Origin of low-energy photoluminescence peaks in single carbon nanotubes: *K*-momentum dark excitons and triplet dark excitons

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We performed photoluminescence (PL) spectroscopy on single carbon nanotubes to investigate the satellite PL peaks, which are much lower in energy than the lowest (E_{11}) bright exciton peak. From the temperature and tube-diameter dependences of the PL spectra, we clarified two origins of the low-energy PL peaks. The weak peak, lying about 130 meV below the E_{11} bright exciton state, is well explained by the phonon sideband of the *K*-momentum dark exciton states above the lowest-bright exciton state. In addition, a strong PL peak appears after pulsed-laser irradiation, and its peak energy depends strongly on the tube diameter. This PL peak comes from the triplet dark exciton states.

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The optical properties of carbon nanotubes originating from one-dimensional excitons with very large binding energies are an important subject from the viewpoints of both fundamental physics and potential applications.[1–3] The degenerate band structures between the *K* and *K′* valleys, together with the spins of carriers, create 16 exciton states, which results in complex excitonic properties of carbon nanotubes.[4–8] Only the spin-singlet, odd-parity, and zero-angular-momentum exciton state is optically allowed (bright), and all the other exciton states are optically forbidden (dark). Many theoretical[4–8] and experimental studies[9–12] have been carried out to improve understanding of the dark exciton states, especially for optical transitions with lower energies than the E_{11} bright exciton state, because the low-lying exciton states may be the cause of the low-quantum efficiency of the photoluminescence (PL) in carbon nanotubes.[4] Recent magneto-PL spectroscopy studies of single carbon nanotubes[11,12] have directly shown the existence of an even-parity singlet dark exciton state through the Aharonov-Bohm effect[13] and revealed that the splitting energy between the bright and the even-parity dark exciton state is only a few millielectron volts.

Recently, satellite PL peaks have been observed, with much lower energies than the E_{11} bright exciton peak.[14–19] Since the lower exciton states have considerable influence on the optical properties of carbon nanotubes, the origin of the low-energy PL peaks has been a matter of intense debate. Determining the energy separation between the low-energy PL peaks and the bright exciton peak is important to identify the origins of the satellite peaks. However, based on the experimental data reported so far, what this energy separation is remains unclear. It was first reported that this energy separation is in the range of 90–140 meV and depends on the diameter of the nanotube and that the low-energy PL peak is due to deep-dark excitonic states.[14] However, other studies have shown that the energy separation is approximately 140 meV, almost constant with the nanotube diameter, and that the low-energy PL peaks come from the upper dark excitonic states called K-momentum dark exciton states.[16,17] Moreover, very recently, appearance of the pronounced satellite PL peak was reported to be ~190 meV below the bright exciton peak and the low-energy PL peak to arise from triplet excitons.[18] Because of the broad distribution of the reported energy separations, the origins of these lower satellite peaks are still unclear. A more detailed optical study of the tube-diameter and temperature dependences of the low-lying PL peaks is needed to understand the excitonic fine structure in carbon nanotubes.

In this work, we performed PL spectroscopy of single carbon nanotubes to investigate the low-energy PL peaks. We found that the weak PL peak ~130 meV lower than the E_{11} peak diminishes at low temperatures and that the energy separation depends only weakly on the tube diameter. These results support that the weak low-energy peak is the phonon sideband of the *K*-momentum dark exciton states above the bright exciton state. An additional low-energy PL peak appears under intense pulsed-laser irradiation, the intensity, of which increases with decreasing temperature, and the energy separation depends strongly on the tube diameter. Our results suggest that the laser-induced PL peak shows a brightening of the triplet dark exciton states.

The samples used in this work were single-walled carbon nanotubes synthesized using the alcohol catalytic chemical vapor deposition method.[20] Each nanotube was spatially isolated and suspended over patterned grooves, which were 10 μm wide and 10 μm deep, and were fabricated on Si substrates using electron-beam lithography. PL spectroscopy for single carbon nanotubes was performed using a custom-built variable-temperature confocal microscope.[11,21–24] PL spectra were taken under continuous-wave excitation with a He-Ne laser (1.96 eV) or a Ti:Sapphire laser (1.37–1.75 eV) and detected using a 30-cm spectrometer equipped with a liquid nitrogen-cooled InGaAs photodiode array having a spectral range of 0.78–1.38 eV. The spectral resolution of the system was about 1.4 meV. A Ti:Sapphire laser with a 100-fs pulse width was also used for intense pulsed irradiation to induce the low-energy PL peak.[18] The irradiation of the intense femtosecond pulsed-laser was performed in a vacuum condition ($\sim 10^{-3}$ Torr) in order to reduce the sample degradation such as oxidation and burning out of the nanotubes.

Figure 1(a) shows a typical contour map of PL excitation (PLE) for a single (9,4) carbon nanotube with E_{11} bright exciton peak. A sharp PL spectrum of a single carbon nanotube provides a clear feature of the low-energy PL band be-

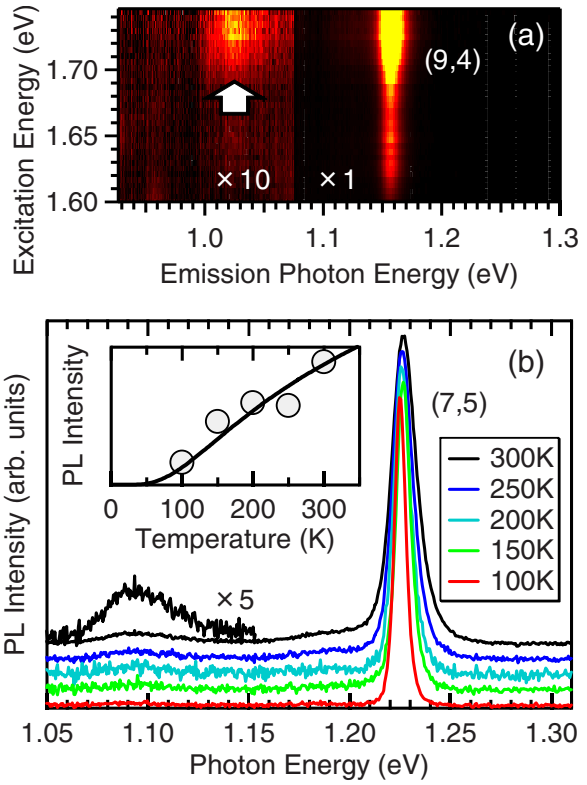

FIG. 1. (Color online) (a) PLE contour map of a single (9,4) carbon nanotube. The arrow shows the weak satellite PL peak far below the bright exciton PL peak. (b) Temperature-dependent PL spectra of a single (7,5) carbon nanotube. The inset shows the temperature dependence of the PL intensity ratio of the satellite peak to the bright exciton peak.

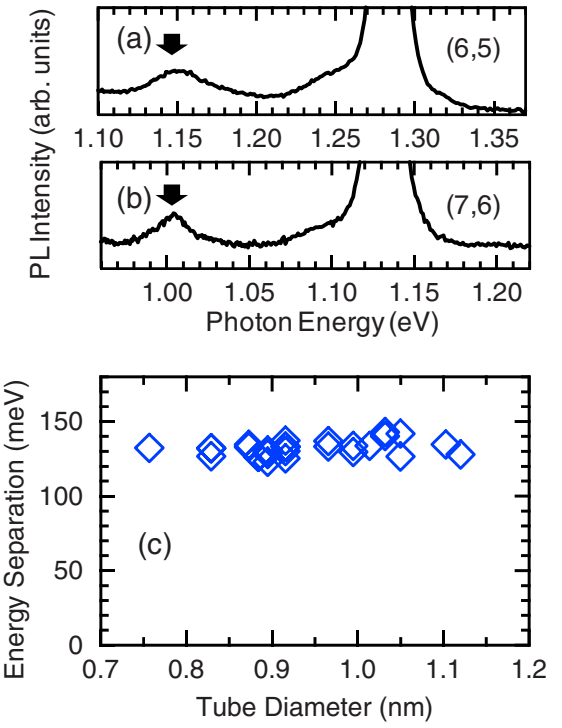

FIG. 2. (Color online) (a) and (b) PL spectra of single (6,5) and (7,6) carbon nanotubes, respectively. The arrows indicate the weak low-energy peaks. (c) Tube-diameter dependence of the energy separation between the bright exciton peak and the weak low-energy peak.

low the E_{11} peak. As indicated by the arrow in Fig. 1(a), we can observe a weak low-energy PL peak ~130 meV below the bright exciton peak, arising from the same (9,4) nanotube. This weak PL peak has been observed by recent PL spectroscopy.[14,16,17] Figure 1(b) shows the temperature dependence of PL spectra of a single (7,5) carbon nanotube. Each PL spectrum was normalized by the bright exciton peak intensity. With decreasing temperature, the PL intensity of the weak low-energy peak decreases.

The ratio of the weak low-energy PL peak to the bright exciton peak is shown in the inset of Fig. 1(b) as a function of temperature. The decrease in this ratio with decreasing temperature shows that the low-energy PL peak does not come from the lower dark exciton states because the exciton population in the lower exciton states should increase at lower temperature. To evaluate the experimental data, we assumed that the low-energy peak is the phonon sideband of the K-momentum dark exciton states, emitting an in-plane transverse optical (iTO) phonon at K-point,[16,17] which appears as the D-band in the Raman spectroscopy of graphite-related materials. The temperature dependence of the PL intensity ratio of the phonon sideband I_{phonon} to the bright exciton state I_{bright} can be expressed as the product of the Boltzmann factor and the probability of emitting a phonon, i.e.,

$$\frac{I_{\text{phonon}}}{I_{\text{bright}}} \propto \exp\left(-\frac{\Delta_K}{k_B T}\right)(n_{\text{ph}}+1), \tag{1}$$

where Δ_K is the energy separation between the K-momentum dark and the bright exciton states, $n_{\text{ph}}=1/[\exp(\Delta_{\text{ph}}/k_B T)-1]$ is the phonon occupation number, and Δ_{ph} is the phonon energy. The solid curve in the inset of Fig. 1(b) shows the calculated result from Eq. (1) using $\Delta_K=40$ meV and $\Delta_{\text{ph}}=170$ meV and reproduces the experimental data well. These values are consistent with theoretical[25] and experimental studies[16,26] on the phonon-mediated absorption peak ~200 meV ($\sim\Delta_K+\Delta_{\text{ph}}$) above the bright exciton peak due to the K-momentum excitons. This result shows that the temperature dependence of the weak low-energy PL peak can be explained by considering the phonon sideband of the K-momentum dark exciton states.

We investigated the low-energy PL peak for many single carbon nanotubes with different chiralities. Typical PL spectra are shown in Figs. 2(a) and 2(b). In Fig. 2(c), we plotted the energy separation, Δ_1, between the weak low-energy PL peak and the bright exciton PL peak as a function of the tube diameter. Although some of the data are slightly scattered even in the same-chirality tubes, $\Delta_1=\Delta_{\text{ph}}-\Delta_K$ is about 130 meV and almost independent of the tube diameter. This result is consistent with the considerations of the phonon sideband discussed above because the energy of the iTO phonon mode, Δ_{ph}, is dominant in Δ_1, and almost independent of the tube diameter within the diameter range shown in Fig. 2(c).[27] We found that $\Delta_1 \sim 130$ meV is slightly smaller than the

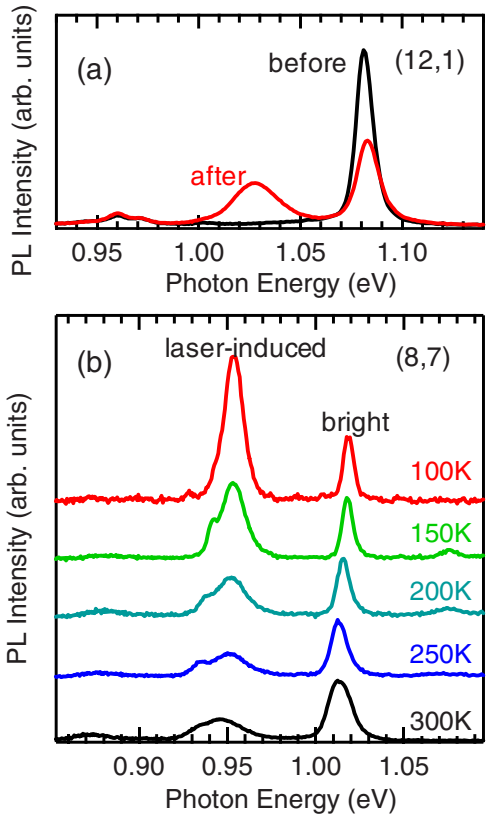

FIG. 3. (Color online) (a) PL spectra of a single (12,1) carbon nanotube before and after pulsed-laser irradiation. (b) Temperature dependence of PL spectra of a single (8,7) carbon nanotube after pulsed-laser irradiation.

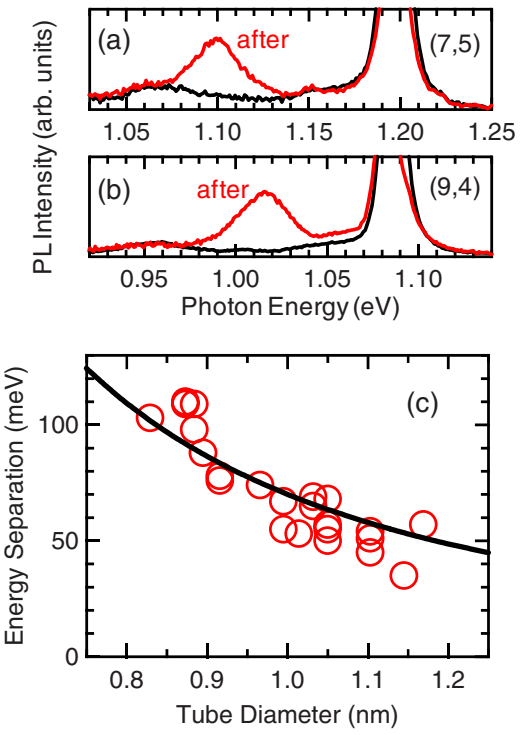

FIG. 4. (Color online) (a) and (b) PL spectra of single (7,5) and (9,4) carbon nanotubes, respectively, before and after laser irradiation. (c) Tube-diameter dependence of the energy separation between the bright exciton and the strong low-energy peak induced by the laser irradiation. The curve shows a fit with the splitting energy proportional to $1/d^2$.

value reported in Ref. 17, and attributed it to the difference in Δ_K due to the environmental effect: our nanotube samples are spatially isolated on a groove, while the samples used in Ref. 17 are dispersed by fluorine polymers with higher dielectric constants. The smaller dielectric constant in our suspended nanotubes enhances the energy separation of the excitonic states, Δ_K, due to the reduced screening of the Coulomb interactions,[28] leading to the smaller value of Δ_1. Therefore, both the temperature and diameter dependences of the weak low-energy PL peak strongly indicate that it arises from the phonon sideband of the K-momentum dark exciton states.[16,17]

Here, we investigated the effect of the strong pulsed-laser irradiation to single carbon nanotubes, since the strong pulsed-laser irradiation has been reported to induce the appearance of a low-energy PL peak.[18] We irradiated the strong pulsed-laser with 735-nm wavelength and ~2 mW for ~5–60 s to single carbon nanotubes. Figure 3(a) shows PL spectra of a single (12,1) carbon nanotube before/after the pulse irradiation, respectively. Additional satellite PL peak appears 70 meV below the bright exciton peak, and the spectral change occurs abruptly due to the pulsed-laser irradiation. Moreover, the weak phonon sideband discussed above is simultaneously observed 130 meV below the bright peak.

Figure 3(b) shows temperature dependence of the PL spectra for an (8,7) carbon nanotube after pulsed-laser irradiation. As temperature decreases, we observed that the intensity of the low-energy PL peak induced by the laser irradiation increases, in contrast with the phonon sideband at 0.87 eV, which decreases at low temperatures. This result clearly shows that the origin of the laser-induced PL peak is completely different from the phonon sideband of the K-momentum dark exciton states and that some light-emitting states lie at much lower energies than the E_{11} exciton state.

We investigated the laser-induced low-energy PL peak for many carbon nanotubes, as typically shown in Figs. 4(a) and 4(b), and plotted the separation energy Δ_2 between the bright exciton peak and the laser-induced peak in Fig. 4(c). Δ_2 is strongly dependent on the tube diameter, with a smaller-diameter tube having a larger Δ_2. We fit the data to $\Delta_2 = A/d^2$, where A is a coefficient and d is the tube diameter, as shown in Fig. 4(c), which reproduces the experimental results with $A \sim 70$ meV·nm^2.

It has been reported that the low-energy PL peak appears ~190 meV below the bright exciton state for (5,4) nanotubes by means of pulsed-laser irradiation.[18] Moreover, very recently, Mohite *et al.* showed that the low-energy photocurrent peak is ~20 meV below the bright exciton for nanotubes with diameters between 1.44 and 1.82 nm by coating the nanotubes with EuS.[29] Even though these splitting energies and the sample preparation methods are very different, note that our results and these observations show a universal behavior of the tube-diameter dependence, which suggests that these low-energy peaks have the same origin.

Capaz *et al.* predicted that the tube-diameter dependence of the splitting energy between the singlet and triplet exciton

states is proportional to $1/d^2$ (Ref. 30) because of the tube-diameter-dependent exchange interaction.[31] The theoretically predicted proportionality coefficient is ~ 40 meV·nm^2 for the micelle-wrapped carbon nanotubes with a relative dielectric constant, ε, of ~ 3. In our work, the samples suspended in vacuum have a smaller dielectric constant, $\varepsilon \sim 1.8$.[30] It has been proposed that the singlet exciton binding energy in carbon nanotubes scales with $\varepsilon^{-1.4}$.[5] Assuming that the binding energy of the triplet exciton has a similar screening dependence, the singlet-triplet splitting coefficient of 40 meV·nm^2 for $\varepsilon=3$ corresponds to about 80 meV·nm^2 for $\varepsilon=1.8$, which is consistent with our results of $A=70$ meV·nm^2. This suggests that the origin of the laser-induced low-energy PL peak is the triplet dark exciton states. Although the spin-orbit interaction is small in carbon nanotubes and graphene due to a small mass of the carbon atoms, a recent theoretical study showed that impurities on graphene lead to a large increase of the spin-orbit coupling.[32] Therefore, we believe that defects created by the laser irradiation, or any impurities trapped by the defects, would result in an increase in the spin-orbit coupling, leading to the spin-flip process and PL from the triplet exciton states. Understanding the mechanism of spin flipping and the development of a spin-controlling technique in carbon nanotubes and related materials are very important for future applications of spin-electronic devices.

In conclusion, we investigated PL peaks at much lower energies than the bright exciton state and found that they are the result of two separate physical processes. The intensity of the weak PL peak ~ 130 meV below the bright exciton state decreases at low temperatures, and the energy separation is almost independent of the tube diameter. This indicates that the weak PL peak is the phonon sideband from the K-momentum dark exciton states ~ 40 meV above the bright exciton state. We found that the pulse laser-induced low-energy PL peak becomes strong at low temperatures and that the energy separation is inversely proportional to the square of the diameter. This result indicates that the low-energy PL peak comes from the triplet exciton states due to the increase in the spin-orbit coupling caused by defects.

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