Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Luminescence 112 (2005) 287–290

JOURNAL OF LUMINESCENCE

www.elsevier.com/locate/jlumin

Temperature dependence of time-resolved luminescence spectra for 1D excitons in single-walled carbon nanotubes in micelles

Masao Ichida[a,b,*], Ikurou Umezu[a], Hiromichi Kataura[c], Mio Kimura[c], Shinzo Suzuki[c], Yoji Achiba[c], Hiroaki Ando[a]

[a]*Department of Physics, Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada-ku, Kobe 658-8501, Japan*
[b]*PRESTO, JST, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan*
[c]*Faculty of Science, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan*

Available online 24 November 2004

Abstract

We have investigated exciton luminescence spectra, decay behaviors, and their temperature dependence in single-walled carbon nanotubes in micelles. The temperature dependence of luminescence spectra can be explained by the one-phonon process associated with the radial breathing mode in the single-walled carbon nanotube. The luminescence decay behavior suggests that the signal is composed of various exponential decays with different decay times. These experimental results are explained by the existence of trapping centers on the nanotube.

PACS: 78.47.+p; 78.55.−m; 78.67.Ch

Keywords: Luminescence properties; Exciton–phonon interaction; Trapping centers

1. Introduction

Much effort has been expended to study the electronic and optical properties in one-dimensional (1D) systems. The theories predict that both binding energy and oscillator strength of the lowest exciton drastically increase as a cross-sectional size of a quasi-1D system decreases. The exciton transition plays an important role in the optical properties of 1D system. The single-walled carbon nanotubes (SWNTs) is regarded as a quasi-1D system because of the high aspect ratio (length/diameter) of a fundamental structure. The van Hove singularity in optical transition have been theoretically and experimentally studied and revealed the properties of the quasi-1D system

*Corresponding author. Department of Physics, Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada-ku, Kobe 658-8501, Japan. Tel./fax: +81 78 435 2679.

E-mail address: ichida@konan-u.ac.jp (M. Ichida).

0022-2313/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2004.09.104

[1–3]. Ando has theoretically pointed out the importance of excitonic effects on optical transitions of SWNTs [4], and we have observed the exciton transition in semiconducting SWNTs [5]. Excitonic effects increase the radiative recombination rate in the lowest excited state. Recently, photoluminescence (PL) due to the exciton transition has been observed for SWNTs in micelles [6]. Bachilo et al. have assigned the PL peaks to the individual SWNT with different chiral index (n, m) which determine the tube diameter and chiral angle of the tube's roll-up vector on a graphene sheet [1]. However, the physical origin of PL band width, temperature dependence, and decay behaviors have not been understood. In 1D system, any small fluctuation can cause localization. Thus, defects may strongly affect the electronic states and relaxation dynamics of the excitons in SWNTs, and these effects will appear in the optical spectra and PL decay behavior.

In this paper, we report on temperature dependence of exciton luminescence spectra for SWNTs in micelles investigated by time-resolved PL measurements. The origin of temperature dependence of PL spectra and decay behaviors are discussed in connection with the exciton–phonon interaction and exciton trapping at defect centers in SWNTs.

2. Experimental

Soots containing SWNTs were produced by the laser ablation method. The mean tube diameter of SWNTs is ~1.13 nm which is estimated from the absorption spectrum [7]. The SWNTs were dispersed in D_2O with dodecylbenzene (DBN) surfactant. The suspension was centrifuged, and upper supernatant was collected. In the dispersion, SWNTs are micelled with DBN in D_2O. The collected dispersion was mixed with polyvinyl alcohol (PVA), and then applied on the quartz substrates. PL spectra were measured using a grating monochromator equipped with a cooled InGaAs photomultiplier tube as a detector. A ps mode-locked Ti sapphire laser (1.58 eV) was used as an optical excitation source. Time-resolved PL spectra were measured by means of a time-correlated single photon counting method. The time resolution of this system was about 50 ps by using deconvolution of decay profiles taking into account the time response of measurement system.

3. Results and discussion

Fig. 1(a) shows the PL spectrum of micelled SWNTs in D_2O measured at 300 K. Four PL bands are observed in the spectrum. Compared with the absorption spectra, these PL bands are attributable to the exciton transition in individual semiconducting SWNTs with different tube index (n, m). Bachilo et al. have assigned these bands to (9,7), (10,3) or (10,5), (11,3), (12,1) or (8,6) from lower-energy side, respectively [6]. Fig. 1(b) displays the PL spectrum of micelled SWNTs in PVA at 300 K. The PL bands become broader and shift to the lower-energy side compared with those for the sample without PVA (Fig. 1(a)). The energy shift is ~20 meV. This shift may stem from the difference in dielectric constants between D_2O and PVA.

Figs. 1(c) and (d) show the PL spectra of micelled SWNTs in PVA at 150 and 10 K, respectively. With decreasing temperature, PL

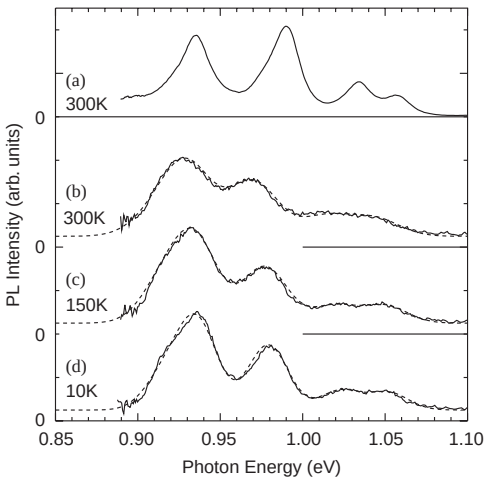

Fig. 1. (a) PL spectrum of SWNTs in micelles measured at 300 K. (b)–(d) PL spectra of micelled SWNTs in PVA measured at various temperature. Fitted spectra are shown in broken curves.

bands become narrower and shift to the higher-energy side. In order to clarify the physical origin of the line shape and temperature dependence of PL spectra, we approximate the shapes of PL bands with analytical functions. The broken curves in Fig. 1(b)–(d) show the best-fit results obtained assuming Gaussian function. The observed spectra are well reproduced by the fitted curves. Because we observed the PL from lots of SWNTs in the sample, one PL band consists of various emission lines from SWNTs having the same chiral index (n, m). The Gaussian-type PL shape for each PL band suggests that there are certain distribution in resonance energy for SWNTs of the same chiral index. Such energy distribution originates in defects of SWNTs or difference in ambience surrounding each SWNT.

Closed and open circles in Fig. 2 display the PL peak energies and line width as a function of temperature. The peak energy shifts to the lower-energy side with increasing temperature. In the weak exciton–phonon coupling regime, the peak energy $E(T)$ at temperature T is expressed as

$$E(T) = E(0) - \Delta \coth\left(\hbar\omega/2k_{\mathrm{B}}T\right), \tag{1}$$

where Δ is a constant, $\hbar\omega$ is a coupled phonon energy, and k_{B} is Boltzmann constant. Solid curves are the best fit results obtained by Eq. (1). Estimated coupled phonon energy is ~28 meV. The homogeneous line width $\hbar\gamma(T)$ of exciton transition is given as

$$\hbar\gamma(T) = \hbar\gamma_0 \coth\left(\hbar\omega/2k_{\mathrm{B}}T\right). \tag{2}$$

As shown in Fig. 1(b)–(d), however, the line shape of PL is Gaussian, which indicates the inhomogeneous broadening of transition dominates. When the homogeneous width is much smaller than the inhomogeneous one, the spectral line shape becomes almost Gaussian. However, since the inhomogeneous broadening does not depend on the temperature, the increase in the line width caused by temperature rise is simply caused by the homogeneous broadening. We assume the temperature dependence of line width $\hbar\Gamma(T)$ as

$$\hbar\Gamma(T) \simeq \hbar\Gamma_0 + \hbar\gamma(T), \tag{3}$$

where $\hbar\Gamma_0$ is a temperature independent width. Broken curve in Fig. 2 shows the fit result, assuming the phonon energy of ~28 meV. Both the peak energy and the line width can be well reproduced by the exciton–phonon interaction model. The coupled phonon energy of 28 meV agrees well with the energy of radial breathing mode in the ~1.13 nm diameter tube sample. Thus, we conclude that the temperature dependence of PL spectra is determined by the one-phonon process with radial breathing mode of SWNT.

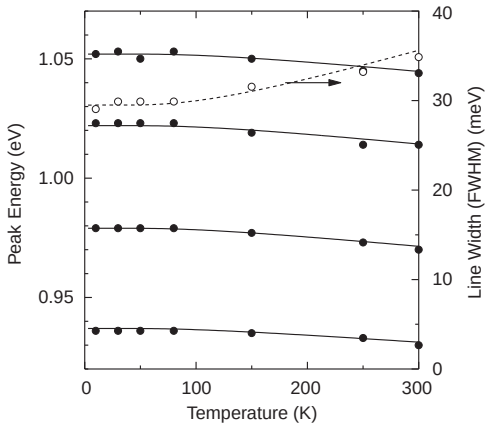

Fig. 2. Temperature dependence of PL peak energy and line width.

Fig. 3 shows the PL decay behavior of micelled SWNT in PVA, measured in a wide temperature range. The PL time evolution does not show single exponential decay. The Gaussian PL shape imply that the PL band stems from various SWNTs with the same chiral index, and the exciton lifetime differs among those SWNTs in the band. In such a case, like an amorphous case, the decay behavior shows non-exponential but stretched exponential function expressed as

$$I(t) = I_0 t^{\beta-1} \exp[(-t/\tau_{\mathrm{eff}})^{\beta}], \tag{4}$$

where β is a constant, and τ_{eff} is an effective decay time. Open circles in Fig. 3 display the decay behavior calculated taking into account the time response of measurement system. The calculated results with β of 0.39 reproduce well the experimental results. The effective decay time increase with increasing temperature, from τ_{eff} of 60 ps at 10 K to 120 ps at 300 K. These results confirm that decay time and resonance energy distribute in each

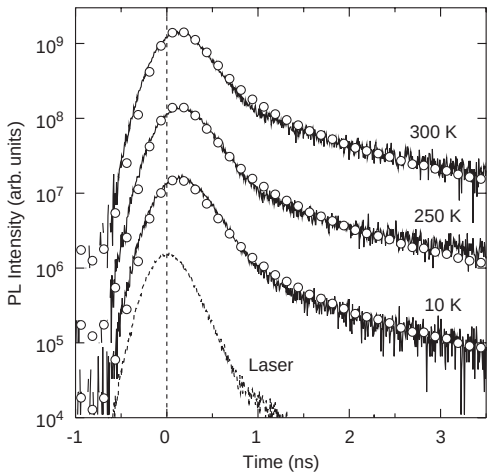

Fig. 3. Decay behaviors of PL of micelled SWNT in PVA measured at ~0.93 eV. Open circles show the fitted results by stretched exponential function.

SWNT have the same chiral index. The origin of such distribution is most likely the defects in the SWNT. We have found that the non-radiative decay rate $\frac{1}{\tau_{nr}}$ of SWNT depends on the tube diameter [8], and the rate is mainly determined by the carrier trapping to the defect in the SWNT [9]. In this case, the measured PL decay rate $1/\tau$ is equal to the sum of radiative and non-radiative rate as $\frac{1}{\tau_r}+\frac{1}{\tau_{nr}}$. The defect density differs among SWNTs even in the same chiral index tube. Thus, the PL decay time has certain distribution, which results in the stretched exponential decay behavior. With increasing temperature, trapped carriers by the defect will be released, and these will increase the chance of radiative transition and prolong PL decay time as we observed in Fig. 3.

We note that Wang et al. measured PL decay time of ~7 ps with a lasting several tens of picoseconds [10]. They attributed the multiexponential nature of the decay to inhomogeneity of the SWNTs sample. In our analysis, such inhomogeneity is included and expressed as the stretched exponential function.

4. Conclusion

We have investigated luminescence spectra, decay behaviors, and their temperature dependence in SWNTs in micelles. The temperature dependence of PL spectra can be explained by the one-phonon process. The coupled phonon energy was determined as ~28 meV which corresponds to the radial breathing mode of SWNT with the mean sample tube diameter. The decay behavior shows the stretched exponential function suggesting that the signal is composed of various exponential decays with various decay times. These experimental results can be understood by the existence of trapping center on the nanotube. Both PL line shape and decay behavior are strongly affected by the trapping centers. The experimental results reflect the main feature of 1D system, that is, the excitonic localization.

This work was partially supported by the grant to private university from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] R. Saito, M. Fujita, G. Dresselhaus, S. Dresselhaus, Appl. Phys. Lett. 60 (1992) 2204.
[2] J.W.G. Wildöer, L.C. Venema, A.G. Rinzler, R.E. Smalley, C. Dekkern, Nature 391 (1998) 59.
[3] H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, Y. Achiba, Synth. Met. 103 (1999) 2555.
[4] T. Ando, J. Phys. Soc. Japan 66 (1997) 1066.
[5] M. Ichida, S. Mizuno, Y. Tani, Y. Saito, A. Nakamura, J. Phys. Soc. Japan 68 (1999) 3131.
[6] S.M. Bachilo, M.S. Strano, C. Kittrell, R.H. Hauge, R.E. Smalley, R.B. Weisman, Science 298 (2002) 2361.
[7] M. Ichida, S. Mizuno, Y. Saito, H. Kataura, Y. Achiba, A. Nakamura, Phys. Rev. B 65 (2002) 241407.
[8] M. Ichida, Y. Hamanaka, H. Kataura, Y. Achiba, A. Nakamura, Physica B 323 (2002) 237.
[9] M. Ichida, Y. Hamanaka, H. Kataura, Y. Achiba, A.Nakamura, unpublished.
[10] F. Wang, G. Dukovic, L.E. Brus, T.F. Heinz, Phys. Rev. Lett. 92 (2004) 177401.