Temperature behavior of the photoluminescence decay of semiconducting carbon nanotubes: The effective lifetime

D. Karaiskaj,1,* A. Mascarenhas,1 Jong Hyun Choi,2 Rachel Graff,2 and Michael S. Strano2
1Center for Basic Science, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401, USA
2Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

The temperature dependence of the photoluminescence decay of excitons in single-walled carbon nanotubes was measured for two nanotube species, (7,6) and (7,5), representative of the two nanotube \( (n-m) \mod 3 \) families. A monotonic increase of the photoluminescence lifetime with decreasing temperature is observed. The external strain induced by lowering the temperature below the freezing point of the solution leads to an overall lowering of the photoluminescence lifetime. This effect indicates that the measured lifetime is defined by the intrinsic electronic properties of carbon nanotubes and could be understood as an exchange interaction between bright and dark excitonic states. We find the lifetime to vary between 223 and 319 ps between 290 and 5 K, obtained by a multieponential fit, well in agreement with previous experiments.

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Determining the effective excitonic lifetime of single-walled carbon nanotubes (SWCNTs) experimentally is not only important for their application in optoelectronics, but it is also an important test in the fundamental understanding of the electronic properties of nanotubes. Although the first experiments on the optical properties of semiconducting carbon nanotubes were interpreted in the context of the noninteracting electron model, it has now become clear that excitonic effects and many-body interactions play an important role. The photoluminescence (PL) quantum yield which is thought to be in the order of \( 10^{-3} – 10^{-4} \) could become a band carrier relaxation. The first PL decay experiments at component in the order of only 5–20 ps, attributed to intermechanism. In this Brief Report, we examine the temperature dependence of the photoluminescence decay and explore some features of the complex dynamics observed in ensemble-averaged pump-probe and time-resolved PL measurements could be attributed to averaging over species with a wide range of lifetimes. In order to explain the low quantum yield and the variety of decay times observed, several different mechanisms have been proposed, such as the existence of bundles and excitonic transfer to metallic tubes leading to nonradiative recombination, exciton-exciton annihilation, deferent densities of nonradiative traps due to defects, and the existence of a much lower lying forbidden state leading to so-called dark excitons.

Different concentrations of localized trap states can account for the variations in the nonradiative exciton decay rates; however, it still remains unclear what the lifetime of carbon nanotubes is, which is solely due to their intrinsic electronic properties, the so-called effective lifetime. Moreover, one of the most promising applications of SWCNTs is their use as biological sensors, and therefore, it is important to understand the effect of external strain on the nanotubes’ excitonic effective lifetime. Recent \textit{ab initio} calculations in combination with symmetry analysis based on group theory predict that the lowest exciton state is dark for any zigzag and chiral semiconducting SWCNT. The dark exciton states originate from a set of interband transitions which are optically inactive and lower in energy than the ones that give rise to bright excitons. These dark excitonic states further enhance the effective radiative lifetime of excited nanotubes, and this is thought to be fundamental in understanding the
The low efficiency of light emission in SWCNT. The overall temperature dependence of the effective radiative lifetime of carbon nanotubes shows a continuous rapid increase with decreasing temperature, in contrast to the behavior of the exciton decay observed in conventional semiconductors, which would be characterized by an increase of the PL lifetime with temperature.

Using a method similar to one previously reported in Ref. 4, the as-produced HiPco SWCNTs were suspended in aqueous (D$_2$O) sodium dodecyl sulfate (SDS). In order to lower the freezing temperature, the aqueous suspension of SWCNTs was mixed with glycerol 1:2 v/v and mounted inside a variable temperature cryostat. For one set of PL decay measurements performed at lower repetition rate, the photoexcitation at 655 nm or any other desired wavelength was provided by an optical parametric amplifier pumped by the output of a mode-locked titanium:sapphire laser (Coherent Mira 900, 76 MHz repetition rate) with a regenerative amplifier (Coherent Rega 9000). The final laser output consisted of a 250 kHz pulse train with a pulse width of 200 fs. For the second set of measurements performed at a higher repetition rate, the excitation pulses were produced by a homebuilt optical parametric oscillator. The repetition rate was reduced from 76 to 15.2 MHz using an external pulse picker (Conoptics). The PL decay curves were measured using the time-correlated single-photon counting technique. The PL signal was detected with a grating spectrometer (SPEX 270 M) equipped with a liquid-nitrogen-cooled and infrared-sensitive photomultiplier tube (Hamamatsu R5509). In order to identify the nanotube species present in the solution, room-temperature PL excitation spectra were taken.

The photoluminescence decay curves from the SDS nanotube solution mixture with glycerol were recorded, starting at 297 K and gradually cooling down to slightly above liquid-helium temperature (5 K). The decay curves for several selected temperatures for the two nanotube species are shown in Fig. 1. The 15.2 MHz repetition rate laser system was used to excite the tubes in order to enhance the signal-to-noise ratio. A moderate increase of the PL decay with temperature could be observed in agreement with theoretical calculations and previous experimental observations. The lifetime increase is monotonic all the way to the lowest measured temperature of 5 K for both nanotube species, and only one exponential decay component could be observed to change with temperature. In order to explore possible longer decay components that would change with temperature, data at a large window of about 100 ns were collected using the 250 kHz repetition rate laser system. The PL decay for the two extreme temperatures of 297 and 5 K shown in Fig. 2 indicates no change of the PL decay with temperature beyond the initial 10 ns. In order to benefit from the larger
The photoluminescence decay of the carbon nanotubes species (7,6) (a) and (7,5) (b) in SDS solution mixture with glycerol at 5 and 290 K. The lines show the best fit using a double-exponential decay model convoluted with the measured instrumental response shown in Fig. 1.

The data were fitted using a simple double-exponential decay:

\[ y(t) = y_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right), \]  

where \( \tau_1 \) and \( \tau_2 \) are the PL decay constants. The double-exponential model decay function was convoluted iteratively via least squares with the measured instrumental response, followed by a comparison with the measured data as suggested in Ref. 17. More than two exponential components were attempted; however, the fitting procedure indicated that additional exponential decay components were redundant. In Fig. 3, the fits for the two extreme temperatures are shown for both nanotube species. The dominating decay constant \( \tau_1 \) was in the order of a few hundred picoseconds and showed a moderate change with temperature. The values obtained by the fitting procedure are listed in Table I. We obtained a decay time of 213.6 ps at 290 K and 223.5 ps at 250 K for the (7,6) and (7,5) nanotube species, respectively, which are similar to values previously reported in the literature. Moreover, the PL decay values at 290 K reported in this Brief Report agree quite well with the larger decay time of 200 ps reported in the single-nanotube study. In addition, a longer temperature independent component \( \tau_2 \) of 2293 and 1895 ps for the (7,5) and (7,6) nanotube species, respectively, was observed. This less dominant decay component is more pronounced at lower temperatures with a weight of 6%–7% and becomes rapidly weaker at higher temperatures, with a contribution of only about 2%. The contribution of a few percent and the rapid reduction of the contribution with temperature indicate that this component originates most likely from excitons trapped at defects and impurities in the nanotubes, which can be quickly thermally dissociated.

Recently, we have reported on the energy shift of the photoluminescence transition lines of SWCNTs with temperature. We also observed a substantial narrowing of the linewidths with decreasing temperature in the same type of suspension mixed with glycerol, which persisted beyond the ice phase transition of the solution all the way to 4.2 K and was attributed to the effect of the electron-phonon interaction. The largest line narrowing at low temperature was observed for the (7,6) tube. The full width at half maximum of 30.5 meV at 297 K is reduced to 20.6 meV at 4.2 K. This behavior indicates a very uniformly induced strain by the ice matrix, since random strains have the opposite effect, leading to line broadening.

In Fig. 4, we plot the PL decay time \( \tau_1 \) versus temperature for the two (7,6) and (7,5) nanotube species. A monotonic increase of the decay time with decreasing temperature is observed, as indicated by the solid arrows in Fig. 4. This behavior is quite similar to the one predicted theoretically, in contrast to the behavior of the exciton decay observed in conventional semiconductors which would be characterized by an increase of the PL lifetime with temperature. As a result, we assign this component to the effective radiative lifetime of carbon nanotubes, which is determined solely by its intrinsic electronic properties. The rapid increase of the effective lifetime with decreasing temperature below the temperature range where the ice matrix induces strain on the nanotubes, marked by the dashed arrows in Fig. 4, indicates that the PL decay times are most likely further increased by the external strain. Previous theoretical studies have estimated the splitting between the bright and dark excitonic

**Table I.** The measured photoluminescence decay times for the selected temperatures obtained by the double-exponential fit [Eq. (1)] convoluted with the instrumental response.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(7,6) ( \tau_1 ) (ps)</th>
<th>(7,5) ( \tau_1 ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>282.1</td>
<td>319.6</td>
</tr>
<tr>
<td>50</td>
<td>265.7</td>
<td>302.7</td>
</tr>
<tr>
<td>100</td>
<td>246.9</td>
<td>264.0</td>
</tr>
<tr>
<td>190</td>
<td>223.0</td>
<td>230.2</td>
</tr>
<tr>
<td>220</td>
<td>214.3</td>
<td>226.2</td>
</tr>
<tr>
<td>250</td>
<td>214.4</td>
<td>223.5</td>
</tr>
<tr>
<td>290</td>
<td>213.6</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 4. (Color online) Photoluminescence decay time versus temperature for the two representative nanotube species (7,6) and (7,5), obtained by the monoexponential fit. The solid arrows are guides for the eyes, while the vertical dashed arrows mark the temperature region where the external strain induced by the ice matrix occurs.

increase in the splitting between the dark and bright excitonic states and, as a result, would increase the excitonic radiative lifetime, where the $1/d^2$ dependence would lead to an even stronger effect. As a result, different nanotubes experiencing different amounts of external environmental strain would possibly exhibit different decay times.

In conclusion, we have measured the temperature dependence of the PL decay for two nanotube species belonging to each $(n-m) \bmod 3$ family and observed two decay components. The longer decay time $\tau_2$ was assigned to excitons trapped at defects and impurities, whereas the shorter decay time $\tau_1$, which increases monotonically with decreasing temperature, is thought to be the effective radiative lifetime. Both decay components have been observed at room temperature in previous studies. The $\tau_1$ decay component ranged from 213 to 319 ps between 290 and 5 K, and may be further increased at low temperatures due to the effect of the external strain.

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*Electronic address: denis.karaiskaj@nrel.gov

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