Confinement of Excitons for the Lowest Optical Transition Energies of Single Wall Carbon Nanotubes*

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The confinement of excitons in a single wall carbon nanotube (SWNT) is discussed based on an analysis of the environmental effect on the optical transition energies, E_{ii} , measured by photoluminescence spectroscopy. We use the effective dielectric constant κ as a function of nanotube diameter and exciton size that has also been used to reproduce excitonic transition energies E_{ii} from resonance Raman spectroscopy experiments. When we focus our attention to the lowest transitions, E_{11} region, we find a systematic deviation of the κ values for semiconducting type-I and type-II carbon nanotubes. We suggest that the E_{11} energies observed by photoluminescence are upshifted to the calculated E_{11} energies due to the confinement of excitons in the SWNTs. Considering this effect, the same energy shift formula for the environmental effect as that for the Raman spectroscopy results can be used to reproduce experimental E_{ii} values from photoluminescence spectroscopy within a good accuracy, hence providing an accurate assignment of many nanotube chiralities. [DOI: 10.1380/ejsnt.2010.367]

Keywords: Many body and quasi-particle theories; Light scattering; Carbon nanotubes

I. INTRODUCTION

The optical transition energies E_{ii} , where $i = 1, 2, 3, \dots$ denotes the transition between the i -th valence and i -th conduction subbands measured from the Fermi level, and the radial breathing mode frequencies (ω_{RBM}) of single wall carbon nanotubes (SWNTs) have been frequently used to assign their structural (n, m) indices [1] based on photoluminescence (PL) and resonance Raman spectroscopy (RRS) measurements [2, 3]. Knowing the (n, m) index of a SWNT allows us to understand the physical properties of the SWNT which are strongly (n, m) -dependent. Thus it is of great importance to have an accurate description of E_{ii} and ω_{RBM} as a function of (n, m) . The concept of excitons has been widely accepted to explain the E_{ii} energies, both from experimental and theoretical points of view, because the exciton binding energies of SWNTs are very large, up to 1 eV, so that the excitons survive even at the room temperature [4–8]. However, the excitonic transition energy E_{ii} for a given SWNT is known to be strongly affected by a change in the surrounding materials around the SWNT, which is called the environmental effect [9].

While the environment effect on ω_{RBM} 's has been understood by some empirical formulas [10, 11], a complete description of the E_{ii} 's environmental effect is still under development, though we now almost get the final conclusion for it [12], where one has to consider the excitonic dielectric screening effect of E_{ii} by the surrounding materials. The “Kataura” plot [13, 14], in which E_{ii} as a function of the nanotube diameter d_t , will be different for one particular environment relative to another, so a general picture for explaining the environmental effect is needed. In the previous works [11, 12], the dielectric constant κ is theoretically expressed as a function of d_t and also exciton size l_k in reciprocal space that can reproduce

many E_{ii} values observed by RRS measurements, namely, $E_{11}^{\text{S}}, E_{22}^{\text{S}}, E_{11}^{\text{M}}, E_{33}^{\text{S}}$ and E_{44}^{S} , where S and M denote semiconducting and metallic SWNTs, respectively. Not only was the method successfully applied to many E_{ii} values of many (n, m) SWNTs synthesized by a particular environmental condition, but it has also been proven to work well for different nanotube environments. In this study, we apply the same treatment to some PL E_{ii} data [15, 16], and we find it is applicable, too, for these datasets. However, we notice that there is a deviated tendency for the κ values for type-I ($\text{mod}(2n + m, 3) = 1$) and type-II ($\text{mod}(2n + m, 3) = 2$) semiconducting SWNTs for E_{11}^{S} only in the PL case. This deviation was not recognized previously in the RRS case because of a limited number of E_{11}^{S} data. Here we suggest a model based on the confinement effect of excitons in a SWNT.

II. THEORETICAL METHOD

The details of the exciton energy calculation used here have been described in some previous papers [17–19]. E_{ii} is calculated as a transition from the ground state to the first bright exciton state by solving the Bethe-Salpeter equation within the extended tight-binding (ETB) model. The ETB model includes the effect of curvature (single particle energy E_{sp}) and many-body effects (self energy Σ and exciton binding energy E_{bd}), so that the exciton energy can be calculated as $E_{\text{ex}} = E_{\text{sp}} + \Sigma - E_{\text{bd}}$. The Coulomb interaction is essential for considering the environmental effect since the shift of E_{ii} is understood by the change of κ in which the unscreened Coulomb potential V between carbon π electrons is modeled by the Ohno potential [4, 5, 22], while the static screened Coulomb potential is expressed as $W = V/\kappa\epsilon(\vec{q})$, where $\epsilon(\vec{q})$ is the polarization function for the π electrons. The effect of electrons in core states, σ bonds, and the surrounding materials are all represented by a single parameter κ . Thus, the expression for W can be understood as the origin of the variation of E_{ii} due to a change to the surrounding materials, because W is a main constituent in the Σ and E_{bd} calculations [17].

Previously, a constant $\kappa = 2.22$ was used by Jiang *et al.*

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to describe E_{ii} of bundled SWNTs for a limited range of diameter, $1.0 < d_t < 1.6$ nm [17, 18]. Miyauchi *et al.* then used $1/\kappa = C_{\text{tube}}/\kappa_{\text{tube}} + C_{\text{env}}/\kappa_{\text{env}}$, where C_{tube} and C_{kappa} are d_t -dependent coefficients, and successfully reproduced some experimental E_{ii} values, though only for a very few number of PL E_{11}^S energies [20]. Araujo *et al.* recently reported a d_t -dependent κ that could reproduce many experimental E_{ii} values and thus represents a breakthrough toward tackling the environmental effect [21]. However, different κ dependencies on d_t were obtained for $(E_{11}^S, E_{22}^S, E_{11}^M)$ relative to (E_{33}^S, E_{44}^S) . Then, we have improved the κ function to include its dependence on the exciton size l_k in reciprocal space [12]. The adopted model for the κ function is

$$\kappa \approx C_\kappa [p^{0.8}(1/d_t)^{1.6}(1/l_k)^{0.4}], \quad (1)$$

where the integer p corresponds to the ratio of the distances of the cutting lines for each E_{ii} transition from the K point in 2D Brillouin zone of graphene [14], and $p = 1, 2, 3, 4, 5$ stand for $E_{11}^S, E_{22}^S, E_{11}^M, E_{33}^S$, and E_{44}^S , respectively. The variable l_k is involved in the κ function because of the screening by the different environments (and metallicity of SWNTs) which modifies the exciton size. The fitted powers $(0.80 \pm 0.10, 1.60 \pm 0.10, 0.40 \pm 0.05)$ for $(p, 1/d_t, 1/l_k)$ have been determined so as to both optimize the correlation between κ and (p, d_t, l_k) , and to minimize E_{ii} differences between theory and experiment [12]. The powers also indicate another scaling relation of excitons similar to the previously reported scaling law which relates the exciton binding energy with the nanotube diameter, dielectric constant, and effective mass [22]. However, the use of the effective mass does not work to describe the difference between M- and S-SWNTs because the polarization functions $\epsilon(\vec{q})$ for M- and S-SWNTs are significantly different from each other even for a similar m^* .

The parameter C_κ is expressed directly by the gradient or slope of the κ function with an assumption that each C_κ characterizes the environmental dielectric constant κ_{env} of each sample, such as determined by different nanotube synthesis methods or particular solvents and wrapping materials around the tubes [12]. Previously we adopted the experimental E_{ii} values of resonance Raman excitation profile for super-growth (SG) [21, 23], alcohol-catalytic CVD (ACCVD) [21, 24], and HiPco [9] based SWNTs. We have set the SG sample as a standard because it has the largest E_{ii} and hence the smallest κ compared to the other samples [23], so that the C_κ values for all other samples should be normalized to the SG's C_κ , giving $\tilde{C}_\kappa = C_\kappa/C_\kappa^{\text{SG}}$ (thus $\tilde{C}_\kappa^{\text{SG}} = 1$). Now for the PL treatment we use E_{ii} data from the work by Weisman *et al.* [15] and Ohno *et al.* [16] which give SWNTs under three different environments: (i) HiPco SWNTs dispersed in sodium decodyl sulfate (SDS) aqueous solution [15], (ii) ACCVD trench-suspended SWNTs immersed in hexane (HEX) [16], and (iii) ACCVD trench-suspended SWNTs immersed in chloroform (CL) [16].

III. RESULTS AND DISCUSSION

In PL spectra, E_{11} energies are given by the emission spectra, while the other higher E_{ii} energies ($i =$

2, 3, 4, ...) are given by the absorption spectra. Since there are no PL spectra for M-SWNTs, only S-SWNTs are considered here. As were obtained previously for the RRS E_{ii} data [12], in Fig. 1 it is now given a series of fitted κ as a function of (p, d_t, l_k) obtained from the PL E_{ii} data. For each sample, all the E_{ii} transitions are unified into a single linear κ function with a slope C_κ as indicated by the violet lines in Fig. 1(a)-(c). The normalized slope values $\tilde{C}_\kappa$ are also mentioned in the figure and they are compared to the RRS data as are given in Table I. In particular, since it is known that the κ_{env} value for chloroform is higher than that for hexane [16], the $\tilde{C}_\kappa$ values obtained for these two samples also follow the same behavior. This fact strengthens the previous assumption that C_κ (or $\tilde{C}_\kappa$) characterizes the environmental dielectric constant of the samples. The physical assumption of $\tilde{C}_\kappa$ can also be justified by dividing κ of each sample with its respective $\tilde{C}_\kappa$ as shown in Fig. 1(d), in which all κ data collapse on to a single line. Another point to note is that the $\tilde{C}_\kappa$ values for HiPco SDS samples measured by PL and RRS spectroscopy are similar to each other, indicating our κ model can be safely used for both PL and RRS.

With the knowledge of $\tilde{C}_\kappa$ for several types of environments, we can use these results in practical applications. To a first approximation, we fit the energy shift $\delta E_{ii}^{\text{env}}$ due to different environments by:

$$\begin{aligned} \delta E_{ii}^{\text{env}} &= E_{ii}^{\text{SG}} - E_{ii}^{\text{env}} \\ &\equiv \tilde{C}_\kappa \left[A + B \left(\frac{p}{d_t} \right) + C \left(\frac{p}{d_t} \right)^2 \right], \end{aligned} \quad (2)$$

where A, B, C , are parameters common to all types of environments and E_{ii}^{env} is calculated using the κ functions. In the previous work [12], Eq. (2) with its corresponding A, B , and C were obtained by considering only the RRS data. The best fits for A, B , and C were found to be -42.80 ± 1.26 meV, 46.34 ± 1.32 meV · nm, and -7.47 ± 0.65 meV · nm², respectively. Now we find this equation is also applicable for the PL data, with $A = -40.10 \pm 1.08$ meV, $B = 47.22 \pm 1.47$ meV · nm, and $C = -6.87 \pm 0.36$ meV · nm². Here the E_{ii} values for the SG sample obtained in RRS measurements are used as a standard because of the SG's smallest environmental dielectric constant among the present data. All E_{ii} values for the other environments are then given by $E_{ii}^{\text{env}} = E_{ii}^{\text{SG}} - \delta E_{ii}^{\text{env}}$. This treatment thus provides a general way to obtain the Kataura plot for SWNTs in any type of environment. A good accuracy of $E_{ii}^{\text{exp}} - E_{ii}^{\text{cal}}$ is obtained within 50 meV for all energy regions (about 0.9–3.0 eV) and diameter ($0.7 < d_t < 2.5$ nm), as shown in Fig. 2.

Unlike the RRS measurements that can give a set of $(E_{11}^S, E_{22}^S, E_{11}^M, E_{33}^S, E_{44}^S)$, the PL data shown in Fig. 1 only give E_{11}^S and E_{22}^S , but the number of E_{11}^S data observed in PL measurements are much more than those in RRS measurements. We can then analyze the E_{11}^S data more carefully. Especially, when we look at the E_{11}^S region, denoted by circles in Fig. 1, there is a deviated tendency of the κ values for type-I (red circles) and type-II (blue circles) SWNTs. For E_{11}^S , since the type-I SWNTs have larger effective mass than type-II SWNTs [14], we expect a smaller exciton size for type-I SWNTs in real space. This means that the type-I SWNTs must have smaller

FIG. 1: The κ function obtained from the PL E_{ii} data. Panel (a) is for the HiPco SWNTs dispersed in SDS aqueous solution. Panels (b) and (c) are for the ACCVD trench-suspended SWNTs immersed in hexane and chloroform, respectively. Circle (cross) symbols are for E_{11} (E_{22}). Red (blue) colors denote semiconducting type-I (type-II) SWNTs. A green line in each plot is a fitted line for the SG sample as a reference. This line is also a guide for eyes to distinguish the slope for different sample. The effective κ values in (a) are determined from the E_{ii} data in Ref. [15], whereas for those in (b) and (c) are determined from the E_{ii} data in Ref. [16]. Panel (d) shows all κ values from (a)-(c) divided by their corresponding $\tilde{C}_\kappa$. Squares, triangles, and stars are for SDS, HEX, and CL, respectively.

TABLE I: List of $\tilde{C}_\kappa$ values obtained within our κ function method.

Measurement	RRS			PL		
Synthesis method (Environment)	SG (as-grown)	ACCVD (as-grown)	HiPco (SDS)	HiPco (SDS)	ACCVD (HEX)	ACCVD (CL)
$\tilde{C}_\kappa$	1.00 ± 0.08	1.42 ± 0.03	1.52 ± 0.05	1.54 ± 0.05	1.77 ± 0.04	2.06 ± 0.06

κ values related to the previous explanation about the electric field lines created by excitons. In fact, if the exciton size is small, only small amount of the electric field can be affected by the environment. However, in Fig. 1, especially in panels (b) and (c), it is clear that type-I SWNTs tend to have larger κ values compared to type-II SWNTs. This opposite behavior suggests that the exciton might be thermally activated by the center-of-mass motions in a finite SWNT length coupled with phonons, so that the E_{11}^S energies obtained from PL measurements are upshifted from the calculated E_{11}^S energies. The upshift value should be larger (smaller) for smaller (larger) effective mass, which will be shown as follows.

In the PL process, the excitons are relaxed from the E_{22}^S states to the E_{11}^S states by the exciton-phonon interaction. This interaction might not perfectly relax the excitons to the lowest exciton states before the electrons and

hole recombination gives the emitted light. The exciton state before the recombination is thus slightly upshifted in energy than the real lowest exciton state considered in the calculation because of the quantum confinement of an exciton. We denote this energy difference by ΔE_{11}^S that can be understood as the energy upshift of the E_{11}^S in the plot of κ . Since κ is obtained from the experimental E_{11}^S energies, the ΔE_{11}^S values should shift the effective κ depending on the tube type. A good parameter for this situation is the center-of-mass $M_{CM} = (m_e^* + m_h^*)/2$ (here m_e^* and m_h^* are the electron and hole effective masses, respectively), because M_{CM} of a type-I SWNT is generally larger than that of a type-II SWNT for a similar d_t . Then, we expect that $\Delta E_{11}^S \sim \hbar^2 k_{CM}^2 / 2M_{CM}$ for the type-I SWNTs should be smaller than that for the type-II SWNTs, so that the κ values for type-I SWNTs will be upshifted smaller. This will result in the correct tendency of the κ values, that is, the κ values for type-I SWNTs are smaller than those for type-II SWNTs, or at least if we cannot make it, the κ values for both type-I and type-II SWNTs are not separated too much.

We can make a model for ΔE_{11}^S by considering the exciton motion is restricted in a finite length, analogous to the problem of a particle in a box. ΔE_{11}^S is expressed as

$$\Delta E_{11}^S = \frac{\int_0^\infty ED(E)f(E)dE}{\int_0^\infty D(E)f(E)dE}, \quad (3)$$

where $D(E)$ is the electronic density of states and $f(E) = e^{-(E/k_B T)}$ is the Boltzmann distribution function, k_B is the Boltzmann constant, and T is temperature. If we approximate $D(E)$ with the 1D nanotube DOS, $D(E) \propto 1/\sqrt{E}$, it will result in a constant $\Delta E_{11}^S = \frac{1}{2}k_B T$ at a given temperature, independent of M_{CM} , which does not

FIG. 2: Evaluation of the differences between experimental (exp) and calculated (cal) E_{ii} values for all samples, showing good agreement between experiment and our model. Open and filled squares are for PL and RRS data, respectively.

FIG. 3: ΔE_{11}^S as a function of M_{CM} for the hexane PL data. To get the values shown in the horizontal axis, $1/M_{CM}$ should be multiplied by a factor $(\hbar^2 \pi^2 / 2L^2) / k_B T$. Red and blue circles denote type-I and type-II SWNTs, respectively. $L = 20$ nm and $T = 300$ K are used in this calculation.

explain the phenomena. Thus we have to model the exciton motion quantum mechanically as a particle in a box which gives discrete energy states E_n as a function of center-of-mass:

$$E_n = \frac{\hbar^2 \pi^2}{2M_{CM} L^2} n^2, \quad (4)$$

where L is length in which the exciton is confined. The DOS in Eq. (3) becomes a delta function and thus the integral turns to a summation:

$$\Delta E_{11}^S = \frac{\sum_{n=0}^{\infty} E_n e^{-(E_n/k_B T)} dE}{\sum_{n=0}^{\infty} e^{-(E_n/k_B T)} dE}. \quad (5)$$

Since E_n is inversely proportional to M_{CM} , ΔE_{11}^S is also roughly inversely proportional to M_{CM} , as shown by a solid line in Fig. 3.

Therefore, we can achieve the expectation to have smaller (larger) ΔE_{11}^S for the type-I (type-II) SWNTs

because M_{CM} for the type-I (type-II) SWNTs is larger (smaller). A plot of ΔE_{11}^S calculated from Eq. (3) for the hexane data is given in Fig. 3 with a fixed $L = 20$ nm and $T = 300$ K. The ΔE_{11}^S correction can then be applied to the determination of κ from E_{11}^S original data,

$$E_{11}^S = E_{11}^S(\text{exp}) - \Delta E_{11}^S, \quad (6)$$

where E_{11}^S is now the exciton state free of the center-of-mass motion, that can be used to determine the effective κ .

With the use of $L = 20$ nm, ΔE_{11}^S for type-I and type-II SWNTs are about 20 – 30 meV and 25 – 35 meV, respectively. The corresponding κ upshifts are then about 0.4 – 0.6 and 0.5 – 0.7 for type-I and type-II SWNTs, respectively. If we use larger L , for example $L = 200$ nm similar to a typical nanotube length found in experiments, ΔE_{11}^S will be close to a constant $\frac{1}{2} k_B T$. We conclude that the exciton motions are very restricted in a short finite length L in the center part of the nanotube axis. We do not have a clear image why the exciton is confined in such a short region. A possible explanation is that the exciton is self-trapped by the lattice deformation or defects of a SWNT. These are open issues for the future work.

IV. CONCLUSION

In conclusion, we have developed the κ function for SWNTs surrounded by several different types of materials using a simple dielectric constant model. The treatment is applicable for E_{ii} values obtained from both RRS and PL spectroscopy. For the E_{11}^S region in the PL case, the opposite behavior of the κ values for type-I and type-II SWNTs is expected to originate from the confinement of exciton motions that makes the experimental E_{11}^S values are upshifted from the calculated values.

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