

Excited-state carrier lifetime in single-walled carbon nanotubes

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We measured the near-infrared photoluminescence decay time in several different-chirality single-walled carbon nanotubes by time-resolved picosecond luminescence spectroscopy. Together with the results of resonant pump-and-probe spectroscopy this leads to a carrier lifetime in the first excited state of semiconducting nanotubes exceeding 30 ps, which is one order of magnitude larger than the carrier dynamics observed in nanotube bundles. Our findings show that the absence of photoluminescence in nanotube bundles is due to a tunneling of the free carriers from semiconducting into metallic nanotubes.

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Optical techniques are powerful methods used to study the electronic band structure of materials away from the Fermi level. Photoluminescence and excitation spectroscopy yield information on the electronic energies and the symmetries of the states. The dynamics of the excited carriers and their recombination is studied by time-resolved measurements. One-dimensional systems like single-walled carbon nanotubes are again special in that they are expected to have particularly intense and strongly structured emission and absorption spectra, because of their square-root-like singularities in the electronic density of states. In contrast to this expectation, however, as grown samples of nanotubes—which occur in bundles of 50–100 individual tubes—did not show photoluminescence. Moreover, their absorption spectra are broad and unstructured.¹

Large progress in the spectroscopy of carbon nanotubes was made when O’Connell *et al.*² reported that photoluminescence and narrow optical absorption peaks could be observed in carbon nanotubes if the originally bundled tubes were isolated in micelles.^{3–5} While the broadening of the optical absorption spectra in bundled nanotubes is due to the intertube electronic dispersion perpendicular to the tube axis,⁶ the absence of photoluminescence in bundles remained unclear. It was suggested that the photoluminescence is quenched by the presence of metallic tubes; although the physical mechanism for the quenching remained unelucidated.² For the understanding of these processes, it thus became essential to determine the radiative lifetime in isolated single-walled carbon nanotubes.

Here we report the relaxation times of photoluminescence of isolated semiconducting nanotubes tuned into several distinct chiral indices. The observed decay times (≈ 30 ps) are more than ten times longer than in nanotube bundles. The much more rapid quenching in bundled tubes is explained by tunneling of the free carriers into metallic tubes. Resonant pump-and-probe experiments confirmed that our decay times correspond to a minimum of ≈ 30 ps for the lifetime of carriers in the excited state.⁷ Combined with the rapid depopu-

lation of the higher excited states our findings suggest the application of individual carbon nanotubes in optoelectronics such as light-emitting nanodevices or even four-level lasers.

The dynamics of photocarriers in single-walled carbon nanotubes bundles was studied by Hertel *et al.*^{8,9} with time-resolved photoemission spectroscopy to probe metallic nanotubes. They found that the carriers in metallic tubes first relax to the Fermi energy by electron-electron scattering within 10–200 fs. The relaxation time depends strongly on the energy of the electrons. This process is followed by a much slower (several picoseconds) cooling of the electron gas by electron-phonon interaction. Pump-and-probe optical spectroscopy by Lauret *et al.*¹⁰ showed a depopulation of the second van Hove singularity E_{22} in semiconducting tubes within 130 fs. In contrast, the valence and conduction band were depopulated only after 1 ps.

More recently, an unusually large radiative lifetime of excited-state carriers was suggested by Wang *et al.*¹² They based their indirect estimate of $\tau_{rad} \approx 110$ ns on the determination of the quantum efficiency of nanotubes, which in turn is given by the theoretical absorption coefficient of a nanotube and a number of assumptions about the experimental setup and the surfactant used; their result still awaits confirmation from direct experiment. Ostojic *et al.*⁷ reported in pump-probe transmission spectroscopy of isolated nanotubes a fast and a slow component, the latter (5–20 ps) appearing only under resonant excitation, which they interpreted as due to interband carrier recombination. They also investigated a curious pH dependence of their fast decay component; the pH value, however, did not have an influence on the slower intraband component, a finding that we confirm in the experiments reported here.

The samples used in the present study were isolated nanotubes coated by a surfactant layer. The preparation of the isolated tubes from HiPco material was described in detail in Ref. 2. Time-resolved photoluminescence was excited at 1.7 eV by spectrally narrow (≈ 1 meV) ps pulses of a Ti:sapphire laser. The luminescence was dispersed by a 0.35 m

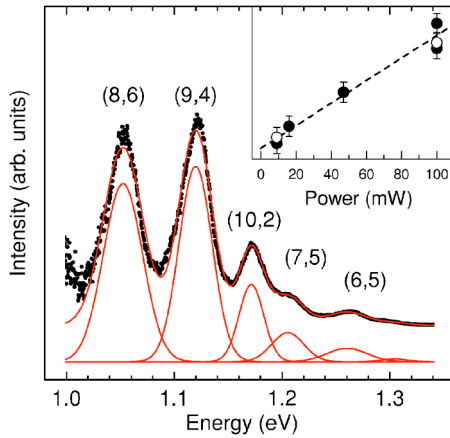


FIG. 1. (Color online) Photoluminescence of single-walled carbon nanotubes excited with 1.70 eV (728 nm) excitation energy. Black dots are the measured spectra; red lines show the fit and the decomposition into single peaks (shifted vertically for clarity). The (n_1, n_2) assignment of the luminescence peaks was taken from Bachilo *et al.* (Ref. 11). The inset shows the dependence of the luminescence intensity for the (9,4) nanotube on excitation intensity. Filled dots are for pulsed excitation; open dots for cw excitation. The two black dots at 100 mW excitation power correspond to the intensity measured before and after the time-resolved experiments.

subtractive double-grating monochromator and detected by a multichannel plate multiplier with an S1 cathode in photo-counting mode. The system response with a full width at half maximum of ≈ 40 ps was taken into account in the analysis of the transients using Fourier deconvolution techniques. The integrated photoluminescence spectra were corrected for the sensitivity of the experimental setup. Our samples were stored in sealed containers; during the experiment the sample was exposed to air, and we noticed a slight decrease in luminescence intensity ($\approx 20\%$) throughout the experiment (see inset of Fig. 1). This may be related to a sidewall protonation as recently described by Strano *et al.*¹³ The measured decay times were unaffected by the exposure, confirming the results in Ref. 7.

Figure 1 shows the time-integrated photoluminescence of five semiconducting nanotubes, which were excited at 1.70 eV laser energy. The photoluminescence intensity increased linearly with increasing laser power as can be seen in the inset. The large width of the luminescence peaks in Fig. 1 is due to the poor energetic resolution (≈ 30 meV) of our experimental setup. We assigned the peaks in the spectra to (n_1, n_2) nanotubes as suggested by Bachilo *et al.*,¹¹ an assignment recently confirmed independently and extended to many more chiral indices by Telg *et al.*¹⁴

The photons are absorbed into the second van Hove singularity in the (8,6), (9,4), and (10,2) nanotube. The situation is different for the (7,5) and the (6,5) nanotube detected in Fig. 1, since for those tubes the energy of the incoming light is below the second van Hove singularity.^{11,15} Instead we excite into higher states of the E_{11} band, i.e., the carriers only relax within the lowest valence and conduction band. This single-electron view of absorption into E_{11} and E_{22} does not

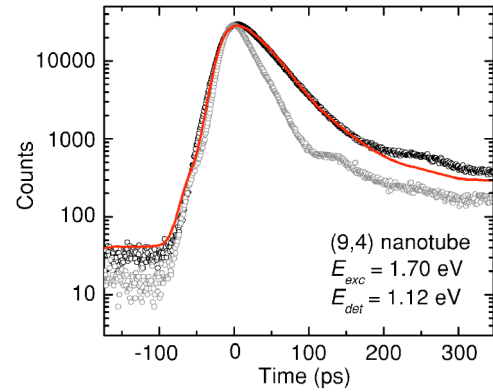


FIG. 2. (Color online) Time-resolved photoluminescence measured at 1.12 eV with laser excitation at 1.70 eV. The luminescence energy corresponds to E_{11} recombination in the (9,4) nanotube. The photoluminescence is shown by the black dots, the system response to the exciting laser pulse by gray dots. The red line is a fitted convolution of the system response (40 ps) and a luminescence signal with a decay time of 28 ps.

consider many-electron effects, which are currently discussed controversially.^{16–18}

We measured the time-resolved luminescence at the maxima of the nanotube signals. In Fig. 2 we present the transient of the (9,4) nanotubes. A decay time of (28 ± 2) ps was obtained from the deconvolution of the luminescence and the laser signal. The decay times for the other tubes are summarized in Table I. All of them are very similar; in particular, within our error they do not systematically depend on the nanotube diameter d or the chiral angle Θ . The assignment of Ref. 11 was recently confirmed and extended to many more chiral indices by Telg *et al.*¹⁴

The photoluminescence of the (7,5) and (6,5) tubes, where the absorption and emission of the photon takes place within the same electronic bands, has a similar dynamics as in the three other tubes where the absorption is into a higher state. This shows that the measured time scales are indeed limited by the last step, i.e., the recombination of the electron-hole pair at the nanotube band gap. We confirmed that the decay times are not determined by the relaxation

TABLE I. Diameter d , chiral angle Θ , E_{11} photon energy, and measured photoluminescence decay times τ of the five (n_1, n_2) nanotubes observed in the photoluminescence measurements. Note that the three tubes with the highest photoluminescence intensity [(8,6), (9,4), and (10,2)] form a series with slightly decreasing diameters. At the same time the chiral angle varies from close to the armchair direction ($\Theta = 30^\circ$) to the zigzag direction (0°).

(n_1, n_2)	d (nm)	Θ ($^\circ$)	E_{11} (eV)	τ (ps)
(8,6)	0.95	25.3	1.05	25
(9,4)	0.90	17.5	1.12	28
(10,2)	0.87	8.9	1.17	22
(7,5)	0.82	24.5	1.20	29
(6,5)	0.75	27.0	1.26	30

from higher states by pump-and-probe experiments exciting resonantly into E_{11} where we found similar decay times (see also Ref. 7). The relaxation from the first excited state in isolated semiconducting nanotubes is thus a striking factor of ten slower than in bundled tubes.

The difference to decay time measurements in bundles of nanotubes can only be explained by tube-tube interactions, because intertube processes such as, e.g., multiphonon emission or nonradiative recombination by defects, yield the same time scale for isolated and bundled tubes. In bundled tubes the free carriers can tunnel into metallic tubes or into semiconducting nanotubes with smaller energy gaps. If they encounter a metallic tube the electron-hole pair recombines nonradiatively by electron-electron scattering. In semiconducting tubes with very small band gaps (≈ 0.2 eV), on the other hand, optical phonon emission will be another nonradiative decay channel. Since the tunneling rate is ten times higher than the recombination probability, bundles of nanotubes do not emit photons.

Ab initio calculations by Reich *et al.* showed that the energy gap in bundled semiconducting nanotubes is reduced by the intertube electronic dispersion perpendicular to the z axis. At the same time, the tube-tube interaction strongly broadens the optical absorption spectra.⁶ Thus even for bundles composed entirely of semiconducting tubes the optical excitation profile and the carrier relaxation will be different from the isolated tube. The transfer of free carriers from semiconducting into metallic tubes in a bundle may somewhat influence the analysis of the slow component in the time-resolved photoemission experiments,^{8,9} since additional carriers are injected into the metallic tubes on a picosecond time scale. Indeed the photoelectron spectrum below ($E - E_F = 0.2$ eV) between 0.5 and 5.0 ps in Ref. 8 is very well described by a Fermi-Dirac distribution at elevated temperatures. Around 0.5 eV, however, a noticeably higher intensity is observed in the spectra than expected from the Fermi-Dirac distribution. This energy range is in good agreement with the energy of the lowest conduction bands in single-walled nanotubes.¹⁵ The additional carriers from semiconducting nanotubes would also explain the systematic deviation of the electronic temperature at longer time scales and increase the electron-phonon interaction parameter measured by Hertel *et al.*^{8,9}

A 30-ps-long decay time in the first van Hove singularity implies that the intrinsic width of the photoluminescence maxima in individual semiconducting nanotubes is extremely small, below 0.1 meV. Up to now, such narrow luminescence has not been reported in single-walled carbon nanotubes. The width of the single lines in the original photoluminescence experiment by O'Connell *et al.*² was between 25 and 50 meV. Although there is little direct evidence for a breaking of the tubes, the separation of bundles into individual tubes by the ultrasonication process may produce an inhomogeneous distribution, e.g., in tube lengths or

in surfactant coverage.¹⁹ The luminescence of unprocessed tubes reported by Lefebvre *et al.*³ was much narrower (between 8 and 13 meV). This is still orders of magnitude larger than expected from a lifetime of at least 30 ps. However, improvement of the preparation methods will surely further decrease the widths of the peaks.

After having discussed the dynamics of the first valence and conduction bands, let us turn briefly to the higher states, i.e., the E_{22} state in which the photons were absorbed in our time-resolved measurements. The electron-hole pairs created in the second valence and conduction band relax to the band gap, where they recombine radiatively. The rise of the photoluminescence signal was on the order of or shorter than our time resolution. Nevertheless, since this relaxation takes place between different electronic states within the same tube, the dynamics are expected to be similar for isolated and bundled nanotubes. At the electronic energies excited in our experiment (≈ 0.85 eV for symmetric valence and conduction bands) electrons in metallic nanotubes relax within 10 fs.⁹ In semiconducting tubes, on the other hand, the depopulation of the E_{22} state takes 130 fs and the population of the lowest state less than 200 fs.¹⁰ These relaxation rates are also in very good agreement with the broadening of the electronic states in resonant Raman measurements on isolated and bundled tubes.^{14,20-24} The reported broadening parameters range from 8 to 40 meV corresponding to lifetimes on the order of $\approx 10-100$ fs.

In summary, we studied the excited states in several chirality-selected single-walled carbon nanotubes by direct time-resolved photoluminescence spectroscopy. We conclude that the radiative lifetime of the carriers in the first excited state of these tubes is ≈ 30 ps or larger. The decay times are independent of the nanotube diameter (between 0.75 and 0.95 nm) and chirality ($9-27^\circ$); our results are consistent with resonant pump-and-probe measurements. The carrier relaxation time in individual tubes is thus at least ten times larger than in nanotube bundles, where the carriers tunnel into metallic or small band-gap semiconducting tubes and subsequently recombine nonradiatively. We could not confirm the very long radiative lifetimes reported by Wang *et al.*, but showed results consistent with those of Ostojic *et al.* The relaxation to the first excited states after the absorption of a photon into the higher valence and conduction bands takes place on a much shorter time scale and was beyond the resolution in our experiment. The combination of a short lifetime of the E_{22} transition with the long recombination time in the E_{11} states make semiconducting carbon nanotubes very attractive for applications in optoelectronics.

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