciting the corresponding $E_2$ transition at 660 nm and by tuning the probe wavelength to its $E_1$ transition at 953 nm. The data are plotted as the inverse of the signal amplitude $[1/\Delta A(t)]$ or the inverse of its squared amplitude $[1/\Delta A^2(t)]$ over delay time $t$, and the former gives a good linear dependence except at short decay times ($<1$ ps). A linear dependence is also found for the kinetics measured by directly pumping the $E_1$ transition of the (8,3) tube, plotted as $1/\Delta A(t)$ versus time delay (figure 6(b)). In contrast, the plots of $1/\Delta A^2(t)$ versus delay time for both data sets deviate from linearity. The linear time dependence observed for $1/\Delta A(t)$ provides strong evidence for the excitonic nature of the elementary excitations. It is pertinent to mention that the same approach has been applied to distinguish the nature of elementary excitations in semiconductor quantum rods [30].

The attribution of the elementary excitations in semiconducting SWNT to excitons is further supported by the square root dependence of the overall amplitude of the fluorescence kinetics on the excitation intensity (figure 3(b), insert). For $E_2$ excitation, the following rate equations can be used to describe the dynamics:

$$\frac{dn_{E_2}(t)}{dt} = G(t) - k_{21}n_{E_2}(t) + \frac{1}{2} \gamma n^2_{E_1}(t), \quad (6)$$

$$\frac{dn_{E_1}(t)}{dt} = k_{21}n_{E_2}(t) - \gamma n^2_{E_1}(t) - k_{12}n_{E_1}(t), \quad (7)$$

where $G(t)$ is the exciton generation rate, and $k_{12}$ is the rate of $E_2 \rightarrow E_1$ relaxation and $k_{1g}$ is the rate of exciton relaxation to the ground state (i.e. the electron–hole recombination). In the case when the exciton–exciton annihilation process dominates the linear relaxation, the quasi-stationary conditions of equations (6) and (7) are fulfilled in the vicinity of the excitation pulse maximum. In this case, simple dependence of the population, $n_{E_1}(0)$, on the amplitude of the excitation pumping $G(t_{\text{max}})$ is obtained,

$$n^2_{E_1}(0) \approx \frac{k_{21}}{\gamma} n_{E_2}(0) \approx \frac{2}{\gamma} G(t_{\text{max}}). \quad (8)$$

According to equation (8), the overall amplitude of the fluorescence kinetics should scale linearly with the square root of excitation intensity, which is consistent with the result shown in the insert of figure 3(b). The qualitative relation given by equation (8) is further confirmed by a numerical calculation based on equations (6) and (7), with the following...
parameters: $\frac{1}{k_{21}} = 20 \text{ fs}$ [18, 32], $\frac{1}{\gamma} = 800 \text{ fs}$ [33], an excitation pulse duration of 100 fs and $\frac{1}{k_{12}} = 100 \text{ ps}$. The result of this numerical calculation is shown in figure 7(a) and confirms the dependence of $n_{E_1}(0)$ on the square root of the excitation intensity.

The same intensity dependence is also expected for direct $E_1$ excitation. In this case, the first term in equation (7) should be replaced by $G(t)$, the exciton generation rate. Following the same procedure as used to derive equation (8), a square root dependence of the amplitude on the pump intensity is obtained. This square root dependence is in accord with the transient absorption measurement with direct $E_1$ pumping for the $(6, 5)$ tube as shown in figure 7(b). In contrast to the time-resolved fluorescence data shown in the insert of figure 3(b), a clear offset at zero pump fluence is noticed in figure 7(b), which likely results from a superposition of a constant induced absorption (IA) signal with the transient response. This square root dependence on pump intensity, together with the other spectroscopic and dynamic signatures of exciton–exciton annihilation observed in frequency-resolved transient absorption spectroscopy [34], enables unambiguous identification of the excitonic nature of the elementary excitations in semiconducting nanotubes. It is interesting to point out that dissociation of the excitons as a result of this annihilation was observed recently [35], following possibly a similar process to that predicted and experimentally verified in molecular crystals a few decades ago [36, 37].

3.4. Evidence for the formation of biexcitons in semiconducting nanotubes

In addition to the exciton–exciton annihilation discussed in the preceding sections, simultaneous creation of multiple excitons in a single nanotube under high excitation levels can result in the formation of biexcitons or excitonic molecules, each exciton involving two Coulombically bound electron–hole pairs [38–41]. For low-dimensional systems such as semiconductor quantum dots and wires, SWNTs and quantum wells, the spatial confinement results in greatly enhanced multiparticle interactions and, consequently, a significant increase in biexciton binding energy ($E_{xx}$) with respect to bulk semiconductors [42–45]. Formation of stable biexcitons in SWNT with an $E_{xx}$ of several tens of meV was predicted theoretically by Pedersen and coworkers [43]. As this $E_{xx}$ is larger than the characteristic bandwidth of the exciton absorption and/or fluorescence emission, the authors concluded that the biexcitons in SWNT should be observable as photoinduced absorption features in frequency-resolved pump-probe spectroscopy, with an energy that is equal to the difference between $E_1$ and $E_{xx}$. While such spectroscopic characteristics were observed for semiconductor quantum dots [40] and conjugated oligomers [44], no experimental observation has been reported so far for SWNT.

Figure 8(a) shows the TA spectrum recorded at a delay time of 2 ps with pump pulses centered at 953 nm. The spectrum contains two partially overlapped IT bands peaking at 954 and 975 nm, respectively, together with a weak band at 1026 nm. These IT bands correspond to the $E_1$ transitions of the $(8, 3)$, $(6, 5)$ and $(7, 5)$ nanotubes, concurrently excited via either electronic resonance [for the $(8, 3)$ and $(6, 5)$ tubes] or the phonon subband of the $E_1$ state [for the $(7, 5)$ tube] [34, 46]. In addition, an IA band peaking at 1010 nm is observed. This IA band shows distinct time evolution from the IT bands associated with the $(8, 3)$ and $(6, 5)$ tubes, which is
evident from the kinetics probed at 953, 975 and 1010 nm (figure 8(b)). The transient measured at 1010 nm initially exhibits a fast recovery from an IT signal. It further develops into a positive IA signal and finally decays mono-exponentially with a lifetime of 7 ps. In contrast, the kinetics detected at 953 and 975 nm for the (8, 3) and (6, 5) nanotubes are dominated entirely by IT signals, which recover in a multi-exponential decay. Distinct differences are also found in the dependence of the amplitudes of the kinetics on pump intensity (figure 9a). The data collected at 1010 nm with different pump intensities show a linear dependence on pump intensity for both the amplitudes of the initial IT maximum and of the IA signal at 1.5 ps. In contrast, the amplitudes of the IT signal maxima associated with the (8, 3) and (6, 5) nanotubes scale linearly with the square root of pump intensity. Based on the differences in the time evolution and the intensity dependence shown in figures 8(b) and 9(a), we conclude that the IA band peaking at 1010 nm does not arise from the single excitonic transitions of the (8, 3) or (6, 5) nanotubes.

According to the spectroscopic signatures of biexcitons calculated for SWNT [43] and the experimental observation of semiconductor quantum dots [40], we tentatively assign the IA band at 1010 nm to biexcitons from either the (8, 3) or (6, 5) tubes. To verify this assignment, we now analyse the intensity dependence shown in figure 9(a). Considering the simplest

![Figure 8](image_url)  
**Figure 8.** (a) Transient absorption spectrum measured in the NIR region at a delay time of 2 ps for excitation at 953 nm. The thin dashed line is the baselines (ΔOD = 0). (b) Comparison of kinetics detected at 953, 975 and 1010 nm. The kinetics are vertically offset for clarity, and the dashed lines are the baselines. All the data are normalized to the signal maxima.

![Figure 9](image_url)  
**Figure 9.** (a) Plot of the amplitudes of the transient absorption kinetics probed at 975 and 1010 nm vs. the pump intensity: the amplitudes of the 1010 nm data at the signal maxima (A1) and at 1.5 ps (A2), the maximum amplitude at 975 nm (A3). The dashed lines are the linear fits. The insert shows the same data at 975 nm, A3, but plotted vs. the square root of the pump intensity. The solid line is the linear fit. (b) Schematic description of the dynamical processes of multie excitons. See text for details.
kinetic scheme depicted in figure 9(b), we can obtain the following rate equations:

\[
\frac{dn_{E_1}(t)}{dt} = G(t) - \frac{1}{2} \gamma n_{E_1}^2(t) - k_{1g} n_{E_1}(t) - \alpha n_{E_1}^2(t) + \beta n_{xx}(t) \tag{9a}
\]

\[
\frac{dn_{E_2}(t)}{dt} = \alpha n_{E_1}^2(t) - \beta n_{xx}(t) \tag{9b}
\]

where \(n_{xx}(t)\) is the population of biexcitons, \(\alpha\) and \(\beta\) are the rates for biexciton formation and dissociation, respectively, \(\gamma\) is the nonlinear annihilation rate and \(k_{1g}\) is the rate of exciton relaxation to the ground state. When \(\gamma, \alpha, \beta\) are significantly greater than \(k_{1g}\), the quasi-stationary solutions of the equations (9a) and (b) give

\[
n_{E_1}(0) \approx \sqrt{\frac{2}{\gamma} G(t_{\text{max}})} \quad (10a)
\]

\[
n_{xx}(0) \approx \frac{2\alpha}{\gamma \beta} G(t_{\text{max}}). \quad (10b)
\]

According to equations (10a) and (b), the TA signal probed at the biexciton band should be linearly dependent on the intensity of the excitation pulses, while the data obtained at the \(E_1\) excitonic transition will scale linearly with the square root of the intensity. The intensity dependence described by equations (10a) and (b) is indeed consistent with the experimental results shown in figure 9(a). This consistency strongly supports the assignment of the IA band at 1010 nm to the transition from exciton to biexciton.

While the IA signal observed at delay time > 500 fs in the kinetic profile detected at 1010 nm can be straightforwardly attributed to the transition from exciton to biexciton, the origin of its initial IT part is unknown. One possibility is the stimulated emission from the biexcitons \([47]\), which should occur at the same frequency as the photoinduced absorption, corresponding to the transition from the biexciton to the exciton states. This attribution, if correct, can also explain the same intensity dependence observed for both the initial IT maximum and the IA signal at 1.5 ps of the kinetics at 1010 nm (see figure 9(a)). From the peak positions of the IA band of biexciton and its corresponding IT band of excitons, one can further determine the \(E_{xx}\) value. Although the (8,3) and (6,5) tubes are excited simultaneously by our pump pulses, the IA band originating from the (8,3) may be hidden due the superposition of the IT band of the (6,5) tube. We thus tentatively attribute the IA band peaking at 1010 nm to the (6,5) tube, and a binding energy of 44 meV is obtained. This result is fairly close to the predicted value for this tube, ~52 meV \([43]\). Further detailed study for unambiguous identification of biexcitons in selected nanotube types are currently in progress and the results will be reported elsewhere.

4. Conclusions

Application of femtosecond fluorescence up-conversion and frequency-resolved femtosecond transient absorption to a micelle-dispersed SWNT preparation reveals unique spectroscopic signatures of specific tube types (9,5), (6,5) and (8,3), by optical excitation of their lowest and second exciton states. We demonstrate that selective detection of the spectroscopic response and dynamics associated with a desired nanotube species is possible, even though the sample used contains a mixture of many types of metallic and semiconducting nanotubes. Analysis of the temporal and intensity profiles of the signals enables us to unambiguously identify the predominant dynamical process as a remarkable manifestation of exciton–exciton annihilation. Our observations provide strong experimental evidence that the elementary excitations in individual semiconducting nanotubes are excitons. After this paper was completed a paper by Heinz and coworkers appeared that provides strong evidence for the bound nature of excitons in semiconducting SWNTs \([48]\). Transient absorption experiments with resonant excitation of the lowest electronic transition of selected nanotubes further enable us to obtain evidence for biexciton formation in semiconductor SWNT.

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References

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