

Diameter dependence of exciton-phonon interaction in individual single-walled carbon nanotubes studied by microphotoluminescence spectroscopy

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We have investigated the diameter dependence of the exciton luminescence linewidth in individual single-walled carbon nanotubes (SWNTs) by means of microphotoluminescence (μ -PL) spectroscopy. The line shapes of μ -PL spectra for single SWNTs suspended on a patterned Si substrate at room temperature can be fitted by single Lorentzian functions. It is found that the μ -PL linewidth depends strongly on the diameter of SWNTs and the exciton-phonon interaction is enhanced with a decrease of the diameter.

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Over the past decade, electronic and optical properties of single-walled carbon nanotubes^{1,2} (SWNTs) have attracted much attention both from the fundamental physics view point and due to the potential applications to opt-electronic devices. The recent discovery of efficient photoluminescence (PL) from isolated semiconducting SWNTs (Refs. 3 and 4) has stimulated considerable efforts in understanding optical properties of SWNTs. The semiconducting SWNTs are one-dimensional (1D) materials with direct-gap band structures.² Because of the extremely strong electron-hole interactions (excitonic effects) in 1D materials,⁵ it has been predicted that their unique optical properties are determined by the dynamics of 1D excitons.⁶⁻¹⁰ Recent experimental results^{11,12} support the excitonic picture of SWNTs. In addition, it has been reported that the electronic structure and the PL energy of SWNTs strongly depend on their diameter (chiral index).^{2,3} However, the diameter dependence of the PL spectral shape of SWNTs is not clear.

The SWNTs samples are usually inhomogeneous systems in the sense that many different species of nanotubes exist: The inhomogeneous broadening and the spectral overlapping of PL spectra cause the complicated PL spectra of SWNTs. It is, therefore, needed to perform PL measurements on single SWNTs¹³⁻¹⁶ for clarifying the optical properties of each SWNT species. Single nanotube spectroscopy provides essential information on the intrinsic excitonic properties of SWNTs, such as exciton-phonon interaction. The exciton-phonon interaction plays an important role to understand the optical properties of SWNT.^{17,18}

In this paper, we have studied PL spectra from spatially isolated single SWNTs (diameter: $d \sim 0.75-1.25$ nm) by means of micro-PL (μ -PL) spectroscopy. The PL spectra of about 180 different single SWNTs suspended on a Si substrate were measured at room temperature. Their spectral shapes can be approximately fitted by single Lorentzian functions. The PL linewidth becomes broad in small diameter SWNTs. Our observation suggests that the exciton-phonon interaction becomes stronger with a decrease of the diameter (i.e., with an increase of the surface curvature). The origin of the PL linewidth broadening of single SWNTs will be discussed.

The samples used in this work were isolated SWNTs synthesized on patterned Si substrates by an alcohol catalytic chemical vapor deposition (ACCCVD) method.^{19,20} The Si substrates were patterned with parallel grooves typically from 300 nm to a few μ m in width and 500 nm in depth using an electron-beam lithography technique. The isolated SWNTs grow from one side toward the opposite side of the groove or hang down toward the bottom of the groove. We prepared several SWNT samples by changing the growth temperature and time. In this work, the single nanotube PL spectroscopy was performed on the sample grown at 750 °C for 30 s. The average number density of isolated SWNTs in the sample is $0.1-1/\mu\text{m}^2$.

Single SWNT PL measurements were carried out at room temperature using a home-built scanning confocal microscope.¹⁶ The SWNT samples mounted on a scanning stage were excited with a continuous-wave He-Ne laser (1.959 eV), and the laser beam was focused on the sample surface through a microscope objective (NA 0.8). The PL signal from SWNTs was spectrally dispersed by a 30 cm spectrometer equipped with a liquid-nitrogen (LN₂)-cooled InGaAs photodiode array (spectral range: 0.78–1.38 eV) or a LN₂-cooled charge coupled device (spectral range: ≥ 1.20 eV). The spectral resolution of our system is less than 0.7 meV. The detector accumulation time was typically between 30 s and 1 min. We also obtained PL images of the luminescent SWNTs on the sample, using a Si avalanche photodiode or an InGaAs photodiode.

Figure 1 shows a typical PL image of isolated semiconducting SWNTs at room temperature. The monitored PL energy range is between 1.18 and 1.38 eV. Several spatially isolated bright spots can be seen in the image. Each bright spot represents the PL signal from a single luminescent SWNT because the PL spectrum obtained just on each bright spot has only a single PL peak, as shown later [Fig. 3(b) and 3(c)]. The spot size estimated from the spatial profiles of the PL intensity is about 500 nm. Here the elongated feature of nanotubes cannot be resolved in our PL images because the SWNTs in this sample have shorter lengths in comparison with the laser spot size.

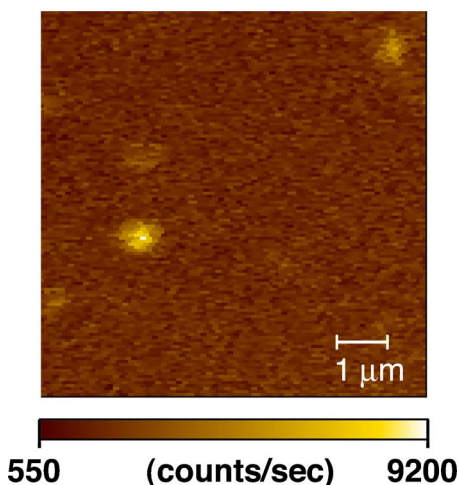


FIG. 1. (Color online) PL image ($7.6 \mu\text{m} \times 7.6 \mu\text{m}$ area) of isolated SWNTs suspended in air on a patterned Si substrate at room temperature.

Figure 2 shows PL spectra obtained from a typical single SWNT [assigned chiral index: (10,5)] at various excitation laser powers. Each spectrum has a single peak located at 1.016 eV. Even in high excitation region above $10 \mu\text{W}$, the PL spectrum shows a single peak without change in the peak energy. The spectrally integrated PL intensity and the linewidth (full width at half maximum, FWHM) are plotted as a function of the excitation laser power in the inset of Fig. 2. In the low power excitation region below $10 \mu\text{W}$, the PL intensity grows almost linearly with the excitation power (as indicated by a solid line), and there is no significant change in the spectral linewidth. In the higher excitation power region ($>10 \mu\text{W}$), on the other hand, both the saturation of the spectrally integrated PL intensity and a small increase in the emission linewidth are observed. The above results show that in the weak excitation region there is no broadening of the

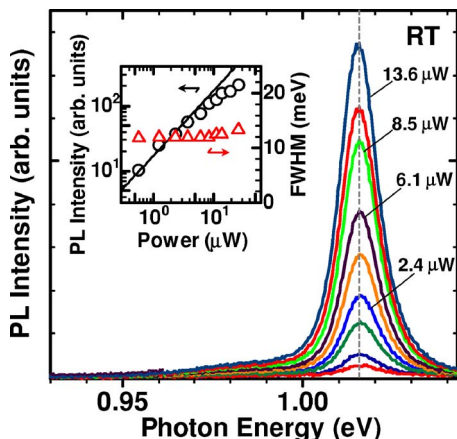


FIG. 2. (Color online) Excitation power dependence of PL spectra of a single SWNT, assigned as a (10,5) nanotube. The inset shows the excitation power dependence of the integrated PL intensity (circles) and the spectral linewidth (FWHM, triangles). Under weak excitation below $10 \mu\text{W}$, the PL intensities show almost linear power dependence as indicated by the solid line and the linewidth shows the constant value.

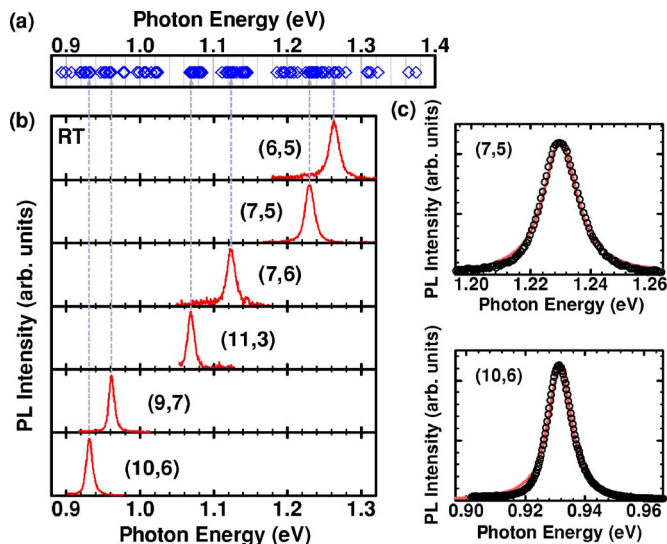


FIG. 3. (Color online) (a) PL peak energy distribution of obtained PL spectra from ~ 180 different isolated SWNTs. (b) PL spectra for several species of single SWNTs at room temperature. SWNTs with higher PL emission energy tend to have a larger spectral linewidth. (c) Typical PL spectra of a relatively small diameter tube [0.83 nm, (7,5)] and a large diameter tube [1.11 nm, (10,6)] in the sample (black circles). Solid red line corresponds to a Lorentzian function.

spectral linewidth due to many-body effects arising from exciton-exciton scattering²¹ or due to temperature rise induced by the laser light. Thus the PL spectral linewidth data were measured with excitation powers less than $10 \mu\text{W}$, in order to discuss the diameter dependence of the PL linewidth.

We obtained PL spectra from about 180 different isolated SWNTs with a variety of chiral indices. Figure 3(a) shows a distribution of the PL peak energies for the single SWNTs (indicated by diamonds). The chiral index assignment for each PL spectrum is based on the previous data of the emission energies ($\sim 10 \text{ meV}$) even within the same chiral index. In Fig. 3(b), we show some of the PL spectra from isolated SWNTs with various emission energies. Only a single sharp peak can be seen in each spectrum. This is certain evidence that the PL comes from a single SWNT. In addition, the PL linewidth tends to become broader with an increase of the PL peak energy. Figure 3(c) shows, in more details, the typical PL spectra of single isolated SWNTs with relatively small and large diameter [up: (7,5), $d=1.11 \text{ nm}$, down: (10,6), $d=0.83 \text{ nm}$] in the sample. The solid lines in Fig. 3(c) represent single Lorentzian functions and approximately reproduce the experimentally obtained PL spectra. In addition, it is found that the Stokes shift of SWNTs was very small (less than 5 meV) for each nanotube species by comparison between absorption and PL spectra of ensemble ACCVD SWNTs in gelatin matrices,²⁵ similar to the case of SDS (sodium dodecyl sulfate)-wrapped SWNTs synthesized by HiPco process.³ These facts show that the observed PL peaks correspond to the zero-phonon lines of free excitons and the spectral linewidth of the PL spectra is determined by the homogeneous broadening.

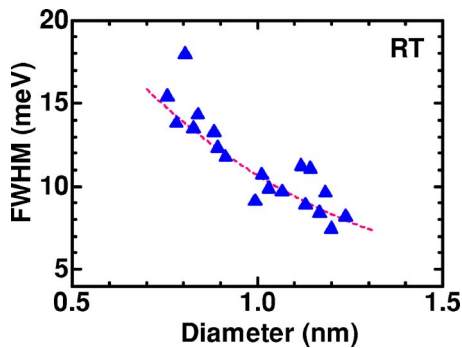


FIG. 4. (Color online) Diameter dependence of the linewidth of PL spectra for isolated single SWNTs. The dotted line corresponds to a guide for eyes.

In Fig. 4, we summarize the PL linewidth as a function of the nanotube diameter from the PL spectra. Here we plot the smallest values as the intrinsic linewidth for nanotubes with the same chiral index, because the extrinsic factors (defects, impurities, and so on) cause the linewidth broadening.¹⁵ The PL linewidth clearly becomes broader as the diameter decreases. This suggests that the exciton-phonon interaction is stronger in smaller diameter tube. Next we discuss the origin of the PL linewidth broadening in single SWNTs at room temperature.

Under weak excitation conditions, the homogeneous broadening of the free-exciton PL spectra from SWNTs is attributed to the phase relaxation due to phonon scattering rather than the energy relaxation. This is because the PL lifetime of excitons is reported to be considerably long (≥ 10 ps)²⁶ and this contribution to the linewidth is negligibly small ($\leq 10^{-2}$ meV). Here we have to take into account the excitonic picture even at room temperature, because the exciton binding energy in a SWNT (~ 200 – 400 meV)^{11,12} is much larger than the thermal energy of room temperature. Thus the homogeneous broadening originates from the dephasing time of excitons in the lowest excited state. In Fig. 4 it is found that the PL spectral linewidth varies as the tube diameter changes. This suggests that the exciton-phonon interaction is stronger and the dephasing time of excitons is shorter in smaller diameter tube (i.e., higher curvature tube).

Jiang *et al.*²⁷ calculated the electron-phonon matrix element for each phonon mode and photoexcited electron. They

showed the electron-phonon interactions for some phonon modes in SWNTs are enhanced compared to graphite, especially the RBM (radial breathing mode), TW mode (twisting mode), and oTO mode (out-of-plane transverse optical mode). This is because of the curvature of the cylindrical SWNT surface. In the case of graphite, π -electron clouds are parallel to each other to the out-of-plane direction. In SWNTs, on the other hand, π -electron clouds oriented inward of the nanotube sidewall are located closely to the neighboring π -electron clouds due to the surface curvature. Thus, as the surface curvature gets greater, the lattice vibration perpendicular to the tube axis will cause the larger fluctuation in the orbital overlap, i.e., the larger deformation potential. This means the exciton-phonon interaction is enhanced in smaller diameter tube, and is consistent with our experimental results. The temperature dependence of the spectral linewidth showed almost linear behavior in the range 4–300 K.^{25,28} This linear temperature dependence implies that the very low energy phonon modes ($\ll k_B T$) dominantly contribute to the linewidth broadening. Among the enhanced phonon modes mentioned above, the TW mode is the only low energy mode. It is thus believed that the TW mode has the dominant contribution to the diameter dependence of the exciton dephasing mechanism. Further theoretical studies are needed for the quantitative understanding of exciton-phonon interaction in 1D systems.

In conclusion, we have performed μ -PL spectroscopy on about 180 single isolated SWNTs suspended in air at room temperature. The line shape of each PL spectrum was found to be described approximately by a Lorentzian function. The PL linewidth increases with a decrease of the diameter. This diameter dependence of the PL linewidth shows that the exciton-phonon interaction is enhanced in a smaller diameter SWNT.

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