Spectroscopic Studies of Carbon Nanotubes

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Abstract

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Spectroscopic Studies of Carbon Nanotubes (104 pp.)

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Spectroscopic studies were performed on carbon nanotubes including single-walled carbon nanotubes (SWNTs) and double-walled carbon nanotubes (DWNTs).

First, we followed the reported method to obtain the individually dispersed SWNTs with the assistance of surfactants in aqueous phase. The absorption and fluorescence spectra of this surfactant/SWNTs suspension were captured and the species distribution for the semiconducting tubes was assigned as well. Afterwards, we studied how the surfactant/SWNT suspension is affected by sonication temperature, centrifugation time, pH, and the surfactant structures.

Further we describe a new method to probe the absolute energy levels of SWNTs. The first conduction band edge of the semiconducting SWNTs was obtained via measuring the redox chemistry.

Finally, the optical property of DWNTs was investigated collaborating with people in Dr. Jie liu’s group in Duke University. Our current results suggest that the inner layer of a DWNT can not fluoresce, which is contrary to the conclusion in the published literature.
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Chapter 1 Introduction

1.1 Background

Over the past decade carbon nanotubes (CNTs) have become one of the most attractive subjects in Condensed Matter Physics. CNTs are unique one dimensional (1D) nanostructures with remarkable properties. The electronic properties of single-walled carbon nanotubes (SWNTs) depend uniquely on the geometric structure, which is arguably the most significant characteristic of this material. A single SWNT can be either metallic or semiconducting, depending only on diameter and chirality.\(^1\text{-}^7\) This phenomenon is unusual among solid-state materials.

In 1991, Iijima, using high resolution transmission electron microscopy (HRTEM) and electron diffraction, reported the existence of helical carbon microtubules (now called nanotubes).\(^8\) Nanotube research accelerated greatly following the independent discoveries of SWNTs by Bethune at IBM\(^9\) and Iijima at NEC.\(^10\) Nowadays, CNTs can be produced by several techniques, such as high-pressure CO gas decomposition with Fe catalyst (HiPCO),\(^11\) Co/Mo catalyst-assisted chemical vapor deposition (CoMoCAT CVD),\(^11\) arc discharge, laser ablation,\(^12\) direct injection pyrolytic synthesis,\(^13\text{-}^14\) and so forth.

CNTs are allotropes of carbon (Fig. 1.1a). A SWNT, having a cylinder shell with only one atom in thickness, can be considered as the fundamental structure unit (Fig. 1.1b).\(^15\) Such structural units form the building blocks of both multi-walled carbon nanotubes (MWNTs), containing multiple coaxial cylinders about a common axis (Fig. 1.1c),\(^8\) and nanotube bundles, consisting of ordered arrays of SWNTs (Fig. 1.1d).\(^16\)
Figure 1.1 (a) Raw HiPCO SWNT powders (b) A SWNT showing that the structure consist of an individual graphene cylinder (After Mauricio Terrones\cite{15}) (c) MWNTs. The second tube is a double-walled carbon nanotube (DWNT) (After Iijima\cite{8}). (d) A SWNT bundle (After Thess, A\cite{16})

Scientists and engineers around the world are exploring the wide range of technological applications for this material. For example, the outstanding mechanical properties of CNTs are used in the fabrication of new, strong composites;\textsuperscript{17-19} their field-emission properties are employed to fabricate flat panel displays;\textsuperscript{20-22} the ballistic character of electronic transport in SWNT has been utilized to demonstrate that SWNT transistors that outperform corresponding state-of-the-art silicon devices;\textsuperscript{23, 24} while the sensitivity of
their electrical characteristics on interactions with their environments is being used to produce chemical and biological sensors.\textsuperscript{25, 26}

This thesis will look into tube-surfactant, tube-aqueous environment, and tube-tube interactions in the SWNT and DWNT dispersions using near infrared (NIR) absorption and fluorescence spectroscopy. Parameters such as sonication temperature, centrifugation time, pH level and surfactant structures will be varied. The electronic structures of SWNTs, as well as the optical properties of DWNTs will be studied. This research not only offers the basic physics understanding for the bulk tube dispersion system, but also demonstrates several new discoveries in the chemical, electronic and optical properties of the carbon nanotubes.

1.2 Outline

The thesis will begin with a concise introduction to the geometric and electronic structure of CNTs. The definition of CNTs and parameter calculations are given there. The electronic structure of SWNTs will be deducted using a basic tight binding model.

In the second chapter, the general optical physics, especially the absorption and fluorescence process, will be discussed following by the mechanism of SWNTs’ absorption and fluorescence spectra.

In the Chapter 3 I shall discuss the early work done in Dr. Chen’s lab. We used the reported method to obtain the SWNT spectra in the bulk system and assign the \((n, m)\)
species for semiconducting tubes in our sample. Afterwards, we studied how the surfactant/SWNT suspension is affected by the sonication temperature, centrifugation time, pH, and surfactant structures.

Probing the absolute energy levels of SWNTs will be discussed in Chapter 4. We approached the energy levels for the semiconducting SWNTs’ first conduction band edges ($E_{v1}$) via measuring the redox chemistry in the tube dispersion system.

The final chapter deals with our studies on the optical properties of double-walled carbon nanotubes (DWNTs) with collaborators in Dr. Jie liu’s group in Duke University. Our current results suggest that the inner layer of a DWNT does not fluoresce, which is contrary to the published conclusions.


Chapter 2 Electronic Properties of Single-walled Carbon Nanotubes

2.1 Geometric Structure of Carbon Nanotubes

CNTs are considered as a 1D nano material because of the high aspect ratio. They can be thought of as graphene sheets rolled into cylinders (Fig. 2.1). With this in mind, the structure of a SWNT is expressed in terms of a roll-up vector:

\[ \mathbf{C}_h = n \mathbf{a}_1 + m \mathbf{a}_2 = (n, m), \quad (2.1) \]

where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the unit vectors of the hexagonal honeycomb lattice of the graphene sheet (Figure 2.1). The translation vector, \( \mathbf{T} \), which corresponds to the length of the \( (n, m) \) SWNT unit cell, is given by:

\[ \mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2 = (t_1, t_2), \quad (2.2) \]

where \( t_1 = \frac{2m+n}{d_R} \), \( t_2 = \frac{2n+m}{d_R} \), and \( d_R \) is the greatest common divisor of \((2m+n)\) and \((2n+m)\). The diameter \( (d_t) \) and chiral angle \( (\theta) \), can be determined:

\[ d_t = (3^{1/2} / \pi) a_{cc} \left( m^2 + mn + n^2 \right)^{1/2} \quad (2.3) \]

and

\[ \theta = \tan^{-1} \left[ 3^{1/2} m / (2n + m) \right], \quad (2.4) \]

where \( a_{cc} \) is the nearest-neighbor carbon atom distance of 0.142 nm. Three distinct types of nanotube structures can be generated based on the different chiralities. The vectors \((n, 0)\) and \((0, m)\) denote zigzag nanotubes \((\theta = 0^\circ)\) and the vectors \((n, n)\) denote armchair
nanotubes \( (\theta = 30^\circ) \). All other vectors \((n, m)\) correspond to chiral nanotubes \( (0^\circ < \theta < 30^\circ) \).^{28}

\[
\theta = 0.3^\circ
\]

Figure 2.1 Schematics of graphene sheet and typical SWNT structures (After Ming Ouyang)\(^{27}\)

MWNTs consist of rolled multiple graphite layers on themselves. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 0.33nm.\(^{29}\) DWNTs, composed by two roll-up graphite lays, are interesting because they benefit from a synergetic useful blend of both SWNT and MWNT characteristics, exhibiting the electrical and thermal stability of MWNTs and the flexibility close to SWNTs.\(^{30}\)
2.2 Electronic Structure of Graphene

Similar to the physical structure, the energy dispersion of CNTs can be obtained by zone folding of the two-dimensional (2D) energy dispersion relations of graphite. Carbon has four electrons in its outer valence shell; the ground state configuration is $2s^2 2p^2$. In graphite, $sp^2$ hybridization occurs, in which each atom is connected evenly to three carbons ($\sigma$ bond). A unpaired electron is present in the $\pi$ orbital, which is perpendicular to carbon hexagonal network.\textsuperscript{15} We now want to find the electronic band structure of the graphene $\pi$ orbital, i.e., we solve the Schrödinger equation:\textsuperscript{28}

$$H\Psi(k) = E(k)\Psi(k). \quad (2.5)$$

$H$ is the Hamiltonian, and $E(k)$ is the eigenvalue at wave vector $k$, and $\Psi(k)$ is the eigenfunctions. The eigenfunctions can be written as a linear combination of Bloch functions $\phi_{l,k}(r)$ due to the periodicity of the lattice:

$$\Psi(k) = \sum_l C_l \phi_{l,k}(r). \quad (2.6)$$

In the tight-binding approximation, the Bloch function is the product of a plane wave envelop function and a periodic function: $\phi_k(r) = U_k(r)e^{ik\cdot r}$. Instead of using this most general form, we consider the specific problem here: The unit cell of graphene contains two carbon atoms, which are labeled as A and B. We construct a Bloch function for the graphene sublattice A with the normalized $\pi$ orbital of the isolated carbon atom $\varphi_k(r)$

$$\phi_A = \frac{1}{\sqrt{N_0}} \sum_{\mathbf{R}} e^{ik\cdot R_A} \varphi_k(r - R_A) \quad (2.7)$$
and an equivalent function \( \phi_b \) for the second sublattice, where \( N_0 \) is the number of unit cells in the solid and \( \mathbf{R}_A \) is a lattice vector.

To solve the Schrödinger equation (2.5) we substitute \( \Psi(k) \) by a linear combination of the Bloch functions in Eq. (2.6). After multiplying both sides with \( \phi_a \) and \( \phi_b \) we find

\[
\begin{bmatrix}
H_{AA}(k) - E(k)S_{AA}(k) & H_{AB}(k) - E(k)S_{AB}(k) \\
H_{BA}(k) - E(k)S_{BA}(k) & H_{BB}(k) - E(k)S_{BB}(k)
\end{bmatrix} = 0,
\]

where \( H_{IJ} \) are the matrix elements of the Hamiltonian and \( S_{IJ} \) are the overlaps between Bloch functions

\[
H_{IJ} = \langle \phi_i | H | \phi_j \rangle, \quad S_{IJ} = \langle \phi_i | \phi_j \rangle
\]

Since the two carbon atoms in the unit cell of graphene are identical, \( H_{AA} = H_{BB}, S_{AA} = S_{BB}, H_{BA} = H_{AB}^{*} \) and \( S_{BA} = S_{AB}^{*} \). By substituting (2.7) and (2.9) into (2.8), we obtain:

\[
H = \begin{pmatrix}
\varepsilon_{2p} & \gamma_0 f(k) \\
\gamma_0 f(k)^* & \varepsilon_{2p}
\end{pmatrix}, \quad S = \begin{pmatrix}
1 & sf(k) \\
sf(k)^* & 1
\end{pmatrix}
\]

where \( \varepsilon_{2p} \) is the site energy of the 2p atomic orbital, \( \gamma_0 \) is C-C interaction energy, \( s \) is the overlap of the electronic wave function on adjacent sites and

\[
f(k) = e^{ik \cdot R_1} + e^{ik \cdot R_2} + e^{ik \cdot R_3} = e^{ik_1 a/\sqrt{3}} + 2e^{-ik_1 a/2 \sqrt{3}} \cos \frac{k_y a}{2}
\]

where \( R_i \) (\( i = 1, 2, 3 \)) is denoted as the bond vectors of the graphene sheet while \( a = |a_1| = |a_2| = \sqrt{3} a_{C-C}. \) The solution of the secular equation \( \det(H - ES) = 0 \) implied by (2.10) leads to the eigenvalues
for $\gamma_0 > 0$, and $E^+/E^-$ corresponds to the $\pi^*/\pi$ energy bands. The function $\omega(k)$ in (2.12) is given by

$$\omega(k) = \sqrt{|f(k)|^2} = \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}}$$

By neglecting the overlap between wave functions centered at different atoms ($s=0$) and adapting $\varepsilon_{2p} = 0$, a common approximation for the electronic structure of a graphene layer is obtained:

$$E_{g2D}^\pm(k_x, k_y) = \pm \gamma_0 \left\{ 1 + 4 \cos \left( \frac{\sqrt{3} k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right) \right\}^{1/2}$$

Fig. 2.2a shows the 2D graphene sheet band structure in the first Brillouin zone obtained from Eq. (2.14). The Fermi surface of the graphene sheet determined from $H(k_F) = 0$, which describes the highest occupied quantum state, is reduced to the six corners ($K_B$) of the hexagonal first Brillouin zone (Fig. 2.2b). Because there are two atoms per unit cell, the valence band of graphene is completely filled.
2.3 Electronic Structure of SWNTs

The 1D band structure of a SWNT can now be derived from this 2D graphite model by imposing periodic boundary conditions. All allowed wavevectors $k$ is then quantized in the direction perpendicular to the rolled-up vector $\mathbf{C}_h$ (Fig. 2.3a). $\mathbf{WW}'$ represents the Brillouin zone of a carbon nanotube and the line segments are periodic shifts of $\mathbf{WW}'$ by $\mu \mathbf{K}_1$ ($\mu=0, \ldots, N-1$), where $N$ is the number of $\mathbf{K}_1$ in an individual tube. Expressions for the reciprocal lattice vectors $\mathbf{K}_2$ along the nanotube axis and $\mathbf{K}_1$ in the circumferential direction (Fig. 2.3a and Fig. 2.3b) are given by: \(^{28}\)

$$K_1 = \frac{1}{N} (-t_2 b_1 + t_1 b_2), \quad K_2 = \frac{1}{N} (m b_1 - n b_2)$$ (2.15)

where $b_1 = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right)$ and $b_2 = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a}\right)$ are reciprocal lattice vectors of graphene.

---

**Figure 2.2** (a) Three-dimensional plot of the $\pi$ and $\pi^*$ graphene energy bands and (b) a 2D projection. (After Ming Ouyang\(^{27}\))
When $E_{g2D}$ at the line segments are folded so that the wavevectors parallel to $K_2$ coincide with $WW'$ as shown in Fig 2.3a. N pairs of 1D dispersion relations $E_\mu(k)$ are obtained, where $N = |C_\Lambda \times T|/|a_x \times a_z|$. The 1D energy dispersion relations of a SWNT are given by:

$$E_\mu(k) = E_{g2D} \left( k \frac{K_x}{|K_x|} + \mu K_z \right)$$

$$\left( \mu = 0, \ldots, N - 1, \text{ and } -\pi/|T| < k < \pi/|T| \right),$$

(2.16)
Figure 2.3 (a) The Brillouin zone of a SWNT is represented by the line segment WW’ which is parallel to $K_2$. (After Dresselhaus, M.S.28) (b) The condition for metallic energy band: $YK_B/K_1=$integer (After Dresselhaus, M.S.28) (c) Allowed 1D wavevectors for a metallic (9, 0) SWNT. (d) Allowed 1D wavevectors for a semiconducting (10, 0) tube. The white hexagons in (c) and (d) define the first Brillouin zone of a graphene sheet, and the black dots in the corners are the $K_B$ points (After Ming Ouyang27).

If the allowed wavevector passes through Fermi points $K_B$ of the graphene sheet, the SWNT is predicted to be metallic (Fig. 2.3c), and otherwise semiconducting (Fig. 2.3d).

The condition for obtaining a metallic energy band is that the ratio of the length of the vector $YK_B$ to that of $K_1$ (Fig.2.3b) is an integer. Since the vector $YK_B$ is given by $YK_B = \frac{2n+m}{3} K_1$, we thus expect:
\[
\begin{cases}
n - m = 3q : \text{metallic} \\
n - m \neq 3q : \text{semiconducting}
\end{cases}
\]

(2.17)

where \(q\) is an integer.

### 2.3.1 Energy Dispersion of Armchair and Zigzag Nanotubes

To obtain explicit expressions for the dispersion relations, the simplest case to consider is the nanotubes having the highest symmetry.

The appropriate periodic boundary conditions used to obtain the energy eigenvalues for the \((n, n)\) armchair nanotube define the small number of allowed wave vectors \(k_{x,q}\) in the circumferential direction

\[
n \sqrt{3} k_{x,q} a = 2 \pi q, \quad (q=1,\ldots,2n).
\]

(2.18)

Substitution of the discrete allowed values for \(k_{x,q}\) given by (2.18) into (2.14) yields the energy dispersion relations \(E^a_q(k)\) for the armchair nanotube, \(C_h=(n, n),\)

\[
E^a_q(k) = \pm \gamma_0 \left\{ 1 \pm 4 \cos\left(\frac{q \pi}{n}\right) \cos\left(\frac{ka}{2}\right) + 4 \cos^2\left(\frac{ka}{2}\right) \right\}^{1/2},
\]

(2.19)

\((-\pi < ka < \pi), \quad (q=1,\ldots,2n)\)

where \(k\) is a one-dimensional vector in the direction of the vector \(K_2.\)

The periodic boundary condition for the \(C_h=(n, 0)\) zigzag nanotube can be obtained as:

\[
n k_{x,q} a = 2 \pi q, \quad (q=1,\ldots,2n)
\]

(2.20)

The energy dispersion relations for the \((n, 0)\) zigzag nanotube yield:
\[ E_q^z(k) = \pm \gamma_0 \left\{ 1 \pm 4 \cos \left( \frac{\sqrt{3}ka}{2} \right) \cos \left( \frac{q\pi}{n} \right) + 4 \cos^2 \left( \frac{q\pi}{n} \right) \right\}^{1/2} \]  
\[ \left( -\frac{\pi}{\sqrt{3}} < ka < \frac{\pi}{\sqrt{3}} \right), \quad (q=1,\ldots,2n) \]

The resulting calculated 1D dispersion relations \( E_q^z(k) \) for the zigzag (9, 0), (10, 0) and armchair (5, 5) nanotubes are shown in Fig. 2.4. There is no band gap for (5, 5) and (9, 0) nanotubes at \( k=0 \) indicating metallic properties, whereas the (10, 0) nanotube is indeed a semiconducting one with an energy gap.

Figure 2.4 Band structure of (a) armchair nanotube (5, 5) and (b) zigzag nanotube (9, 0) (c) zigzag (10, 0) (After Dresselhaus, M.S.)

Due to the high symmetry, it is easier to calculate the electronic structure of armchair and zigzag tubes. However, because of their lower symmetry, the electronic structure of chiral carbon nanotubes is not well understood so far.
2.4 Density of States

A general expression for the density of states (DOS) $D(E)$ in $d$-dimensions is:

$$D(E)=\left(\frac{L}{2\pi}\right)^d \int \frac{dk^d \delta\left(k\(\bar{E}\) - k\right)}{\left|\nabla_k(E)\right|},$$

(2.22)

where $E$ is the energy, $L$ is the dimension size, and $k$ is the wavevector. At a band edge, the denominator $|\nabla_k(E)| \to 0$, and singularities arise in the DOS at $E$, referred to van Hove singularities (VHS), indicating the characteristic of the dimensionality of a system. In three dimensions, VHS are kinks, while in two dimensions the VHS appear as stepwise discontinuities with increasing energy (Fig. 2.5). Unique to 1D system, the VHS are manifest as peaks. Hence, SWNTs are expected to exhibit spikes in the DOS due to the 1D nature of their band structure.

![Figure 2.5 Schematic of features in the density of states for 3D, 2D and 1D. (After Teri Wang Odom)](image)

Of particular importance is the energy dependence of the nanotube DOS. The DOS near the Fermi level $E_f$ is critical for determining the electronic properties and optical phenomena of the nanotubes. We shall find it also determines redox reaction discussed in
Chapters 4 and 5. Fig.2.6 compares the DOS for metallic (5, 5) armchair and semiconducting (7, 0) zigzag nanotubes where the DOS has a value of zero for semiconducting nanotubes, and non-zero for metallic nanotubes.

Figure 2.6 DOS for (a) armchair tube (5, 5) (b) zigzag tube (7, 0) (After Mauricio Terrones\textsuperscript{15})
The first VHS band gaps for semiconducting and metallic SWNTs are 
\[ E_g^S = 2\gamma_0 a_{cc} / d, \]
and 
\[ E_g^M = 6\gamma_0 a_{cc} / d, \]
respectively, and are independent of chiral angle \( \theta \) to the first order. Both \( E_g^S \) and \( E_g^M \) are plotted as a function of nanotube diameter \( d \) for all chiral angles at a given \( d \) value in Fig. 2.7. Such a plot is commonly referred to as a Kataura plot.\(^{33}\) This plot is very useful for determining the energy in the absorption and fluorescence spectra to assign the (n, m) species of SWNTs.

![Figure 2.7 Gap energy distributions as a function of diameter. Solid circles indicate the metallic SWNTs and open circles the semiconducting ones. Double circles indicate the armchair-type SWNTs. (After H Kataura\(^{33}\))](image)
Chapter 3 Optical Spectra of Single-walled Carbon Nanotubes

3.1 Principle of Optical Process

3.1.1 Major Optical Processes

For most semiconductors, photons of sufficient energy can excite electrons from the filled valence bands to the empty conduction bands. As a result, the optical spectra of semiconductors provide a rich source of information on their electronic properties. Fig.3.1 shows schematically some of the optical processes which can occur when a medium is illuminated by light. At the surface of the medium, a fraction of the incident light is reflected and the rest transmitted. Inside the medium some of the radiation may be absorbed or scattered while the remainder passes through the sample. Some of the absorbed electromagnetic radiation may be dissipated as heat or reemitted at a different frequency. The latter process is known as photoluminescence, which includes phosphorescence and fluorescence. Electromagnetic waves are scattered by inhomogeneities inside the medium. Scattering of light by acoustic waves is usually referred to as Brillouin scattering. Scattering of light by other elementary excitations, such as optical phonons or plasmons, is known as Raman scattering. The primary analytic tools used in this thesis are absorption and fluorescence. We will therefore focus on these processes in the following discussions.
3.1.2 Absorption and Fluorescence

In the absorption process, a photon of a known energy excites an electron from a lower to a higher energy state. Fluorescence is the reversed process, in which the absorption triggers the emission of another photon with a longer wavelength on a timescale of 10 nanoseconds.\textsuperscript{35}

The selection rule determines whether a given transition is allowed or forbidden. And the transition rate (probability of transition per unit time) from one energy eigenstate of a quantum system into a continuum of energy eigenstates is given by Fermi's golden rule, which is calculated by perturbation theory.\textsuperscript{36}

\[
W = \frac{2\pi}{\hbar} \sum_{u,l} |\langle u |H_I | l \rangle|^2 \delta(E_u - E_l + \hbar\omega)
\]  (3.1)
where \( l \) and \( u \) are transition initial and final states with energy \( E_l \) and \( E_u \), respectively, \( H_I \) is the interaction Hamiltonian.

Within energy level systems we can have a variety of mechanisms for these two processes. Most of these processes can occur in quantum wells, wires (including the tubes), and dots, as well as in bulk material. In this section, the relevant band-to-band and exciton transitions will be discussed. Although there are many other possibilities such as band to impurity, impurity to band, donor to acceptor and intraband transitions, these are not directly relevant to this work.

(1) Band to Band Transition

We treat the band to band transition in the single-particle approximation neglecting the interaction between the photogenerated electron and hole.\(^{35} \) The simplest absorption occurs in between two direct valleys (band gap \( E_g \)), where all the momentum-conserving transitions are allowed (Fig.3.2). Every initial state at \( E_l \) is associated with the final state at \( E_u \) such that

\[
E_u = h\nu - |E_l|.
\]  

(3.2)

The absorption coefficient, which defines the extent to which a material absorbs energy, is:

\[
\alpha (h\nu) = A (h\nu - E_g)^{1/2}
\]

(3.3)
where $A' \approx \frac{q^2 \left( 2 \frac{m^* \mu^*}{m_h^* + m_e^*} \right)^{2/3}}{n \hbar c m_e^*}$. $m_e^*$ and $m_h^*$ are effective masses of electron and hole in the material, respectively. $n$ is index of refraction.

**Figure 3.2** Band to band transition (After Jacques I. Pankove$^{35}$)

As a reversed absorption process, the direct band to band emission spectrum is given by

$$L(\nu) = B \left( h\nu - E_g \right)^{1/2}$$

(3.4)

in which the coefficient $B$ can be evaluated from

$$B = \frac{2q^2 \left( \frac{m^* \mu^*}{m_h^* + m_e^*} \right)^{3/2}}{n \hbar c m_e^*}$$

(3.5)

(2) **Exciton Transition**

The free exciton is an electron excitation which involves correlated motion of electrons and holes, does not carry current, but does carry energy. In direct-gap materials the free
exiton occurs when the photon energy is \( h\nu = E_g - E_x \) (\( E_x \) is the binding energy of the exiton) (Fig. 3.3). Since excitons can be created with some kinetic energy, it is evident that they can also be created by higher-energy photons, thus contributing a component to the absorption coefficient in the region of band to band transitions. In the corresponding exciton fluorescence process, the energy of the emitted photon is again simply \( h\nu = E_g - E_x \).

![Exciton transition (After Jacques I. Pankove)\(^{35}\)](image)

**Figure 3.3** Exciton transition (After Jacques I. Pankove\(^{35}\))

### 3.2 Absorption and Fluorescence Spectra of SWNTs

CNTs were expected to show strongly structured optical spectra because they are 1D system. The singularities in the electronic DOS should give rise to strong absorption and luminescence peaks. Despite these expectations, photoluminescence from SWNTs was not observed for a decade after the tubes are discovered since CNTs normally occur in bundles, in which the metallic tubes quench the fluorescence.\(^{37}\) In order to exploit the
optical properties of SWNTs, the tubes have to be individually dispersed in organic or aqueous media.

Individually dispersed SWNTs can be obtained by covalently functionalizing the end or the sidewall of nanotubes, but the electronic structure of the SWNT is altered arguably.\(^{38-42}\) In 2001, Michael J. O’Connell reported they observed the absorption and especially fluorescence spectra of isolated tubes.\(^{43}\) The SWNT dispersion was obtained by ultrasonicating the as-produced SWNTs in an aqueous sodium dodecyl sulfate (SDS) solution followed by a centrifugation treatment. The micelles (Fig. 3.4a) prevented the tubes from reforming bundles and their electronic structures were preserved as well. Fig. 3.4b shows the optical spectra in near-infrared (NIR) region for the semiconducting tubes with diameter of 0.7 to 1.1nm.

**Figure 3.4** (a) Cross-section model of the nanotube as it would exist in a water-free hydrocarbon environment (b) Absorption spectra (blue) and fluorescence spectra (red) of SWNT suspended in SDS micelles. (After Michael J. O’Connell\(^{43}\))
3.2.1 The Mechanism of SWNT Absorption and Fluorescence

SWNTs can be either metallic or semiconducting depending on whether n-m is evenly divisible by 3 and the band gaps among the nanotubes vary in approximate inverse proportion to the tube diameter. Another important feature of SWNT electronic structure is sets of sharp maxima (VHS) in their DOS. These arise from the tubes’ quasi-one-dimensional character. Nanotube optical spectra are dominated by strong dipole-allowed transitions, polarized along the tube axis, between VHS in matching valence and conduction sub-bands. These are referred to as $E_{ii}$ transitions, with $i=1, 2, 3, \text{etc.}$ Fig. 3.5 illustrates the idealized electronic state density and dominated low-energy optical transitions of both semiconducting and metallic SWNTs.\textsuperscript{44, 45} The metallic tubes do not fluoresce since excited electron will recombine with the hole in the valence band through the channel in between the valence band ($E_{Vi}$) and conduction band ($E_{Ci}$). In general, a SWNT bundle does not fluoresce because the presence of a metallic nanotube quenches the electronic excitation on an adjacent semiconducting tube.\textsuperscript{43}
Figure 3.5 Schematic drawing of absorption and fluorescence mechanisms for (a) a semiconducting tube and (b) a metallic tube (After Sergei M. Bachilo\textsuperscript{45})

### 3.2.2 Typical SWNT Absorption and Fluorescence Spectra

Fig.3.6 is typical absorption and fluorescence spectra of a SDS/SWNT suspension. The $E_{11}$ transition of the direct band gap semiconducting tubes falls in the near infrared 800-to 1600-nm wavelength range (noted $E_g \propto \frac{1}{d} \propto \frac{1}{\lambda}$), slightly overlapping the 550- to 900-nm region of their $E_{22}$ transitions. The lowest energy VHS of the metallic tubes appear between 400 and 600 nm.
The (n, m) assignment is very important for the tube species distribution analysis. The species assignment in Fig. 3.6 is based on Table A1 in Appendix A. The labeled peaks in Fig. 3.6 correspond to specific absorption and emission bands associated with different tube species.

Each absorption component in the spectral region of the first van Hove “band gap” transition of the semiconducting tubes, $E_{11}$, is present in the fluorescence spectrum, red-shifted by ~10 nm. The individual components of the emission spectrum appear to have widths of approximately 0.025 eV, or 200 cm$^{-1}$, very close to the value of thermal energy, $k_B T$ for the room temperature.

The (n, m) assignment is very important for the tube species distribution analysis. The species assignment in Fig. 3.6 is based on Table A1 in Appendix A. The labeled peaks

Figure 3.6 Optical spectra of SDS/SWNT suspension (a) Ultraviolet (UV)-vis absorption spectra (b) NIR absorption spectra and fluorescence spectra excited at (c) 658 nm excitation and (d) 785 nm.
are formed from the transition of metallic $E_{11}$, semiconducting $E_{22}$ \{d (8,4), e (7,5) (7,6), f (12,2), g (8,6) (8,7), h (10,6), i (12,1), j (14,0) (11,6) (13,2) (12,4)\} and semiconducting $E_{11}$ \{P1 (6, 5), P2 (8,3), P3 (7,5), P4 (10,2), P5 (9,4), P6 (12,1), P7 (11,3), P8 (10,5), P9 (9, 7)\}.

In one word, spectroscopy demonstrates a good tool in looking into the electronic structure and charge behavior of CNTs. In the following chapters, we will apply absorption and fluorescence spectra to further investigate the tube suspension system.
Chapter 4 Absorption and Fluorescence Spectra of Bulk SWNT Suspensions

4.1 Motivation

The first detection of absorption and fluorescence spectra from surfactant assisted SWNT suspension, as discussed in Chapter 3, paved the way towards understanding the photo physics of specific tube structures through bulk measurements. Recent developments show that SWNTs can be incorporated into micelles formed by various surfactants in aqueous solutions, such as lipids, DNA, and commodity polymers. The force and charge interactions in the surfactant/SWNT aqueous suspension can be affected by experimental variables. To verify our procedures and gain experience in the SWNT spectroscopy field we began with established methods to obtain the SWNT spectra and understand (n, m) species assignment. We then studied how the surfactant/SWNT suspension is affected by sonication temperature, centrifugation time, pH, and the surfactant structures. The effects are probed by the NIR absorption and fluorescence spectroscopy.

4.2 Experimental

4.2.1 Materials

Raw HiPCO SWNTs were purchased from Carbon Nanotechnologies Inc. (<35% ash content). Sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS) and poly (St-alt-Ma) (PSMA) (Fig. 4.1) were applied respectively to disperse the raw HiPCO
SWNTs in aqueous phase. SDS and SDBS, the widely used surfactants, were purchased from Sigma-Aldrich Co. of ~98% and ~80% purity, respectively. PSMA (80% purity) is a uniquely designed molecule for dispersing SWNTs in Dr. Chen’s group (Fig. 4.1).52

\[
\text{(a)} \quad \text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{O}^\text{SO}_4^\text{SO}_4^\text{ONa} \\
\text{(b)} \quad \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{S}_2\text{O}_4^\text{ONa} \\
\text{(c)} \quad \text{[Diagnosis]} \\
\]

**Figure 4.1** Molecular structures of (a) SDS, (b) SDBS, and (c) PSMA

### 4.2.2 Techniques

**SDBS/SWNT Dispersion Preparation**

We followed established experimental methods described in the literature\textsuperscript{43} to prepare the SDBS/SWNT aqueous suspension for the spectroscopic studies and tube (n, m) species distribution analysis. The 1wt% SDBS solution was firstly mixed with 0.4mg/ml raw HiPCO SWNTs. Then the 1h sonication (VCX 130 ultrasonics processor from Sonics & Materials Inc.) at a power level 5W in ice water bath was applied to the mixture. Right
after that, the product was treated by the centrifugation for 2h at 13500g (Centrifuge 5417C from Eppendorf North America Inc.). The bundles, ropes and catalysts were brought to the bottom while the supernatant, which is dominated by the individually dispersed tubes, was withdrawn using a pipet for further test (Fig. 4.2).

**Figure 4.2** Schematic drawing of experimental process to obtain the SDBS/SWNT suspension: (1) Sonication probe; (2) SDBS and SWNT mixture; (3) Ice-water bath; (4) Individually dispersed SWNT suspension

**Stability Studies of SDS/SWNT and SDBS/SWNT Suspensions**

To obtain some fundamental understandings for the tube dispersion system, we compared the stability of SDS/SWNT and SDBS/SWNT suspensions under different sonication temperature and centrifugation time. The 1wt% SDS or SDBS was firstly mixed with 0.4mg/ml raw HiPCO SWNTs following by the sonication and centrifugation processes. The experimental variables are listed in Table 4.1 and Table 4.2.
Table 4.1  Experimental parameter setup for suspension stability test at different sonication temperatures

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Sonication time/ power</th>
<th>Sonication temperature</th>
<th>Centrifugation time/speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>1h/~5W</td>
<td>0, 20, 40, 60, 80°C</td>
<td>2h / 13500g</td>
</tr>
<tr>
<td>SDBS</td>
<td>1h/~5W</td>
<td>0, 20, 40, 60, 80°C</td>
<td>2h / 13500g</td>
</tr>
</tbody>
</table>

Comments: The sonication temperature is tuned by changing the temperature of the water bath.

Table 4.2  Experimental parameter setup for suspension stability test at different centrifugation time

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Sonication time/ power</th>
<th>Sonication temperature</th>
<th>Centrifugation time/speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>1h/~5W</td>
<td>Ice water bath</td>
<td>1, 2, 3, 4h / 13500g</td>
</tr>
<tr>
<td>SDBS</td>
<td>1h/~5W</td>
<td>Ice water bath</td>
<td>1, 2, 3, 4h / 13500g</td>
</tr>
</tbody>
</table>

Comments: In the centrifugation process, the suspension samples were filled in a 1.5ml testing tube and centrifuged around a fixed perpendicular axis.

The pH Dependence Studies of SWNT Suspensions

pH response of the tube dispersion is an interesting issue currently. In order to observe the pH effect, after obtaining the SDS/SWNT and SDBS/SWNT suspensions via 1h sonication in ice water bath and 2h/13500g centrifugation treatment, the product was separated into several equal volumes and their pH levels were modified to different values by adding the equal amount of HCl or NaOH liquid. These samples were incubated overnight.
Spectroscopic Studies of PSMA-pyrene/SWNT Complex

Optical spectra of SWNT dispersion can be affected by surfactant structures. In order to study surfactant structure effect, PSMA/SWNT dispersions were produced: PSMA (containing 0, 1, 2, 5, 10% pyrene side) solution was firstly prepared by mixing PSMA powder with 60mM NaOH solution in the ratio of 1mg: 1ml. 0.4mg/ml raw HiPCO SWNTs was then added to this solution. The suspensions were obtained after sonicating the mixture for 1h with ~5W power and centrifuging for 2h with 13500g.

4.2.3 NIR Spectroscopic Measurements

The NIR spectroscopy was studied via Model NS1 NanoSpectralyzer (purchased from Applied NanoFluorescence) where the integration time was set to 100ms, and the averaging parameter was chosen to be 5. The NIR absorption and fluorescence spectra are measured in the range of 900-1600nm (3nm spectral resolution) with 512 element InGaAs array detector. There are two excitation sources: 90 mW at 658 nm and 70 mW at 785 nm (diode lasers). This spectrometer can cover SWNT diameter range from 0.7-1.4nm. The optical schematic is shown in Fig. 4.3.
Figure 4.3 Optical schematic of Model NS1 NanoSpectralyzer (After Applied NanoFluorescence, LLC)
4.3 Results

4.3.1 Sonication Assisted Dispersion of SDBS/SWNT

The SDBS/SWNT NIR spectra (Fig. 4.4) we obtained exhibit similar structures to those reported in the literature.53 The 1D direct band gap semiconducting tubes in the SDBS/SWNT suspension sample are found to fluoresce brightly in the NIR wavelength range 900 to 1600nm (Fig. 4.4a and Fig. 4.4b). Also this dispersion shows well resolved optical absorption spectra (Fig. 4.4d).
Figure 4.4 Spectra of SDBS/SWNT suspension and HiPCO SWNT (n, m) species distribution analysis (a) NIR fluorescence spectra excited at 658nm and (b) 785nm. The blue curves are the measured spectra and the red are simulated spectra. The basis functions of individual (n, m) species are indicated. (c) (n, m) distribution of the HiPCO SWNTs. The thickness of each hexagonal cell border represents the content for the enclosed (n, m) structure. (d) Absorption spectra of this SDBS/SWNT suspension.

A global fit algorithm was applied to find the (n, m) distribution of the raw HiPCO SWNTs. The $E_{11}$ position of the SDBS/SWNT template (supplied by the fitting program) was imported to the program firstly. We allowed 0.1% variation for the $E_{11}$ and $E_{22}$ position and 5% variation for $E_{11}$ width, $E_{22}$ width, $E_{11}$ shape, excitation profile, and laser
ratio per fitting round. (Further description seen in Appendix A) The simulated spectra and individual (n, m) components were obtained after 3 rounds (Fig. 4.4a and Fig. 4.4b). A graphene sheet map of possible nanotube structures with (n, m) values labeling semiconducting species is shown in Fig. 4.4c. It was computed via multiplying signal intensity of specified tubes by correction factors, which describe the individual excitation efficiencies. The thickness of each hexagonal cell border represents the distribution of the enclosed (n, m) structure. Fig 4.4c exhibits that the raw HiPCO SWNT diameters cover the range of 0.7-1.3nm, which agrees well with the product illustration. And the graphene sheet map indicates the most abundant species are (8, 7) and (13, 2).

4.3.2 Stability of SWNT Suspension

1) Thermal Stability

The absorption spectra were obtained from SDS/SWNT (Fig.4.5a) and SDBS/SWNT (Fig. 4.5b) suspensions sonicating at 0, 20, 40, 60, and 80°C, respectively. The figures illustrate that as sonication temperature increases, the concentration of the suspensions decreases, and meanwhile SDBS/SWNT always results in a higher concentration at every sonication temperature.
Figure 4.5 Absorption spectra of (a) SDS/SWNT and (b) SDBS/SWNT sonicated at 0, 20, 40, 60, and 80°C

2) Stability under Centrifugation

We observed a decreasing concentration as longer centrifugation in both suspensions. However, the fluorescence spectra of SDS/SWNT (Fig. 4.6a) decrease as longer centrifugation, while SDBS/SWNT (Fig. 4.6b) almost does not change.

Figure 4.6 Fluorescence spectra (785nm excitation) of (a) SDS/SWNT and (b) SDBS/SWNT aqueous suspensions with 1h, 2h, 3h, and 4h centrifugation
4.3.3 pH Dependence of SWNT Suspensions

Fig. 4.7a and Fig. 4.7c are NIR absorption spectra of SDS/SWNT and SDBS/SWNT suspensions at different pH. The peaks of SDS/SWNT are broadened considerably with increasing acidity, while SDBS/SWNT still shows well resolved spectra even at pH 1.4. After plotting normalized absorbance as a function of pH for the labeled peaks in both absorption spectra, we clearly see the trend that the absorbance increases as pH is raised and the increase is faster for the larger diameter tubes in both cases (Fig. 4.7b and Fig. 4.7d). However, SDBS/SWNT is not as sensitive as SDS/SWNT.
Figure 4.7 pH titration for individually dispersed SWNT suspensions (a) Absorption spectra of SDS/SWNT suspension at pH3, 4, 5, 6, 7, 8, 10, and 12 (b) Normalized absorbance of SDS/SWNT plotted as a function of pH (c) Absorption spectra of SDBS/SWNT suspension at pH1.4, 3.4, 6.9, 10.1, and 12.7 (d) Normalized absorbance of SDBS/SWNT plotted as a function of pH

Fig. 4.8 represents the corresponding fluorescence spectra of the two SWNT suspensions. Again SDS/SWNT (Fig. 4.8a and Fig. 4.8b) exhibits the same trend as its absorption spectra and the emission almost vanishes at pH3. However, as pH increases, the fluorescence of SDBS/SWNT increases firstly and decreases after the suspension reaches a neutral condition (Fig. 4.8c and Fig. 4.8d).
Figure 4.8 Fluorescence spectra at different pH of (a) SDS/SWNT excited at 658nm and (b) 785nm and (c) SDBS/SWNT excited at 658nm and (d) 785nm

It is discovered that the optical signal of SWNT suspension at low pH can be increased when heated at 80°C under Ar for 1h in order to desorb O₂ and the increasing is faster for the tubes of larger diameters. The signal can be recovered in the time scale of a week with air admitted (Fig. 4.9). The recovery is also faster for the tubes of larger diameters. However, the fluorescence can not be recovered without the air addition.
Figure 4.9 The gradual fluorescence recovery of SDS/SWNT after degas

It is also discovered that the fluorescence spectra of SDS/SWNT (Fig. 4.10a) and SDBS/SWNT (Fig. 4.10b) can be recovered if the pH is modified to the initial value from the other value.
Figure 4.10 Recovery of nanotube fluorescence (a) SDS/SWNT (b) SDBS/SWNT. Nanotube fluorescence spectra show weaker signals when lowering down pH (red line), and the spectra are recovered after increasing pH to the initial value (blue line).

4.3.4 Spectra of PSMA-pyrene/SWNT Complex

The concentrations of the five PSMA/SWNT samples (containing 0, 1, 2, 5, and 10% pyrene side) were manually modified to reach approximately the same absorbance (Fig. 4.11a). Their fluorescence spectra increase as pyrene content in the PSMA molecule increases (Fig. 4.11b). Figure of normalized intensity vs. pyrene content (Fig. 4.11c) indicates the increase is faster for the peak at the shorter wavelength. The trend is reversed compared to previous pH titration experiment.
Figure 4.11  (a) Absorption spectra of concentration modified PSMA (0, 1, 2, 5, and 10%)/SWNT suspensions (b) Corresponding fluorescence spectra excited at 758nm (c) Normalized intensity of P1, P3, P5, P6 and P8 vs. pyrene content
4.4 Discussion

4.4.1 Sonication Assisted SDBS/SWNT Dispersion

There is an important difference between the information one can obtain by absorption and by fluorescence: The absorption spectrum is broader since the excitation process can involve all the states. Even for a bundle composed of exclusively one type of tube we expect broadened optical absorption spectrum because the tube-tube interaction introduce an electronic dispersion to the SWNTs.\textsuperscript{54} Meanwhile our absorption spectra show a nearly linear background which also appears in the published literature.\textsuperscript{43, 55} This background will be discussed in the next chapter. However, the fluorescence process couples a narrow band of states containing the thermalized electrons with a narrow band of empty states, therefore, produces a narrow spectrum.

4.4.2 Stability of SWNT Suspension

The energy of the system increases as sonication temperature is raised. However, the tubes aggregate to low down their internal energy to weaken this tendency. These bundles are easier to be brought to the bottom of the centrifuge tube during the centrifugation process (Fig. 4.5). Therefore we observed higher sonication temperature results in lower tube concentration. Moreover, SDBS can disperse more tubes than SDS at each temperature. This phenomena agrees with the results reported in the other literature\textsuperscript{53, 56}. The SDS can disperse the SWNTs in aqueous environment because of the hydrophobic interaction between the hydrophobic tail in the SDS molecule and the side walls of CNTs. However, SDBS can disperse tubes not only because of the hydrophobic
interaction but also a so called π-π interaction. The π-π interaction between the benzene ring in the SDBS molecule and the SWNT surface may contribute to more dispersed tubes in the solution.

When we increase the centrifugation time, it is not unexpected that the concentration decrease since more tubes and catalysts (added during the tube growth process) are brought to the bottom. However, the fluorescence spectra of SDBS/SWNT almost do not vary, which can be attributed to the bundle removal during the centrifugation process. The fluorescence from SDS/SWNT decrease demonstrates that the individual tubes in SDS/SWNT are not as stable as SDBS/SWNT. It is also interesting to observe that the largest diameter tubes in SDS/SWNT suspension are firstly removed under centrifugation. In summary, due to the additional π-π interaction, SDBS/SWNT suspension is more stable than SDS/SWNT.

4.4.3 The pH Effect on the SWNT Suspensions

Let’s firstly observe the pH effect of the widely studied SDS/SWNT suspension. The trend of our SDS/SWNT spectra sequence agrees well with the literature.\(^{57-63}\) The absorption and fluorescence increases with increasing pH. The increase is faster for the larger-diameter tubes. Fig. 4.7 and Fig. 4.8 demonstrate H\(^+\) is a necessary factor for the valence electron depletion and fluorescence quenching, while Fig. 4.9 illustrates O\(_2\) is another necessary factor. It is also proved that the pH sensitivity phenomenon is
reversible when recovering the O$_2$ content (Fig. 4.9) or H$^+$ concentration (Fig. 4.10) in the SWNT suspension.

So far, there are two mechanisms to explain this pH sensitivity phenomenon. One is proposed by Ming Zheng$^{61}$ called redox reaction (Fig. 4.12a). As pH increases, the reaction would move toward the positive direction and produce more electron holes to the tube side walls. Since the absorbance is proportional to the joint DOS, the removal of electrons from the valence band would result in bleaching of the absorption and meanwhile fluorescence quenching. A gradual oxidation by oxygen from smaller to larger band gap tubes takes place as the pH drops since the reduction potential of CNT increases with increasing band gap, providing an explanation for the diameter dependence. The other mechanism was reported by Gordana Dukovic.$^{63}$ The SWNT network firstly reacts with oxygen to produce the 1, 4-endoperoxide SWNT-\(\text{O}_2\) (Fig. 4.12b). In a low pH condition, protonation of the endoperoxide forms a carbocation (structure SWNT-\(\text{O}_2\text{H}^+\)), i.e., a hole in the \(\pi\)-system valence band which depletes the valence band.
Figure 4.12 Two proposed mechanisms to explain the pH sensitivity. (a) Redox reaction (After Ming Zheng\textsuperscript{61}) (b) Formation of carbocation (After Gordana Dukovic\textsuperscript{63})

Both mechanisms can explain the experimental phenomena. However, the second mechanism requires exposing the sample under light to significantly accelerate the nanotube oxidization, while the redox reaction needs not. More discussions on these two mechanisms are stated in the next chapter.

The pH response of SDBS/SWNT suspension we observed is puzzling. The SDBS/SWNT shows less sensitivity than SDS/SWNT in both absorption and fluorescence spectra. We deduce it is possibly because the benzene side in SDBS molecule can refill electrons to the depleted valence band in the acidic condition. The
fluorescence intensity of SDBS/SWNT increases firstly and decreases afterwards as pH is raised. The reason is not understood yet.

4.4.4 The Pyrene Side Effect on the PSMA/SWNT Suspensions

The bundles result in the peak broadening in the absorption spectra since the tube-tube interaction introduces an electronic dispersion to the SWNTs. Therefore, Fig. 4.11a indicates a better dispersion as pyrene content increases. Fig. 4.11b and Fig. 4.11c exhibit the increasing fluorescence as pyrene content increases and the increase is fastest for the smallest diameter tubes. The bundle formation could cause a non-radiative recombination because of the presence of metallic tubes. However, whatever the (n, m) species are, they are considered to have equal chance to aggregate; therefore the trend shown in Fig. 4.11c appears not solely due to the bundles. We attribute electron donation from the pyrene side a possible reason for the special diameter dependence: The larger diameter tubes of narrower band gap tend to more easily accept the donation. The donated electron in the valence band decreases the emission efficiency, so that we observed less fluorescence increasing in the longer wavelength region as pyrene content increases.
Chapter 5 Probing SWNT Electronic Structure via Redox Chemistry

5.1 Motivation

The absolute energy levels of SWNTs are important physical quantities of great interest. Several groups have reported their approaches via theoretical studies\textsuperscript{64-66} and experimental measurements.\textsuperscript{67-69} However, there is no consensus among them so far. Since the redox reaction discussed in Chapter 4 is determined by Fermi energy $E_F$, it may provide an opportunity to probe the absolute energy levels of SWNTs by measuring this redox chemistry.

The O$_2$/H$_2$O redox pair in the SDS/SWNT dispersion can be expressed as:

$$4H^++O_2+4e^- \rightarrow 2H_2O \quad (5.1)$$

Let the electrode potential be $\varphi_1$, which can be derived simply from the Nernst equation:

$$\varphi_1 = \varphi_0 - \frac{0.0591}{n} \log \left( \frac{[Ox]}{[Red]} \right), \quad (5.2)$$

where $\varphi_0$ is the formal electrode potential, $n$ is the number of electrons transferred in the half reaction, $[\text{Red}]$ is the concentration of oxidizing agent, and $[\text{Ox}]$ is the concentration of reducing agent. In this specific case, the Nernst equation can be rewritten as:

$$\varphi_1 = \varphi_0 - \frac{0.0591}{4} \log \frac{1}{[H^+]^4 pO_2} \quad (5.3)$$

By substituting $\varphi_0 = 1.229 V$, $[H^+] = 10^{-nH}$ and $pO_2 = 0.2\text{bar}$,
\[
\phi_1 = 1.229 - 0.0591 \log \frac{1}{(10^{-\phi_1})^4 \times 0.2} = 1.22 - 0.06 \cdot \text{pH}
\] (5.4)

Due to the abundance of the dissolved O\textsubscript{2} and the solvent H\textsubscript{2}O, the chemical potential of electrons in the dispersion \(\phi\) is determined by the O\textsubscript{2}/H\textsubscript{2}O redox pair, therefore \(\phi = \phi_1\).

Assuming electronic equilibrium in the dispersion, the Fermi energy of tubes would align with the chemical potential of the suspension, thus the Fermi energy of the tubes can be expressed as:

\[
E_f (\text{eV}) = -(4.44 + \phi) \quad (5.5)
\]

where 4.44 (V) represents the absolute standard potential of the hydrogen electrode (NHE), and \(\phi\) is electrode potential of this reaction vs. NHE. By substituting \(\phi = \phi_1\), we obtain

\[
E_f (\text{eV}) = -(4.44 + \phi_1) = -(5.66 - 0.06 \cdot \text{pH}) \quad (5.6)
\]

This equation indicates the Fermi energy \(E_f\) of this SWNT aqueous solution can be tuned by changing pH. Moreover, the absorbance in the NIR absorption spectra indicates the electron occupation status at the band edge in the E\textsubscript{11} transition process, while the Fermi-Dirac distribution \(f(E) = \frac{1}{1 + e^{(E-E_\text{F})/kT}}\) indicates the electron occupation probability at energy level \(E\). This probability is significantly affected when the \(E_f\) shifts if the energy of the electron is close to \(E_f\). All these above facts offer us a possibility to approach \(E_{\text{v1}}\) of
SWNT (n, m) species by measuring the SDS/SWNT NIR absorption spectra in different redox levels.

As described in Chapter 4, two mechanisms can contribute to the absorption bleaching as pH is raised. In order to calculate the absolute energy of the first valence band edge (E_v1) via the redox reaction, it is necessary to experimentally exclude the endoperoxide formation. However, as produced SDS/SWNT dispersion is not stable under high temperature, avoiding endoperoxide by simply heating may introduce errors to the experiment. We design a new method to remove the endoperoxide defects on the SWNT side walls.

5.2 Experimental Methods

10ml 1wt% SDS solution and 4mg raw HiPCO SWNTs were mixed and heated under Ar at 80°C for 4h to clear the oxygen in the starting material. Afterwards, the mixture was sonicated in an ice-water bath Ar for 1h with ~5W power following a 10 min centrifugation treatment at 16400g to remove the insoluble material. We expect that there is no redox reaction or endoperoxide formation in the SDS/SWNT dispersion right after this step. The product is separated into several equal volumes and the pH is modified to different values by adding the same amount of HCl or NaOH solution. The samples were incubated for one week or even more with air admitted to allow the completion of the redox reaction.
5.3 Results

The black curve in Fig. 5.1 was obtained from the sample right after the 10min centrifugation. Compared to the spectra of SDS/SWNT obtained from the traditional method described in Chapter 4 (red curve), we claim that the two proposed reactions do not affect the SWNT suspension system after the special sonication and centrifugation treatments since the black curve exhibits much more resolved peaks at longer wavelength, which behaves as ~pH12, which indicates that the O$_2$ has been desorbed.

![Figure 5.1 Absorption spectra of SDS/SWNT obtained from thermal desorption of endoperoxide (black curve) and traditional method (red curve)](image)

One concern is that the carbon endoperoxide may compete with the redox reaction during the incubation with air addition. We did an experiment to look into this possibility. Firstly, the pH of the SDS/SWNT suspension was adjusted to 3 immediately after the 1h sonication step. The suspension was then separated into two equal volumes. Let one
sample sit under room light and the other in the dark. Pure oxygen with the same gas flow was introduced to the two samples for 1h following the overnight incubation. The spectra of the two samples (Fig. 5.2) express the same bleaching after this process. As mentioned in Chapter 4, the formation of endoperoxide requires light while redox reaction needs not; therefore we can conclude redox reaction occupied the suspension during the incubation.

**Figure 5.2** Test of the endoperoxide formation effect during the incubation

The NIR absorption spectra (Fig. 5.3) were obtained from samples of different pH after soaking for one week. The spectroscopic parameters were chosen to be the same as described in Chapter 4. The labeled peaks P3, P4, P5, P6, P8 and P9 correspond to SWNT (n, m) species: (7, 5), (10, 2), (9, 4), (12, 1), (10, 5), and (9, 7). This figure exhibits the same trend as Fig. 4.7a, namely that the absorbance increases with increasing
pH and the increase is faster for the larger diameter tubes. However, Fig. 5.3 exhibits consistently more structure than Fig. 4.7a.

**Figure 5.3** NIR absorption spectra of the SDS/SWNT suspension in different pH environments. The labeled peaks correspond to SWNT (n, m) species: (7, 5), (10, 2), (9, 4), (12, 1), (10, 5), and (9, 7).

The absorbance of the labeled semiconducting tubes in Fig.5.3 are plotted as a function of $E_f$ (markers in Fig. 5.4), where $E_f$ (eV) can be obtained from Eq. (5.6). In an ideal model, where the instrumental error, thermal effects and interaction with the suspension environment is neglected, and only the semiconducting $E_{11}$ transition is considered, the absorbance ($\text{abs}$) for a specific (n, m) species should obey:

$$\text{abs}=f(E_{\nu 1})(1-f(E_{c1})) \cdot A,$$  \hspace{1cm} (5.7)
where $A$ is a constant. The minimum $0$ appears when $f(E_{v1})=0$ or $f(E_{c1})=1$, i.e.

$$E_f \ll E_{v1}. \text{ And the maximum is } \left(\frac{1}{1+e^{(E_{v1}-E_{c1})/2kT}}\right)^2 \text{ obtained while } \frac{d\left[f(E_{v1})[1-f(E_{c1})]\right]}{dE_f} = 0,$$

i.e. $E_f = \frac{E_{c1}+E_{c1}}{2}$.

![Figure 5.4](image)

**Figure 5.4** Repotting for labeled peaks in Fig. 5.3 as a function of $E_f$, which are shown as markers. The curves are fitting based on Eq. (5.9).

Nevertheless, the ideal model does not fit the experimental absorption data, i.e. the experimental minimal absorbance is not $0$. In our approach, based on the experimental absorption data, we assume the absorption process yields:

$$f(E_{v1})(1-f(E_{c1})) = \frac{\text{abs-min}}{\text{max-min}}, \quad (5.8)$$

where max and min represent the two absorption extremes for each peak. By substituting

$$f(E_{v1}) = \frac{1}{1+e^{(E_{v1}-E_f)/kT}} \quad \text{and} \quad f(E_{c1}) = \frac{1}{1+e^{(E_{c1}-E_f)/kT}},$$

we rewrite the above equation:
\[
\text{abs = min + (max-min) } \frac{1}{1 + e^{(E_{v1} - E_g)/kT}} \left(1 - \frac{1}{1 + e^{(E_{v1} + E_g)/kT}}\right), \quad (5.9)
\]

Here \(E_g\) is the band gap of a specified tube, which can be obtained from

\[E_g = \frac{hc}{\lambda g} = \frac{1240 eV \cdot nm}{\lambda}.\]

\(\lambda\) is the corresponding absorption wavelength in Fig. 5.3. The curves in Fig. 5.4 are obtained by fitting Eq. (5.9), where \(T\) is set to the room temperature 298K and \(\lambda\) (nm) is 1020.8, 1052.9, 1106.8, 1170.7, 1248.9 and 1319.6, respectively.

Table 5.1 shows the parameters obtained from the fitting.

<table>
<thead>
<tr>
<th>(n, m)</th>
<th>(E_{v1}) (eV)</th>
<th>max</th>
<th>min</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3: (7, 5)</td>
<td>-5.357 ± 0.007</td>
<td>0.491 ± 0.003</td>
<td>0.413 ± 0.003</td>
</tr>
<tr>
<td>P4: (10, 2)</td>
<td>-5.347 ± 0.007</td>
<td>0.504 ± 0.004</td>
<td>0.398 ± 0.004</td>
</tr>
<tr>
<td>P5: (9, 4)</td>
<td>-5.334 ± 0.007</td>
<td>0.569 ± 0.006</td>
<td>0.392 ± 0.006</td>
</tr>
<tr>
<td>P6: (12, 1)</td>
<td>-5.327 ± 0.010</td>
<td>0.619 ± 0.011</td>
<td>0.392 ± 0.011</td>
</tr>
<tr>
<td>P8: (10, 5)</td>
<td>-5.279 ± 0.009</td>
<td>0.724 ± 0.016</td>
<td>0.393 ± 0.012</td>
</tr>
<tr>
<td>P9: (9, 7)</td>
<td>-5.276 ± 0.015</td>
<td>0.721 ± 0.025</td>
<td>0.388 ± 0.019</td>
</tr>
</tbody>
</table>

5.4 Discussion

The \(E_{v1}\) values of the labeled peaks are around 5.3eV, increasing from -5.36eV to -5.28eV. Since the diameter relation of the six peaks is (7, 5) = (10, 2) < (9, 4) = (12, 1) < (10, 5) = (9, 7), and the chiral angle is (7, 5) > (10, 2) and (9, 4) > (12, 1), the results indicates the
diameter and chirality dependences: As diameter increases, the \( E_{v1} \) increases and the tube of smaller chiral angle tends to have larger \( E_{v1} \). This conclusion is consistent with some of the literature but disagrees with others.

However, the fitting quality is not satisfactory. The fitting function follows the P3 and P4 nicely, but way off for P8 and P9 since the widths of the original absorption data (markers in Fig. 5.4) are broadened. If \( T \) in Eq. (5.9) is not set as 298K, but left as a variable during the fitting process, the fitted curves follow the original absorbance data perfectly, but the \( T \) values are unreasonable, even 800K for P9. The origin of the low quality fitting could be:

1) The apparent pH dependence of baselines

A pH dependent background can be observed in Fig. 5.3: As pH increases, the background increases, where the lifting is faster at longer wavelength. To figure out the effect of these baselines to the fitting quality, we firstly empirically approach the baselines (dash dots in Fig. 5.5) by applying the function \[ \sum_{b=1}^{2} A(\lambda - c)^b, \] where \( A, c \) and \( b \) are constant, and \( \lambda \) is the wavelength.
After simply subtracting the baselines from the original absorption spectra, we obtained flatter new absorption spectra (Fig. 5.6a). The labeled peaks were again fitted by applying the Eq. (5.9). The fitting quality is still unsatisfactory (Fig. 5.6b). Perhaps it should be attributed that the empirical baseline functions does not precisely describe the real physics behind. Or the other two possibilities discussed in the following contribute.
2) Multiple (n, m) species in the dispersion

Though the assigned species for each absorption peak is the dominant species, each peak is in fact the absorbance summation of several (n, m) species, therefore it is unfair to choose one (n, m) species to represent one peak in our model. Moreover, the tube diameter formula $d_i = \left(\frac{3^{1/2}}{\pi}\right) a_c \left(m^2 + mn + n^2\right)^{1/2}$ indicates that more (n, m) species share the same diameter at longer wavelength region. Therefore, neglecting of the multiple (n,
m) species effect, especially for longer wavelength region, could result in a worse fitting quality for the tubes of larger diameters, such as P8 and P9.

3) Broadening of VHS

The SWNT VHS can be perturbed by thermal effect and dynamic interaction with SDS and H\textsubscript{2}O molecules or external tubes. The VHS broadening effect could cause the transition in fact appears at a shifted location with a certain probability, therefore affect the fitting quality somehow.

The fitting quality can be improved by solving the three problems listed above respectively:

1) Plasmonic excitation of the metallic tubes was discovered to contribute to the increasing baselines.\textsuperscript{71} Recently, ultracentrifugation technique can be applied to separate the metallic and semiconducting tubes apart because of their distinct densities in the liquid gradient.\textsuperscript{72} If plasmonic excitation is indeed the origin of the baseline pH sensitivity, we could observe relatively low and insensitive baselines in the semiconducting enriched SWNT dispersion. This separation work is ongoing recently.

2) SWNTs containing less (n, m) species may result in a more reasonable result in our model since each peak could be constructed by almost one species in the absorption spectra. People in Dr. Yuan Chen’s group in Nanyang Technological University (NTU)
are able to produce SWNTs with less \((n, m)\) species. They were asked to repeat the experimental procedure established in our group. We are looking forward to see how pH affects their SDS/SWNT suspensions.

3) The VHS broadening effect is expected to influence the fitting quality to a degree. This effect could be simulated by Gaussian distribution. We are currently building up a theory to approach this electron energy perturbation. We expect this simulation applying in our fitting model improves the fitting equation.
Chapter 6 Optical Properties of Double-walled Carbon Nanotubes

6.1 Motivation and Background

DWNTs have attracted much attention during the past several years as a special class of carbon nanotube materials.\textsuperscript{73-79} DWNTs are expected of higher thermal and chemical stability compared to SWNTs, meanwhile they are the thinnest member of MWNTs, which have a preferred structure for investigating interlayer interaction.\textsuperscript{80} So far, people have paid many efforts in making applicable use of this material, however, the optical physics, especially the interlayer interaction of DWNTs, is not well understood yet. Several papers claimed they observed the emission from the inner layers of DWNTs.\textsuperscript{80-82} Nevertheless, in theory the excited electrons from the inner tube is expected to transfer to the outer tubes since the band gap of the outer shell is narrower than the inner shell. We collaborate with Dr. Jie Liu at Duke University to study the optical properties of DWNTs. The collaborators prepared the raw DWNTs, purified DWNTs, and functionalized DWNT suspensions. We dispersed the raw tubes and purified tubes in aqueous environment. The functionalized DWNTs were processed by us via sonication and centrifugation treatment for better dispersion. Model NS1 NanoSpectralyzer was applied for DWNT spectroscopy studies in our lab.

6.2 Experimental Methods

In order to study the optical properties of DWNTs, a well dispersed DWNT suspension has to be obtained first. People in Dr. Liu’s group produced raw DWNTs by carbon
monoxide chemical vapor deposition (CO-CVD) method using binary catalysts Co/Mo supported on MgO. The purified DWNTs were obtained after a two-step purification process. The raw DWNTs were firstly oxidized to remove the carbonaceous impurities and chemically active SWNTs, following the addition of the HCl water solution to remove the support MgO and the catalyst Co/Mo. More than 95% double-walled tubes were obtained in the purified DWNTs after the purification process. We prepared SDBS/DWNT suspensions following the same method described in Chapter 4 using their raw DWNTs and purified DWNTs as a starting material, respectively. The spectrometer parameters were set the same as in Chapter 4.

The five water soluble DWNT-COOH samples are prepared by the collaborators following this method: 0.01/0.03/0.05/0.10/0.15g KMNO₄ was firstly dissolved in 20ml H₂SO₄ solution. Afterwards it was dropwise added into the mixture of 5mg purified DWNTs and 20ml 0.5M H₂SO₄ solutions while sonicating. After 5h sonication, the product was mixed with 30ml concentrated HCl and heated to boil for 20mins or longer until the KMNO₄ turned to be dark pink. Right after that, the solution was filtrated and washed with 40ml KOH for 4 times. In order to better disperse the tubes, these five samples were processed with a 1h sonication treatment with ~5W power following 2h centrifugation in our lab.

They also produced the C₁₂H₂₅ drafted DWNT in tetrahydrofuran (THF). Firstly the collaborators added the purified DWNTs (20mg), naphthalene(30mmol) and slight excess
of lithium to a dry 100 ml, three-neck, round-bottomed flask followed by the addition of THF(50ml) under an atmosphere of argon to allow the reaction to carry out. The mixture was then sonicated at room temperature for 4h. Afterwards 4.2 ml iodododecane was added to the solution followed by the sonication at room temperature for another 3h. Next, the product was quenched by slow addition of ethanol followed by water and acidification with 10% HCl, filtered through a 0.45µm polytetrafluoroethylene membrane, and washed successively with water and ethanol at the final step. The C_{12}H_{25} drafted DWNT were again processed with sonication and centrifugation treatment in our lab for better dispersing.

In order to test the spectra of DWNT-COOH and DWNT-C_{12}H_{25}, the spectrometer parameters were set to integration time 100ms for absorption spectra and 16000ms for fluorescence spectra. The average was chosen to be 5 for both.

6.3 Results and Analysis

6.3.1 NIR Spectra of DWNT Dispersion

We started with the NIR fluorescence spectra of SDBS/purified DWNT (Fig. 6.1). These spectra reveal that only a few structures dominate the semiconducting nanotube distribution in the pure DWNT sample. This NIR spectrometer can detect the emission in the region of 900-1600nm. Since the diameter of the DWNT outer shells is around 1.6nm, which emits at ~2000nm, this instrument is not able to detect the emission from the outer
tubes. Therefore, the emission can be attributed to either inner layers of DWNTs or the less than 5% SWNT content.

![Florescence spectra of SDTS/pure DWNT suspension excitated at (a) 658nm and (b) 785nm. The blue curves are the measured spectra and the red one is simulated spectra. The basis functions of individual (n, m) species are indicated.](image)

**Figure 6.1** Florescence spectra of SDBS/pure DWNT suspension excitated at (a) 658nm and (b) 785nm. The blue curves are the measured spectra and the red one is simulated spectra. The basis functions of individual (n, m) species are indicated.

The global fit was applied to find out the (n, m) distribution in the purified DWNTs. The E_{11} position of the SDBS/SWNT template (supplied by fitting software) was manually red shifted for 30cm\(^{-1}\). We allowed 0.1% variation for the E_{11} and E_{22} position and 5% variation for E_{11} width, E_{22} width, E_{11} shape, excitation profile, and laser ratio per fitting round (Further description seen in Appendix B). The simulated spectra and individual (n, m) components were obtained after more than 3 rounds, which are also plotted in Fig.6.1. A graphene sheet map of possible nanotube structures with (n, m) values is shown in Fig.6.2, which indicates that the sample diameters cover the range of 0.68-1.25nm and the average is 0.86nm. The most abundant structures are (6, 5) and (10, 2) corresponding to 0.757nm and 0.886nm in diameter. The collaborators discovered that the inner-tube diameters, measured by HRTEM, are mainly 0.76nm and 0.90nm, which was confirmed
by their Raman analysis. This global fitting result surprisingly agrees very well with the HRTEM and Raman results.

Figure 6.2 (n, m) distribution of fluorescence spectra of SDBS/DWNT suspension. The thickness of each hexagonal cell border represents the content for the enclosed (n,m) structure.

Figure 6.2 (n, m) distribution of fluorescence spectra of SDBS/DWNT suspension. The thickness of each hexagonal cell border represents the content for the enclosed (n,m) structure.

However, Fig. 6.3 exhibits the NIR spectra of SDBS assisted raw DWNT (containing a fair amount of SWNT impurities) and pure DWNT (containing <5% SWNTs) dispersions. After the purification process, the absorption is broadened and the emission decreases dramatically. Importantly, the absorption and fluorescence peaks of the two suspensions appear at the same positions.

The raw DWNTs exhibit better resolved absorption spectra than the purified DWNTs, which implies two possibilities. One is that the well resolved spectra structure are due to the fairly amount of SWNT content, and the peaks disappear in the pure DWNT sample simply because of the removal of SWNTs. The other possibility is the peaks of the raw
DWNTs are from excitation of the inner tubes. The double-walled tube structures are damaged in the purification process, which results in the peak broadening.

The single-walled tubes are expected to emit at slightly different positions compared to the same (n, m) inner tubes if the inner tubes really fluoresce. However, since the peak positions of the raw DWNTs and pure DWNTs are consistent, this seems that the emissions of the two samples are both from the SWNT impurities.

![NIR absorption and fluorescence spectra](image)

**Figure 6.3** (a) NIR absorption and (b, c) fluorescence spectra of SDBS assisted purified DWNTs and raw DWNTs dispersions
6.3.2 NIR Spectra of Functionalized DWNTs

To address the problem “whether the inner tubes fluoresce”, collaborators in Dr. Liu’s group prepared two groups of functionalized pure DWNT dispersions. We expect the structures of SWNT impurities are destroyed in the functionalization process, and hence the obstacle of SWNT emission can be avoided. Moreover, if the covalent functionalization is in a good control, only the DWNT outer wall is modified while the structural integrity of the inner tubes is preserved. Therefore, any detected emission from that suspension is only from the inner tubes.

Fig. 6.4a is the photo of the five DWNT-COOH samples obtained right after the sonication and centrifugation process in our lab. Fig. 6.4b, Fig.6.4c and Fig. 6.4d are absorption spectra, fluorescence spectra excited at 658nm and 785nm, respectively. The numbers labeled on the test tubes and indicated in the spectra denote the concentrations of KMNO₄ in H₂SO₄ are 0.01, 0.03, 0.05, 0.10 and 0.15g/20ml at the very beginning step. Fig. 6.4a and Fig. 6.4b show that as KMnO₄ concentration increases, the solution concentration increases which indicates an increasing functionalization level. The 0.01g sample was weakly functionalized since the solution is transparent (Fig. 6.4a and b), while 0.1g and 0.15g samples achieved a high oxidization degree since the concentrations of these solutions are very high (Fig. 6.4a and Fig. 6.4b). Therefore, we should have obtained appropriate samples among the five, neither insufficiently nor excessively functionalized. Fairly strong emission, comparable to SDBS/pure DWNT suspension, was expected to be detected, but none of the five samples fluoresce (Fig. 6.4c and d) even
though the integration time was set to 16000ms, 160 times of the parameter setup in the previous chapters.

Figure 6.4 (a) the photo of the five DWNT-COOH samples and (b) absorption spectra, (c) fluorescence spectra excited at 658nm and (d) 785nm

Since –COOH is an electron withdraw group, which could result in the fluorescence quenching. Therefore, DWNT-C_{12}H_{25} dispersion in THF was prepared instead, where -C_{12}H_{25} is a neutral group. Fig 6.5(a) is absorption spectra of DWNT-C_{12}H_{25} and the control sample SWNT-C_{12}H_{25}. The fluorescence spectra of DWNT-C_{12}H_{25} (Fig.6.5b and
Fig. 6.5c) show finer structure than the control sample SWNT-C_{12}H_{25}. However, the emission is still very weak, only about 0.3% of the SDBS/pure DWNT fluorescence.

![Graphs showing absorption and fluorescence spectra](image)

**Figure 6.5** (a) absorption and fluorescence spectra excited at (b) 658nm and (c) 785nm of DWNT-C_{12}H_{25} and the control sample SWNT-C_{12}H_{25}.

### 6.4 Discussion on Whether Inner Tubes Fluoresce

Though several published papers claimed DWNTs fluoresce, they didn’t take a serious account of the fluorescence emitted from the small SWNT containment mixed in DWNTs. One paper explained the emission signal they obtained is from the inner layers of DWNTs but not SWNT impurities because the high temperature burns the SWNTs in the growth process. But in fact, the high temperature can not kill all the SWNTs. The other
paper argued one would need to assume that the effective quantum efficiency (QY) is over an order of magnitude higher than that of pure SWNT suspensions if the emission from the DWNT suspension is not due to the inner tubes. However, it is unfair to make such a comparison since the two types of tubes were produced with different (n, m) distributions, different defects and impurities.

The research ongoing in Dr. Liu's group supports the conclusion that the inner tubes do not fluoresce. People in Dr. Liu's lab carefully compared the kinetics of diazonium salts reacted HiPCO SWNTs with pure DWNTs. NIR Fluorescence signals from HiPCO tubes and pure DWNTs both dramatically decreased to zero in a very short time scale after the addition of diazonium. If the emission of pure DWNTs is from the inner tubes, it is expected to show a slower kinetics because of the protection from out tubes. Another experiment was designed to further study this problem. They tested mechanical properties of the emitted tubes in the pure DWNTs and HiPCO SWNT suspensions. Comparison reveals that the emitted tubes in these two samples have the same persistence length. Since DWNTs' stiffness is stronger than SWNTs, it is more likely that pure DWNT emission is from the SWNT impurity.

Our results shown in Section 6.3.1 and 6.3.2 also support a “no” answer to this problem. To further clarify it, we propose two experiments here:
1) Density gradient ultracentrifugation is reported to succeed in SWNT separation. This technique could separate the tubes with the significant difference in diameter and density. We expect this method can be used to separate the raw DWNTs into two samples: DWNTs with very low SWNT content, and SWNTs with a low fraction of DWNTs. Therefore the fluorescent wavelength and efficiency could be compared to identify the origin of the emission light.

2) We are currently building a new setup in Dr. Eric Stinaff’s lab. We expect to obtain the spectra extended to 2000nm or even more there, so that the detection region can cover emission from both inner tubes and outer tubes. These advanced instruments open a door for us to look into the possible energy transfer in the DWNT emission process. Recently, we have collected some primary data from his lab (Fig. 6.6).

The experimental setup for absorption spectra is shown in Fig. 6.6. The specialty of this setup is that InSb detector in the light path can extend the detection range to ~2000nm currently. We tested the absorption spectra of SDBS/raw SWNT and SDBS/raw DWNT D$_2$O dispersions. The black curves, which exhibited weak structures, in Fig.6.6a and Fig.6.6b are obtained from the new setup. However, the noise signal ratio is large compared to the feature obtained using the Model NS1 spectrometer (red curves). In the future, we are going to increase the experimental parameters such as integration time to decrease the noise ratio. Also we will try to broaden the detection range even more.
Figure 6.6 (a) Experimental setup (b) Absorption spectra of SDBS/SWNT in D₂O obtained from Model NS1 spectrometer (red curve) and from the new setup (black curve) (c) Absorption spectra of SDBS/raw DWNT in D₂O obtained from Model NS1 spectrometer (red curve) and from the new setup (black curve)
Chapter 7 Conclusion

First, we obtained SWNT spectra in the bulk suspension following the reported method and gained specified assignment \((n, m)\) species for raw HiPCO SWNTs from the global fit program. Afterwards, we studied how the surfactant/SWNT suspension is affected by sonication temperature, centrifugation time, pH, and the surfactant structures. The results indicate that higher sonication temperature decreases the concentration of the dispersed tube. The SDBS/SWNT is more stable than SDS/SWNT under centrifugation. Less \(H^+\) or \(O_2\) in the SWNT suspension were proved to increase the optical spectra signal and the larger diameter tubes are affected more. Meanwhile the pH sensitivity phenomenon is reversible. Two mechanisms to explain this phenomenon proposed in the literature were discussed. In the PSMA-pyrene/SWNT suspensions, we observed the pyrene dependence phenomenon, which is reversed to the observation in the pH titration experiment. We attribute the electron donation a possible mechanism.

Further we describe a new method to probe the absolute energy levels of SWNTs. The first conduction band edge of the semiconducting SWNTs was obtained via measuring the redox chemistry in the tube dispersion system. The \(E_{v1}\) values we obtained showed consistent trend as some of the published papers. However, the results need more modification since the fitting quality is not satisfactory. Plasmatic excitation, multiple \((n, m)\) species and broadening of VHS are the three possible factors. We proposed the corresponding methods to address these problems in the future studies.
Finally, the optical property of DWNTs was investigated collaborating with people in Dr. Jie Liu’s group in Duke University. Comparison between the absorption and fluorescence spectra of raw DWNT and pure DWNT dispersion and the studies of functionalized purified DWNTs optical spectra indicate that the inner tubes can not fluoresce. This conclusion is contrary to the published literature. We consider the ultracentrifugation technique and the spectra of extended region can lead to the final answer.
Reference


40. Barkauskas, J. Biological Applications of Functionalized Carbon Nanoparticles. (Springer Netherlands, 2006)


## Appendix A Table of Van Hove Optical Transitions for Semiconducting SWNTs

Table A1. Structures and first and second van Hove optical transitions for semiconducting SWNT structures with diameters between 0.48 and 2.0 nm. (After R. Bruce Weisman).

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99
Appendix B How to Find Out the SWNT \((n, m)\) Species Distribution from the Global Fitting

The global fitting methodology is explained in the manual of the Model NS1 NanoSpectralyzer. The general approach to spectral fitting with a new sample is first to load the template intended for or most to that surfactant by entering its path and filename into the box and selecting the **Import** button to load its parameters (Figure S1).

![Global Fit Parameters](image)

**Figure S1** Global fit parameters (After Applied NanoFluorescence, LLC)
The lower right quadrant shows two tables. When one template is selected, a list appears below showing its current value or values. Note that any parameter may be manually revised by an entry into the appropriate field. At the end of a fit, the parameter called **Solution Vector** contains the deduced emission amplitudes of all \((n, m)\) species in the spectral basis set. The fit analysis should be run with some of the below parameters allowed to vary.

**E_{11} Position** is the set of specific \((n, m)\) peak frequencies in cm\(^{-1}\), for the E\(_{11}\) emission features. These values will shift with the surfactant and, perhaps, the sample preparation protocol that is used. When applying a set of frequencies that are appropriate for the surfactant, only slight variations (within ca. 0.2\%) should be permitted. Larger tolerances may lead to misidentification of some peaks.

**E_{22} Position** is the set of specific \((n, m)\) peak frequencies in cm\(^{-1}\), for the E\(_{22}\) absorption features. These values are less critical than the E\(_{11}\) positions and may be safely allowed to vary by ca. 0.5\%.

**E_{11} Width** is the set of specific \((n, m)\) peak widths in cm\(^{-1}\) for the emission features. Variations of ca. 10\% per round may be safely allowed.

**E_{22} Width** is the set of specific \((n, m)\) peak widths in cm\(^{-1}\) for the absorption features. Variations of ca. 5\% per round are safe.
**$E_{11}$ Shape** is a set of $(n, m)$-specific ratios of Lorentzian to Gaussian character used in modeling the emission spectrum. It is possible to allow variations of ca. 30% in these parameters.

**Shared $E_{11}$ Width** is a single peak width in cm$^{-1}$ used to describe all of the emission features (as an alternative to $(n, m)$-specific peak widths). Selecting a variation in this parameter disables variations of the $E_{11}$ Width. A 20% variation range can be allowed in exploratory fitting.

**Shared $E_{11}$ Shape** is a single ratio of Lorentzian to Gaussian character used in modeling all of the peaks in the emission spectrum (as an alternative to $(n, m)$-specific peak shapes). Selecting a variation in this parameter disables variations of the $E_{11}$ Shape.

**Excitation Profile** is a set of common parameters used in modeling the vibronic structure of the $E_{22}$ absorption features. This parameter can be varied by ca. 20% during exploratory fitting.

**Laser Ratio** is a single parameter involving the relative laser powers and optical efficiencies at the two excitation wavelengths. A variation limit of ca. 5% per fitting round is recommended.
After the template is imported and the parameter variation tolerances are set up, the fitting is started by clicking **OK**. Clicking the **Calculate** button (Fig. S2) again will cause fitting to continue for another round, with all parameters starting with their last adjusted values. The MSD, which indicates the relative standard deviation between the original spectra and simulated spectra, is generally possible to reduce to 0.005.

![Figure S2 Experiment and simulations (After Applied NanoFluorescence, LLC)](image)

**Figure S2** Experiment and simulations (After Applied NanoFluorescence, LLC)

After a satisfactory fitting is obtained, the data can be saved by clicking **Save Results**. The data of the analysis appear in an Origin project composed of several worksheets and graphs. The names and contents are:

**Fluor_658/Fluor_785**
This is a graph of the fluorescence spectrum measured with the excitation laser, overlaid with the computed spectral simulation obtained from nonlinear least-squares fitting with individually varied \((n, m)\) species amplitudes. Spectra of these individual \((n, m)\) components are also plotted (solution vectors).

**Graphene sheet**

This is a grapheme sheet plot of the relative abundances of various semiconducting \((n, m)\) species in the sample. The thickness of the hexagonal border surrounding an \((n, m)\) label is proportional to the deduced relative abundance, which is again found with the assumptions of equal fluorescence quantum yields and absorptivities per atom among the species.