Mono- and Biexponential Luminescence Decays of Individual Single-Walled Carbon Nanotubes

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We have studied the exciton recombination dynamics of individual (6,4) and (6,5) single-walled carbon nanotubes embedded in aqueous gels or deposited on glass surfaces. CoMoCat nanotubes systematically display short monoexponential photoluminescence (PL) decays presumably due to defects introduced during their synthesis. In contrast HiPco nanotubes can either display mono- or biexponential PL decays depending on the environmental conditions. Transition from bi- to monoexponential decays can be reproduced by a simple three level model taking into account defect-dependent nonradiative decay mechanisms.

The photoluminescence (PL) properties of semiconducting single walled carbon nanotubes (SWNTs) have attracted much attention over the last years. These properties strongly depend on the structure of each nanotube but also on extrinsic factors resulting for instance from synthesis or environmental factors. As a result, PL studies performed on ensemble of SWNTs are affected by inhomogeneities that hinder the development of a detailed understanding of the underlying mechanisms. Experiments on individual SWNTs remove part of this heterogeneity by allowing description of the characteristics of each SWNT in its particular environment. Comparisons between values of a physical parameter extracted from different experimental reports are however difficult because, generally, the studied samples differ by synthesis methods or preparation procedures. For example PL decays performed on individual (6,4) and (6,5) nanotubes by different groups have resulted in distinct behaviors, differing by synthesis methods or preparation procedures. For observations, single-molecule wide-field and confocal PL microscopes were used to image SWNTs excited with a continuous wave laser. The SWNTs were immobilized in aqueous agarose gels (5 wt %) or spin-coated on surfaces. SWNTs concentration was kept well below 1 µm⁻³ such that bright individual nanotubes could be optically resolved. The PL of these bright tubes was sent to a spectrometer for further spectral identifications of individual (6,4) or (6,5) nanotubes. Typically, isolated SWNTs feature narrow PL lines from their bright excitonic state E₁₁, with full width at half-maximum (fwhm) in the range of ~17−22 nm. Following identification of these bright individual nanotubes, the excitation modality was switched to pulsed excitation (~150-fs pulses, 76-MHz repetition rate) using either a Ti:Sa oscillator (for excitation of a vibrational band of the first optical transition at ~800 nm or ~810 nm) or an optical parametric oscillator (for resonant excitation at the second optical transition at ~570 nm). The PL decays were then recorded using conventional time-correlated single-photon counting (TCSPC) setups. Narrow bandpass filters (fwhm = 20/10 nm) centered at the peak wavelength of the PL in front of the avalanche photo diode were used to suppress spurious spectral contributions like, e.g., scattered laser light. The decays were obtained in 10 min integration time with low excitation intensities ≤10¹² photons/(pulse·cm²) to ensure that less than one photon is absorbed per pulse knowing the resonant absorption cross-section of the SWNTs (~10⁻¹⁷ cm² per carbon atom). For data fitting we record the instrumental response function (IRF) of the TCSPC setup at a wavelength close to the peak emission line (~980 nm for (6,5) and ~880 nm for (6,4)) of the nanotubes (see Supporting Information). This is an important point since the penetration depth of light into the photoactive Si layer of avalanche photodiodes is wavelength dependent and measuring the IRF at the excitation wavelength (close to E₂₂) would lead to an erroneous additional decay component as reported for CoMoCat tubes.

Figure 1a shows two representative luminescence decays of (6,5) SWNTs synthesized by HiPco and CoMoCat methods studied in agarose gels. The two recorded PL transients are strikingly different. A long time component is observed in the HiPco nanotube, while it is completely absent in the CoMoCat one. A least-squares fitting algorithm was used to extract the...
decay times and decay dynamics from the transients. The weighted residuals and the corresponding “reduced chi-squared” parameter $\chi^2$ (see caption of Figure 1) are a measure for the quality of the fits and are used to distinguish mono- and biexponential decay behaviors. Data fitting of the PL decays reveals that CoMoCat SWNTs studied in aqueous gels systematically display monoeXponential behaviors as previously reported on glass surfaces (Figure 1b). In contrast, bright HiPco SWNTs recorded in aqueous gels systematically display biexponential decays as previously reported (Figure 1c). Parts a and b of Figure 2 show that the long time component $\tau_{long}$ of the PL decays ranges from 0.4 to 2 ns while the short time component $\tau$ ranges from 35 to 60 ps. The latter is significantly larger than the decay time of CoMoCat nanotubes ($\tau = 10\sim 30$ ps, Figure 2d).

To investigate the influence of the nanotube environments, PL decays from HiPco nanotubes suspended in DOC and spincoated onto bare coverslips were also measured. In this case, the PL decays bridge the two behaviors obtained for CoMoCat and HiPco nanotubes in aqueous gels (parts a and c of Figure 2). Indeed, half of the SWNTs studied on glass surfaces displays a monoeXponential behavior with decay times ranging from 10 to 40 ps while the other half displays biexponential decays with $\tau$ ranging from $\sim 30\sim 50$ ps and $\tau_{long}$ centered at $\sim 450$ ps. This broad range of behavior clearly reflects the heterogeneous environment of the nanotubes lying on glass coverslips. Interestingly, the long time component fractional yield $A_{long}$ decreases with $\tau_{long}$ (Figure 2e), and when the fast components of biexponential fits are shorter than $\sim 35$ ps, experimental decays are in general satisfactorily fitted by monoeXponential curves.

We now consider (6,4) HiPCo nanotubes embedded in agarose gel or deposited on glass. In contrast to (6,5) nanotubes, most of the recorded decays are monoeXponential. Indeed, only few nanotubes in gels display biexponential decays (4 over 42 studied tubes) and none on surface. Figure 3 shows that monoeXponential decays in agarose gel vary between 30 and 80 ps with an average value of 52 ps. On glass the distribution is shifted toward smaller values with an average decay time of 23 ps. This latter distribution is similar to that reported for (6,4) CoMoCat nanotubes on surfaces.

The origin of the biexponential decay was previously attributed to the presence of two closely lying dark (D) and bright (B) excitonic states (see Figure 4a) with recombination rates $\Gamma_D$ (purely nonradiative) and $\Gamma_B$ (mainly nonradiative). Weak PL yields of the bright state (limited to a few percent) are due to nonradiative relaxation pathways (occurring in tens of picoseconds) which are much faster than the radiative recombination time (in the nanoseconds range). Thermalization
between dark and bright states can be promoted through coupling to acoustic phonon modes whose energies match the dark—bright excitonic splitting $\Delta E \approx 5$ meV.\textsuperscript{20,21} The transition rates for downhill and uphill processes are $\gamma_i = \gamma_0(n + 1)$ and $\gamma_i = \gamma_0 n$, respectively, where $\gamma_0$ is the zero temperature bright to dark transition rate\textsuperscript{22} and $n$ is the Bose–Einstein phonon number.\textsuperscript{10}

Two mechanisms have been proposed to interpret the exciton fast nonradiative decay process in nanotubes.\textsuperscript{12} The first one involves an enhanced multiphonon decay of localized excitons in potential fluctuations due to the local environment of the nanotubes. The second one is a phonon-assisted indirect exciton ionization process due to the presence of the free carriers which can create a phonon and an intraband electron–hole pair. Importantly, higher defect densities and local perturbations along the nanotubes make both mechanisms more efficient. By solving the kinetic equations, we derived the dynamics of the bright excitonic state population $P_B(t)$ after excitation at $t = 0$ (see Supporting Information). The average biexponential behavior of nearly pristine nanotubes (e.g., nanotubes in gels in Figure 2a) can be reproduced assuming $\Gamma_{\text{B}} = 20$ ns$^{-1}$, $\Gamma_{\text{D}} = 2$ ns$^{-1}$, $\gamma_0 = 0.05$ ns$^{-1}$, and an equal population of the bright and dark excitonic states at $t = 0$: one obtains $t = 50$ ps and $t_l = 450$ ps and a long time component fractional yield $A_{\text{long}} = 11\%$. The small value of $\gamma_0$, corresponding to a bright-to-dark transition probability $\sim 400$ times weaker than that of the bright excitonic state recombination, clearly shows that branching to dark states is not the main cause for low PL quantum yield (for the present materials) in agreement with ref 12.

Typical values for the rates $\gamma_i$ and $\gamma_i$ are orders of magnitude smaller than the nonradiative decay rates $\Gamma_{\text{B}}$ and $\Gamma_{\text{D}}$. Therefore the measured decay times $t$ and $t_{\text{long}}$ are primarily determined by these rates. The situation is different for the fractional amplitude $A_{\text{long}}$. Its magnitude is mainly determined by $\gamma_0$ and to a lesser extent also by the initial population of the bright and dark states (see Supporting Information).

For nanotubes subject to defects or environmental effects, an additional extrinsic fast nonradiative decay rate, $\Gamma_{\text{B}}$, should be added to $\Gamma_{\text{B}}$ and $\Gamma_{\text{D}}$. Parts b and c of Figure 4 shows the theoretical evolution of $t_{\text{long}}$ as a function of $t$ and that of $A_{\text{long}}$ as a function of $t_{\text{long}}$ when $\Gamma_{\text{B}}$ varies from 0 to $30$ ns$^{-1}$. The hatched areas represent the domains where $t$ and $t_{\text{long}}$ are experimentally indistinguishable and where $A_{\text{long}}$ is extremely small. In these cases, the experimental PL decays are well reproduced with a monoeXponential curve. For example, for a typical rate of $12$ $\Gamma_{\text{B}} = 20$ ns$^{-1}$ added to the previous values of $\Gamma_{\text{B}}$ and $\Gamma_{\text{D}}$, the exciton recombination dynamics becomes fast and monoeXponential with a decay time $t = 25$ ps in agreement with our experimental observation.

In Figure 4 and from our analysis we identify the involved dark state as the even parity $E_{1,1} \approx 5$ meV below the bright state $E_{1,1}$. In addition, there are two degenerate finite momentum states ($K$ and $K'$-momentum excitons) with $\Delta E \approx 36$ meV for the (6,5) SWNT above the bright one.\textsuperscript{23,24} Direct optical excitation of this state is forbidden, but it can be populated via a phonon sideband located at ($-E_{1,1} + 200$ meV $\approx E_{1,1} + 170$ meV).\textsuperscript{23,24} Hertel et al. found that after resonant $E_{1,1}$ excitation a large fraction of the $E_{1,1}$ excitons decay into this $K$ momentum state.\textsuperscript{25} According to our model, a large initial population of the dark state is a prerequisite for a detectable fractional amplitude $A_{\text{long}}$ and thus for observing the biexponential decay. To test if these higher-lying dark states influence the PL dynamic significantly, we recorded PL decays at two different excitation wavelengths. One was chosen to be close to the exciton–phonon state at 834 nm and the other well below at 920 nm. Interestingly, switching between the two excitation wavelengths does not change the decay dynamics substantially: only small changes in the fractional amplitudes and decay times have been observed (data not shown). This would suggest that the K-momentum exciton is not significantly involved in the biexponential decay.

Luminescence decays of (6,4) SWNTs with large decay times ($t > 50$ ps) that do not show biexponential decays cannot be reproduced by only modifying the extrinsic rate $\Gamma_{\text{B}}$ and keeping the other parameters the same as for (6,5) SWNTs. The experimental observation can be explained within our three-level model by a reduced $\gamma_1$ between the two states in the case of (6,4) nanotubes. This would be expected due to a larger bright–dark splitting energy $\Delta E$ that was found to scale inversely with the diameter squared.\textsuperscript{27} Keeping all other parameters constant, a small increase in $\Delta E$ based on the different nanotube diameters (0.74 vs 0.68 nm) would lead to a reduction of $A_{\text{long}}$ by a factor of $\sim 2$, and thus the long time component of the decays would be close to the detection limit.

In this work, we have identified the synthesis methods and environmental conditions leading to the observation of monor biexponential PL decays in individual small diameter SWNTs. A simple model based on a three-level system reproduces the experimental observations taking into account the predominant defect dependent nonradiative decay mechanisms proposed recently.\textsuperscript{12} This work emphasizes the importance of SWNTs processing and observation conditions for obtaining high quality luminescent nanotubes.

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Supporting Information Available: Three-level model describing the biexponential decay of HiPco SWNTs, and figures depicting amplitude factors, initial bright state population $N$ on the measured decay times and fractional yield amplitudes, transition rates vs decay times, and influence of the bright–dark splitting energy on amplitude. This material is available free of charge via the Internet at http://pubs.acs.org.
References and Notes

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