Degradation and exciton energy transfer studies in single-walled carbon nanotube bundles

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To my parents and my brother
Abstract

Single walled carbon nanotubes (SWNTs) due to their unique optical behavior, large surface area, robust mechanical strength and electrical properties make them one of the ideal candidates for sensing and opto-electronic applications. In this work, we explore the energy transfer (exciton energy transfer-EET) phenomena occurring between nanotubes in bundles, using resonance Raman spectroscopy.

Exciton energy transfer (EET) occurs naturally in plant photosystems, where the sun light is harvested to produce high energy hydrocarbons and oxygen as a by-product. Thus making EET, one of the fundamental processes for the very basis of life on this planet. By using photoluminescence (PL) spectroscopy techniques, it was discovered that semi-conducting SWNTs mimics nature, by exhibiting EET. EET is known to occur between semi-conducting SWNTs, where upon photoexcitation, energy is transferred in a non-radiative fashion from a smaller diameter (large band gap), donor (D) nanotube to relatively larger diameter (smaller band gap), acceptor (A) nanotube, via dipole-dipole interaction. Some of the necessary conditions for EET to occur are bundling (the close proximity between donor-acceptor nanotubes is essential, ~ < 10 nm), spectral overlap of photoemission of donor and photoexcitation of acceptor and dipole orientation. PL methods are however not ideal for studying metallic SWNTs. There are no reports on EET between metallic SWNTs. To overcome this issue we investigated for potential EET observation in SWNT bundles using resonance Raman spectroscopy.

For a mixed (metallic and semi-conducting) SWNT sample, we observed EET for both metallic and semi-conducting SWNTs from smaller diameter, donor SWNTs to larger diameter, acceptor SWNTs by studying the changes in the Raman radial breathing modes (RBM) upon changing the
laser excitation power (changing power density) using two different lasers (at 1.96 eV and 2.33 eV). The observed changes in the extent of EET (changes in the Raman RBM spectra), with changing laser power can be attributed to differences in the extent of molecular photodesorption occurring with changing laser power. The EET pathway observed via Raman spectroscopy for SWNTs is different from the EET events observed using PL methods. Here, we propose an alternative EET pathway, where EET is ‘phonon-assisted’, i.e. exciton energy transfer (EET) occurs after energy loss to phonons (Stokes Raman).

Because EET for SWNTs occur between SWNT bundles, one must be able to improve EET by improving inter-nanotube interactions. Here, we investigated the role of mild chemical cleaning procedures such as hydrogen peroxide treatment of SWNTs, on improvement of EET between SWNTs. We observed that both molecular photodesorption and mild chemical cleaning improves EET, by improving inter-nanotube interactions. This allowed us to appreciate the role of the environmental effects on EET between SWNTs.

With improving inter-nanotube interactions we found that the thermal conduction between the SWNTs also improved. We observed that the Raman G band frequency change due to sample heating reduced due to improved photodesorption.

On the other hand we have also studied enzymatic degradation of SWNTs using horseradish peroxidase (HRP) in the presence of hydrogen peroxide over a period of 30 days. Enzymatic degradation of SWNTs was observed for measurement made after 30 day treatment. A faster route for degradation is SWNT treatment with sulfuric/nitric acid mixture (acid mix treatment). We observed that acid mix treatment (strong chemical treatment) in conjunction with sonication yields faster degradation routes.
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**Figure 4.8:** Shows improvement (reduction) of $I_D/I_G$ upon 9M H$_2$O$_2$ treatment of SWNTs (bottom plots) when compared to those of untreated SWNTs (top plots). This is an indication of improvement of first order Raman scattering (G band intensity) upon 9M peroxide treatment, when compared to the D band intensity. It also indicates no breakdown of amorphous carbon with exposure to high power laser.

**Figure 4.9:** Raman G band spectra for (a) HNO$_3$ treated, (b) H$_2$SO$_4$/H$_2$O$_2$ treated and (c) thermally treated SWNTs. It shows that no change in the Raman G band line shape after exposure to high power laser (340 kW/cm$^2$) and the final measurements later at 3.3 kW/cm$^2$. Similar effect is seen for thermally treated SWNT sample. Upon thermal treatment, the G-band intensity increases. (Reprinted with permission from Yu, Z. et al. J. Phys. Chem. A, Vol. 104, No. 47 (2000). © (2000) The American Chemical Society)

**Figure 4.10:** Top left shows the peak fitted G band spectra of untreated SWNTs at 1.96 eV and 1.7 mW and bottom left is its corresponding Raman RBM spectra. Top right is the peak fitted G band of the 9M peroxide treated SWNT sample at the same 1.96 eV and 1.7 mW, power. The bottom right is the corresponding RBM spectra for the 9M peroxide treated SWNTs. The arrows indicate the relative changes in the RBM spectra of the 9M peroxide treated sample to the RBM spectra of the untreated SWNT sample. As seen, due to EET, the corresponding RBM signal for large diameter metallic M$_{11}$ improves. This translates to improvement in the G-band intensity (increased area under the asymmetric BWF fit) for the 9M peroxide treated SWNTs (top right) compared to G band for untreated SWNTs (top left).

**Figure 5.1:** Binding poses of (a) HRP, (b) MPO with carboxylated SWNTs. Fig: (c) is the peroxidase cycle for HRP and MPO (red pathway in acidic conditions in presence of Cl- ions for MPO). Fig: (c) is adapted from Veitch, N. C1. (Figures a, b and c are reprinted with permission from Kotchey. G. P. et al. Accounts of Chemical Research, 1770-178 (2012) Vol. 45, No. 10. © (2012) The American Chemical Society)

**Figure 5.2:** Optical image (left) shows degradation of SWNTs in the HRP + H$_2$O$_2$ SWNT suspension (in the red box) after 30 day period. The absorbance spectra to the right also shows corresponding drop in the absorbance value for HRP + H$_2$O$_2$ SWNT suspension (blue) when
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1. Background

This chapter gives a brief introduction to the structure of single-walled carbon nanotubes (SWNTs) and some of its properties along with its unique Raman response pertinent to the subsequent chapters in this work.

1.1 Introduction

Since the observations made by Iijima, S.\(^1\), for multi-walled carbon nanotubes and subsequent observations on single-walled carbon nanotubes by Iijima, S. \textit{et al.}\(^2\) and Bethune, D. S. \textit{et al.}\(^3\), carbon nanotubes has been a subject of extensive research for a wide range applications such as high speed electronics\(^4\) with high density integration\(^5\), optoelectronics\(^6\) and as sensors\(^7\) including potential bio-sensing of single cells\(^8\). These applications using carbon nanotubes is possible due its interesting material properties such as capacity for high carrier density\(^9\), long mean free path for charge carriers\(^10\), and a very unique optical response, dominated by its discrete optical excitonic\(^11\) transitions that are diameter dependent. It is necessary to study and understand the structure of carbon nanotubes to fully appreciate its optical and electronic response versatility.

1.1.1 Structure of SWNT, notations and nomenclature

Carbon nanotubes (1D) along with fullerenes (0D) and graphene (2D) are unique low dimensional incarnations of \(sp^2\) (C-C) hybridized graphite. Graphene, the 2D incarnation can be considered as a fundamental building material for fullerenes, carbon nanotubes and graphite (Figure 1.1)\(^12\). This also allows us to appreciate the how dimensionality difference leads to potential difference in electronic states vis-à-vis density of states (DOS) for each of these materials (Figure 1.1 (b)).
The material pertinent to this work is 1D single walled carbon nanotubes (SWNTs). SWNTs can...
be grown via various different processes including CVD, arc discharge methods to name a few\textsuperscript{13}. These can simply be visualized as seamlessly rolled up sheet of graphene (as shown in Figure 1.1). The carbon atoms in the SWNT lattice are $sp^2$ hybridized and are arranged in hexagonal, honeycomb fashion\textsuperscript{14}. There are many number of ways in which graphene could be rolled up (rolling up graphene of different lengths and at varying angles) to give rise to different SWNTs that are distinctly different from each other in terms of their properties.

Each SWNT can be uniquely described by so called circumferential vector or wrapping vector (AA’ in Figure 1.2),

$$C_h = na_1 + ma_2 \equiv (n,m) \quad (Eq:1.1)$$

Where $a_1$ and $a_2$ are unit vectors of the graphene lattice and $(n,m)$ are integer indices that uniquely identify and define the structure of SWNTs\textsuperscript{14}. From Eq: 1.1, we can therefore also establish the diameter($d_t$) for the SWNT.

$$d_t = \frac{|C_h|}{\pi} = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \quad (Eq: 1.2)$$

Where ‘$a$’ is the lattice constant of the honeycomb network ($a = \sqrt{3} \times a_{cc}$, $a_{cc} \cong 1.42$ Å, C-C bond length). The angle at which it is rolled up $\theta$, can also be calculated from Eq: 1.1.

$$\cos\theta = \frac{C_h \cdot a_1}{|C_h||a_1|} = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}} \quad (Eq: 1.3)$$

The value of $\theta$ is in the range, $0 \leq |\theta| \leq 30^\circ$. This is because of the hexagonal symmetry of the lattice. This angle, in other words can also be the tilt angle of the honeycomb, hexagons w.r.t. the direction of nanotube axis (nanotube axis is AA’).
Figure 1.2: Graphene sheeting showing the area to be rolled into SWNT (for a (5,3) SWNT) (between the dotted lines). Also indicated are the $a_1$, $a_2$ unit vectors. AA’ forming the nanotube axis for (5,3) SWNT. Here, the circumferential vector, $C_h = 5a_1 + 3a_2$, with a rolling angle of $\theta$. (Reprinted with permission from Charlier. J-C. et al, Rev. Mod. Phys., Vol. 79, No. 2 (2007). © (2007) The American Physical Society)

Figure 1.2, shows a typical graphene rolling scheme for explaining the indexing (n,m) for a given SWNT ((5,3) SWNT in this case).

1.1.2 Electronic structure of SWNTs

Understanding reciprocal space and electronic structure of graphene is necessary to fully appreciate the electronic structure of SWNTs. Graphene’s Brillouin zone is hexagonal with inequivalent vertices called K (and K’) point. High symmetry $\Gamma$ point is at the center and between the K and K’ point is the M point (as shown in Figure 1.3).
Simple tight binding model based calculation\textsuperscript{14} yields electronic energy dispersion of graphene in its reciprocal space (\textbf{Figure 1.4}), showing the most important characteristic feature of this dispersion, vis-à-vis Dirac cones at K and K’ points. At these points, we observe the valence and the conduction band touch each other (thus explaining the semi-metallic behavior of graphene). At the Dirac point (as shown in \textbf{Figure 1.4}), we observe linear dispersion behavior as electrons behave as massless Fermions\textsuperscript{15}.

\textbf{Figure 1.4:} Graphene electronic dispersion in the $k$ space. The zoomed in part at the K (and K’) points or the Dirac points, where the valence and the conduction band touch each other. (Reprinted with permission from Castro Neto et al, Rev. of Mod. Phys., Vol 81, No. 1, Jan-March (2009) 47-99 © (2009) The American Physical Society).

This electronic dispersion of 2D graphene can be used to understand $E$ vs $k$ for SWNTs.
By imposing periodic boundary condition on the electronic wave functions along the circumference of the SWNT, the electronic structure of SWNT can be obtained. This imposition of circumferential, periodic boundary condition, leads to discretization of states in the circumferential direction, resulting in reduction of phase space to just a series of lines (the so called ‘cutting lines’). The spacing of these cutting lines is inversely proportional to the diameter, \( d \), of the SWNT. The orientation of these cutting lines with respect to the Brillouin zone (shaded area in Figure 1.5) of graphene, depends on the circumferential vector or the wrapping vector, \( \theta \). In other words, the cutting lines can also be defined as zone-folded 1D Brillouin zone (of SWNTs) line segments, expressed in relation to their 2D Brillouin zone (of graphene) counterparts\(^{16}\). Samsonidze, G. G. \textit{et al}\(^ {16}\) is a good review source to understand the concept of cutting lines with respect of SWNTs.

When these cutting lines pass through the K (or K’) point (intersecting the Dirac cone, at the Dirac point), the nanotubes satisfy the condition of \([(2n+m)\text{mod}3=0]\). These SWNTs are metallic in nature, as their linear band structure does not have a ‘band gap’ at their Fermi level. When the cutting lines miss the K (or K’) point, it results in hyperbolic sub-bands with a band gap at their Fermi level. This conditions leads to semi-conducting behavior in SWNTs. There are two possible conditions leading to semi-conducting behavior; \([(2n+m)\text{mod}3=1]\) or \([(2n+m)\text{mod}3=2]\). This means depending on where the cutting lines pass through the Dirac cone, there are 3 possibilities:

a) \([(2n+m)\text{mod}3=0]\), leading to metallic behavior in SWNTs.

b) \([(2n+m)\text{mod}3=1]\), leading to semi-conducting behavior in SWNTs.

c) \([(2n+m)\text{mod}3=2]\), leading to semi-conducting behavior in SWNTs.

All these conditions are illustrated in \textbf{Figure 1.5}. 

Thus far, the electronic states of the nanotubes has been discussed. Due to dimensionality is it also important to discuss the density of states (DOS) for nanotubes. DOS is essentially the number of states (or spots) per energy interval that are available for the electron to occupy at each energy level. For SWNTs (for 1D materials), the density of states (DOS) is singular at the vertex of a parabolic band. It falls off as $1/\sqrt{E}$. This results in asymmetric spikes in the DOS usually referred to as van Hove singularity (vHs)$^{14}$. Figure 1.6 shows the Energy vs DOS plots for some of the metallic and semi-conducting SWNTs. The spikes in the plots (Figure 1.6) are the vHs. Another important point to notice in these plots is the band gap. For the metallic SWNTs (left panel-Figure 1.6), there are density of states available at all energy levels (even at Energy = 0). This makes these SWNTs metallic in nature. For the semi-conducting SWNTs (right panel-Figure 1.6), there are no DOS at Energy = 0. Figure 1.7$^{17}$, shows the electronic band structure and its corresponding DOS plot for (5,5) SWNTs. This clearly shows the relation between band structure and DOS (at the vertex points of the band structure we find the corresponding vHs).
Figure 1.6: The left panel is the Energy vs DOS plot for (9,9), (13,4) and (12,3) metallic SWNTs (no band gap). The right panel are the plots for semi-conducting (7,5), (11,1) and (10,3) SWNTs. The spikes are the van Hove singularities (vHs) in DOS, a consequence of one dimensionality of SWNTs.

Figure 1.7: Shows the band structure and corresponding DOS for (5,5) metallic SWNT within the zone-folding scheme. (Reprinted with permission from Charlier. J-C. et al, Rev. Mod. Phys., Vol. 79, No. 2 (2007). © (2007) The American Physical Society)
Initially\(^1\), the optical activity seen via photoluminescence and resonance Raman spectroscopy was primarily thought to be band to band optical transition of electrons, dictated within the dipole selection rules, allowing for only those electronic optical transitions between corresponding DOS (vHs) in valence (\(i^{th}\) valence band) to conduction (\(j^{th}\) conduction band) band for semi-conducting SWNTs (selection rule allows only those transitions where \(i = j\)). These optical transitions are referred to as \(S_{ii}\) or \(E_{ii}^S\). For metallic SWNTs, the lowest transitions between linear bands (those meeting at Fermi level) is banded. But just like the semi-conducting, the higher transitions are allowed. These transitions are referred to as \(M_{ii}\) or \(E_{ii}^M\). It is now known that this optical transitions are not band to band transitions but excitonic in nature\(^1\). However, the conventional way of naming optical transitions as \(S_{ii}\) or \(E_{ii}^S\), for semi-conducting and \(M_{ii}\) or \(E_{ii}^M\), for metallic continues to this day. Kataura plots\(^1\) gives the optical transition energies for each \(E_{ii}^S\) and \(E_{ii}^M\), and their relation to their corresponding diameters. This tells us what laser energies to use to have these transition energies in resonance. Figure 1.8, shows a typical Kataura plot.
1.1.3 Raman spectroscopy for SWNTs

Resonance Raman spectroscopy is a very versatile and useful technique for probing the optical properties of SWNTs. The Raman spectra is dependent on the phonon dispersion of SWNTs. Just like the electronic dispersion, even here, it is first necessary to consider the phonon structure for graphene. As can be seen for Figure 1.9(a), graphene has 3 optical and 3 acoustic phonon branches\textsuperscript{14}. Again, as defined by the dimensional limitation imposed by the circumferential or wrapping vector restricts the reciprocal lattice space to only those at the \textit{cutting lines}, allows for a good approximation of the phonon dispersion for SWNTs.

Figure 1.9: (a) Phonon dispersion and (b) phonon DOS for graphene. (c) Phonon dispersion (showing 6N phonon branches, for N \textit{cutting lines}) and (d) corresponding phonon DOS of SWNTs. (Reprinted with permission from Dresselhaus, M. S. \textit{et al}, Physics Reports 409 (2005) 47-99 © (2005) Elsevier B.V.)

Ferrari, A. C. \textit{et al}\textsuperscript{20} is a very good and comprehensive source for understanding Raman scattering. Inelastic scattering of incident excitation of material is called Raman scattering. This occurs due to either energy loss (Stokes process) or energy gain (anti-Stokes process) to phonons\textsuperscript{14, 20}(it is primarily phonons for Raman spectra for SWNTs and graphene). The Raman processes considered
for this work are first order Raman processes. These involve scattering by a single phonon, such that the only phonon that can participate is from the Γ point (q = 0), because in such cases the photon cannot compensate for any change in momentum (resulting in no change in k space). The Raman features relevant for this work are the G band features and radial breathing modes (RBM). The G band features occur at ~1600 cm\(^{-1}\). These features are due to stretching modes of C-C bonds at the Γ point. Unlike in graphene, where the G band is a single peak (due to degeneracy of longitudinal optical (LO) mode and in-plane transverse optical (iTO) mode), for SWNTs, is degeneracy is lifted due to curvature and confinement effects, leading to observation of modes associated with C-C modes in both axial and longitudinal direction. As observed in Figure 1.9, where zone folding leads to N branches for a SWNT for each LO and iTO, in reality only three of these can be observed. These are A, E\(_1\) and E\(_2\) (Raman active). Experimentally, two peaks from the G band are important. The G\(^+\) and the G\(^-\) bands (for LO and TO respectively). The G peak line shape gives information about what type of SWNTs are present in the sample. Sample heating leads to downshift in Raman G band frequency and mild chemical/or electrostatic doping leads to upshift in the G band frequency. These changes in the G band shape and G band frequency shift due to heating and doping are relevant to Chapter 4 and for understanding SWNT degradation in Chapter 5. Dresselhaus, M. S. et al\(^{14}\) is a very good source to understand the G band properties.

Radial breathing modes (RBM) occurs (at ~100 – 300 cm\(^{-1}\)) due to in-phase vibrations of the atoms in the nanotube in the radial direction. This therefore, give information regarding the diameters. The Raman RBM frequency is inversely related to diameter of the SWNT. It can be given by

\[ \omega_{RB} = \frac{c_1}{d_t} + c_2 \]

where c1 and c2 fitting parameters (depending on the environmental effects).

RBM can be used to for SWNT indexing (assigning (n,m) values to each SWNT) with the help of Kataura plots. RBM are optical phonons at the Γ point and are therefore first order Raman features.
These RBM features are relevant for Chapter 2 and 3 for understanding the changes in the degree of interaction between the SWNTs.

1.1.4 Scope of this project

When carbon nanotubes are closely bundled together, upon excitation with certain energies, they interact in such a way that they transfer energy from smaller diameter, donor SWNT to larger diameter energy acceptor SWNT. This phenomena is called exciton energy transfer (EET). This has been observed using photoluminescence (PL) methods. PLE and resonance Raman spectroscopy are complimentary techniques for studying SWNTs. So much so that SWNT Raman features can also be observed using PL methods. This has been a primary motivation for exploring the possibility of observation of exciton energy transfer (EET) using Raman spectroscopy for SWNTs. There has been no previous report of observation of EET in SWNTs using Raman spectroscopy. With PL, metallic SWNTs cannot be studied. With Raman spectroscopy we can overcome this handicap and can potentially study EET in metallic SWNTs. There has been no previous report on observation of EET within (between) metallic SWNTs. Studying EET in SWNTs is important to explore its potential use as solar energy concentrators and antennas for solar cell applications.

The aim of Chapter 2, is to explore the possibility of potential observation of EET using Raman spectroscopy. Possibility of EET between metallic SWNTs was also investigated along with the exploration of EET pathways.

In Chapter 3, the role of molecular photodesorption and mild chemical cleaning (9M peroxide treatment of SWNTs), was investigated, towards changes in inter-nanotube interaction using Raman spectroscopy in conjunction with XPS, SEM, TEM.
Chapter 4 is dedicated to the investigation of role of molecular photodesorption and chemical cleaning (9M peroxide treatment of SWNT) towards improvement of heat conduction between nanotubes by improving inter-nanotube interaction. This is towards realizing potential application of SWNTs as material for thermal budget management for VLSI\textsuperscript{24}.

Chapter 5 is a study of enzymatic degradation of SWNTs (using Horseradish peroxidase) and also understanding the role of sonication (in conjunction) with strong acid treatment towards complete degradation of SWNTs.
1.2 References


2. Observation of phonon assisted exciton energy transfer (EET) in mixed metallic and semi-conducting single walled carbon nanotube (SWNT) bundles using Resonance Raman Spectroscopy.

In this chapter, exciton energy transfer (EET) in SWNTs is introduced along with the rationale as to why it should be possible to observe EET using Resonance Raman Spectroscopy (RRS) in SWNT bundles. EET is observed in SWNT bundles by comparing their Raman radial breathing mode (RBM) spectra at various laser powers. These measurements were made using two different laser energies to study consistency in observation of EET events across different SWNTs of varying diameters and electrical properties. A proposed pathway is then introduced to explain changes in the resonance Raman spectra for SWNT bundles with changing laser power.

2.1 Introduction

2.1.1 Non-equilibrium carrier distribution dynamics in SWNTs bundles

As with most light based spectroscopy methods like photoluminescence (PL), absorption measurements and others, Raman spectroscopy depends on the optical properties of the material (SWNTs in this case). To understand the optical properties and optical spectra of material, it is important to first understand the various events that occur upon light-matter interaction. These events are explained by Hertel, T. *et al*\(^1\) for SWNTs and by Jorio, A. *et al*\(^2\) for light-matter interaction in general. Light-matter interactions leads to perturbation of the system leading to a
state away from equilibrium. The carriers in this non-equilibrium state undergo changes in order to return to their original thermal equilibrium state. Understanding these non-equilibrium carrier dynamics and distribution gives us insight into the carrier life-time of events which eventually allows us to determine if EET is possible or not in SWNT bundles. Non-equilibrium carrier distribution is generated when the incident light is absorbed by the SWNTs. In case of SWNT bundles, the thermal equilibrium is regained via three major pathways:

1. Electron-electron (e-e) interactions
2. Electron-phonon (e-ph) interactions
3. Electron-hole recombination

The e-e interaction for SWNT bundles is the fastest and most efficient pathway in redistributing the energies of the excited electrons through fast generation of secondary electron-hole (exciton, e-h) pairs in a cascading fashion via e-e scattering events. This is usually called internal thermalization of the electronic systems. This internal thermalization redistributes the energies to a new equilibrium at a slightly higher temperature, beyond which e-e interactions does not play any further role in changes in the carrier distribution function. These internal thermalization processes due to e-e interactions were measured to be in the sub-picosecond time scale at around 0.25 ps, by time-resolved photoemission experiments.

After internal thermalization, the excited electron gas in the above mentioned new transient equilibrium are cooled via e-ph interaction, back to the lattice temperature. The energy losses to e-ph interactions are very low. These e-ph interactions were found to be weak and their consequent rate was found to be slow at >1 ps (and <1 ps). These e-ph interactions were found to work at picosecond time scale. Optical phonon lifetimes at room temperature for semi-conducting and metallic SWNTs were found to be at similar time scale (at 1.2 ps and 0.9 ps, respectively).
The slowest of the three relaxations is the e-h recombination. This results in the final inter-band relaxation of exciton/electron (carrier) back to its ground state, with a corresponding emission of photon (this radiative recombination could be band-gap transition (Rayleigh) or after ‘e-ph’ interaction (Stokes and anti-Stokes)). This is also called as electron-photon interaction step. This radiative recombination has a theoretical lifetime of ~10 ns. The other experimentally reported radiative e-h recombination lifetimes are ~20-180 ps and about ~20-30 ps for shorter diameter SWNTs at room temperature and others report < 1 ns for these electron-photon interactions. Despite these variations in the reported lifetime values, these are still the slowest of the three pathways. With this, excited electrons return to their ground states.

This framework of non-equilibrium carrier dynamics tells us about the time rates of various important relaxation pathways after light is absorbed by the SWNTs. With this framework we can understand exciton energy transfer as observed by other groups using photoluminescence methods.

2.1.2 Exciton energy transfer (EET) in SWNTs

One of the first observations of EET in SWNTs was reported using photoluminescence (PL). It states that resonant excitation of smaller diameter SWNT (larger bandgap) (Donor) results in strong photoluminescence from larger diameter SWNT (relative smaller bandgap) (Acceptor) in a mixed SWNT bundle with SWNTs of varying diameters. This implies energy transfer from larger bandgap SWNTs to smaller bandgap SWNTs in a bundle. Even prior to the first observed reports of EET in SWNT bundles, its presence was long hypothesized to explain signal quenching of semi-conducting SWNTs in presence of metallic SWNTs in nanotube bundles. This quenching was attributed to the possibility of energy or carrier transfer from semi-conducting SWNTs to metallic SWNTs and its eventual non-radiative relaxation.
In SWNT bundles, the wall to wall distance between neighboring SWNTs is within the order of stacking in graphite ~ 0.34 nm regime. In such circumstances, the EET can potentially occur via three different pathways:

a) Exciton tunneling and Dexter charge transfer

b) Photon exchange

c) Förster Resonance Energy Transfer (FRET)

Exciton tunneling and Dexter charge transfer occur when there is carrier transfer from donor SWNT to acceptor. Coupling of neighboring exciton wave functions is required for exciton tunneling. Here, the efficiency of exciton tunneling strongly depends on specific donor-acceptor couples. However, it was found that for SWNT bundles there was no such preference. Thus, ruling it out as a major pathway for EET in SWNTs. Other publications however, do not completely rule out the possibility of carrier transfer in parallel with other pathways. It is not considered to a major EET pathway.

EET in SWNT bundles has been found to be strongly distance dependent, i.e. closer the distance between the donor SWNT and the acceptor SWNT, stronger the EET. EET phenomena in SWNTs is not seen in isolated SWNT solutions, and EET is shown to increase with increase in bundling from isolated SWNTs to bundles in vertically aligned SWNTs, showing strong distance dependency. Photon exchange which involves exciton-photon coupling (It does not directly involve the donor-acceptor interaction, but the photon emitted by the donor is used up to excite the acceptor exciton.) and it has smaller distance dependency (Photon exchange remains significant at greater distance too.) on donor-acceptor distance than seen EET in SWNT bundles. FRET is the most commonly proposed pathway for EET in SWNTs. EET phenomena within SWNT bundles exhibits all the characteristics of FRET. FRET is a non-radiative energy transfer
from large bandgap donor SWNT to smaller bandgap acceptor SWNT via dipole-dipole interaction. FRET has been elegantly explained by Förster in 1959\textsuperscript{13}. It is a very common occurring phenomena in conjugated polymers\textsuperscript{13}, quantum dots\textsuperscript{14}, nano-rods\textsuperscript{15} and even biological systems\textsuperscript{16}. FRET is known to dominate in the short and intermediate distances of \textasciitilde0.5-10 nm (the inter-tube distance in SWNT bundles is within the short-intermediate distances)\textsuperscript{13-16}. The spectral overlap of donor emission and acceptor absorption, along with donor-acceptor distance and relative orientations of the donor, acceptor dipoles are the primary factors that determine the FRET efficiency\textsuperscript{13}. SWNTs in a bundle are parallel to each other, with small inter-tube distances. This leads to maximum overlap of dipole orientation resulting in effectively increasing FRET efficiency\textsuperscript{8, 17}. Other evidences of FRET as EET pathway in SWNTs is the photoluminescence quenching of CdSe-ZnS quantum dots upon conjugation with SWNTs, leading to energy transfer from dots to SWNTs\textsuperscript{18}.

Since the first observations of the energy transfer between semi-conducting SWNT bundles using PL spectroscopy\textsuperscript{7}, FRET pathways have been proposed to explain EET in SWNTs\textsuperscript{8-10, 12}. Figure 2.1 (a), illustrates one such FRET pathways of EET in SWNT bundles using PL. Here, optical excitonic transition, $E_{ii}$, is represented by different notation ‘$eh_{ii}$’ (electron-hole/excitonic level). Figure 2.1 (b), is a typical intensity vs wavelength plot showing the necessary ‘spectral overlap’ between donor emission ($E_{mD}$) and acceptor excitation ($E_{xA}$) needed for EET to occur in SWNT bundles. Also, important to notice is the distinct difference in the donor ($E_{xD}$) and acceptor ($E_{xA}$) excitations. This configuration in photoluminescence spectroscopy of excitation (only providing donor excitation) at one energy, leading to excitation of acceptor due to spectral overlap and probing for emission allows us to observe EET using PL methods.
The other proposed pathways suggest an alternative FRET pathway, i.e. between ‘eh\(_{22}\)-D’ and ‘eh\(_{22}\)-A’, as against between ‘eh\(_{11}\)-D’ and ‘eh\(_{11}\)-A’ shown in Figure 2.1(a)\(^8\). Recently published work by Mehlenbacher, R. D. et al\(^9\), suggest both these energy transfer pathways are possible and extend it by showing all potential EET pathways in SWNT bundles with SWNTs with varying diameters. It is necessary to see where EET rates fall in the overall scheme of non-equilibrium carrier dynamics discussed in section 2.1.1. From the EET observations using PL methods, it has been suggested that EET from donor to acceptor in SWNT bundles via FRET is faster than the slowest and the final step discussed in the non-equilibrium carrier dynamics, i.e. radiative recombination of the exciton\(^10\). This fast EET pathway results in significant increase in the acceptor luminescence intensity and suppressing donor emission\(^8\). It has also been estimated that

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**Figure 2.1:** (a) Schematic of Exciton Energy Transfer (EET) as observed using PL spectroscopy. Here, ‘eh’ represents ‘11’ and ‘22’ optical excitonic transitions of donor (D) SWNT and acceptor (A) SWNT. (a→b) shows excitation of the donor exciton with energies equal ‘eh\(_{22}\)’ leading to ‘eh\(_{22}\)’ transition. (b→e) shows fast relaxation to donor’s ‘eh\(_{11}\)’ level. (c→e) is the EET in form of FRET from donor SWNT to acceptor SWNT with comparatively lower ‘eh\(_{11}\)’. (e→f) is the radiative recombination leading to emission at acceptor ‘eh\(_{11}\)’. (Reprinted with permission from Tan, P. H. et al., Physical Review Letters, 99, 137402 (2007). © 2007 The American Physical Society). Figure (b) is a schematic illustrating how the excitation of donor leads to acceptor emission via FRET using PL spectroscopy and the importance of the spectral overlap of the donor emission (Em\(_D\)) and excitation of the acceptor (Ex\(_A\)). More the spectral overlap better the EET efficiency.
time taken for EET ($\tau_{\text{EET}}$) to be less than 10 ps\textsuperscript{10}. While Mehlenbacher, R. D. \textit{et al}\textsuperscript{20}, conclude that 70\% of the photoexcitation resides on the smallest bandgap nanotubes, after 3 ps.

However, some of the theoretical studies argue that EET in SWNTs cannot be completely expressed in terms of FRET model based on a simple point dipole approximations\textsuperscript{21} (FRET model overestimates energy transfer rates\textsuperscript{22}), for the rate of energy transfer between spatially extended states (as seen in SWNTs). Some works now describe EET in SWNTs as ‘Förster-type electromagnetic coupling’\textsuperscript{23}.

Lüer, L. \textit{et al}\textsuperscript{24}, show ultrafast excitation energy transfer ($<$ 10 fs) in small semi-conducting SWNT bundles. They rule out FRET mechanism for such fast excitation energy transfer and conclude that it may be due to tunneling or Dexter transfer. This ultrafast excitation energy transfer may also be viewed in the scheme proposed by O’Reilly, E. J. \textit{et al}\textsuperscript{25} (original proposed to explain ultrafast EET in light-harvesting photosystems) which suggests EET depends not only on the topology of the electronic couplings of the pigments but more importantly on the molecular motion of the pigments (electron-phonon interactions).

To summarize, we see many different pathways of EET occurring in SWNT bundles at various time scales. Many of the EET events can be explained using Förster type energy transfer mechanisms\textsuperscript{8}, or to a lesser extent via Dexter energy transfer pathways\textsuperscript{10}. Whereas the ultrafast EET\textsuperscript{24} which the authors considered them to potentially be a Dexter type transfer pathway. These ultrafast EET as seen by Luer, L. \textit{et al}\textsuperscript{24} can also potentially be a consequence of electron-phonon interaction as proposed by O’Reilly, E. J. \textit{et al}\textsuperscript{25}. Work by Mehlenbacher, R. D. \textit{et al}\textsuperscript{19} is a great source which talks about observation of many different EET pathways occurring at different $E_{ii}$ levels between different SWNTs within a bundle.
2.1.3 Rationale for potential observation of EET via Resonance Raman method

Before discussing the rationale for potential observation of EET using Raman methods, let us briefly look at the resonance Raman spectroscopy (RRS) pathway for SWNTs and its relation to the Kataura plots. Raman event results in the inelastic scattering of the monochromatic light incident on to the substrate (SWNTs in this case). Figure 2.2 (a) is a representation of the Kataura plot which shows the relationship between optical excitation transition energies \( E_{ii} \) of SWNTs to its diameter. The optical transition energies \( E_{ii} \) is inversely proportional to the SWNT diameter, which is to say that smaller diameter SWNTs have larger \( E_{ii} \) values compared to larger diameter SWNTs. Kataura plots are very important in understanding SWNT’s optical and electronic properties and its relation to its diameter and metallicity.

During a resonance Raman process, as seen in Figure 2.2 (b), upon excitation with monochromatic light \( \lambda_i \), the electrons from their ground state (GS) get excited to its excitonic levels \( E_{ii} \). With resonance Raman methods we probe the various \( E_{ii} \) levels which are in resonance with the excitation energy (In case on Figure 2.2 (b), SWNT-1 and SWNT-2 have their \( E_{ii} \) in resonance).

As seen in Figure 2.2 (b), the smaller diameter nanotube (SWNT-1) has a larger \( E_{ii} \) (further away from ground state) value than SWNT-2 (larger diameter nanotube) and in agreement with Kataura plot (Figure 2.2(a)). In purview of the non-equilibrium carrier dynamics in SWNTs upon excitation with light, we can establish the lifetime values for each of the stages involved in resonance Raman excitation of SWNTs. After excitation, during resonance Raman process, we see two events leading to complete relaxation of excited electrons.

(i) Faster electron-phonon interactions

(ii) Slower electron-photon interactions
The ‘e-ph’ interaction involves energy loss (in a Stokes Raman event) of excited electrons to phonons (represented by green wavy line in Figure 2.2 (b)). These ‘e-ph’ interactions are very fast events, at picosecond time scale\(^{1-3}\) (1.2 ps for semi-conducting and 0.9 ps in metallic SWNTs\(^3\)). These energy losses to phonons is very small (as represented by the small size of the green wavy line) in Figure 2.2 (b). After energy loss to phonons, the excited electrons now exist in a new, albeit lower energy level (this level can be a real or a virtual state) which are still much higher when compared to the ground state. The electrons from these new excited levels finally drop back to their GS via slower, electron-photon interactions or electron-hole ‘e-h’ radiative recombination which takes place at a nanosecond time scale\(^2\). In Figure 2.2 (b), this radiative recombination results in the two scattered photons with different energies (\(\lambda_{f1}\) for SWNT-1 and \(\lambda_{f2}\) for SWNT-2). This difference in inelastic scattering of light is due to difference in energy loss to phonons for SWNT-1 and SWNT-2. This results in two peaks with different Raman shifts in the resulting radial breathing mode (RBM) Raman spectra, where the Raman shift (\(\Delta \omega\)) can be given by:

\[
\Delta \omega \text{(cm}^{-1}) = \left( \frac{1}{\lambda_i(nm)} - \frac{1}{\lambda_f(nm)} \right) \times \frac{10^7 nm}{cm} \quad (\text{Eq: 2.1})
\]

As the electron-photon interaction or the ‘e-h’ radiative recombination is a slower process at nanosecond scale, there is a potential possibility of dipole-dipole coupling or dipole-dipole interaction between the ‘e-h’ (exciton) pairs of neighboring SWNTs of different diameters leading to EET between SWNTs in SWNT bundles. This is possible, as EET in SWNT bundles, occur at a timescale of 10 ps\(^1\). This EET lifetime (\(\tau_{\text{EET}}\)) (time taken for EET to occur between the SWNTs) is more than the time taken for e-ph interaction (< 1 ps) but less than ‘e-h’ recombination (at nanosecond time scale). Therefore, we must be able to observe EET events occurring due to dipole-dipole interactions of excitons in neighboring SWNTs after having lost energy (Stokes Raman
event) to phonons. All the proposed EET pathways thus far only discuss EET between excitons of donors and acceptors without considering energy exchange with phonons (Stokes and Anti-Stokes). Here, we suggest that both the EET pathways between exciton pairs of (i) donor and acceptor SWNT before energy exchange to phonons (as has been proposed by other groups) and (ii) donor and acceptor SWNT after energy exchange to phonons (therefore, ‘phonon assisted exciton energy transfer’) are possible.

As both Raman and PL events are optically related events and can be observed in same plot\textsuperscript{17, 26}

![Figure 2.2](image_url)

**Figure 2.2:** (a) Kataura plot showing the $E_{ii}$ vs SWNT diameter. The blue dots represent the optical excitonic transition of metallic SWNTs and the red dots for the semi-conducting SWNTs. The shaded region is an example resonance window within which the $E_{ii}$ transitions are in resonance with the monochromatic excitation wavelength. Figure (b) illustrates the various steps involved in the resonance Raman process for SWNT bundles.

(As seen in Figure 2.3) and as EET has already been observed using PL\textsuperscript{7-10, 12, 23} it must be highly likely to observe EET events using resonance Raman spectroscopy too.

To this end we hypothesize that, ‘Exciton energy transfer (EET) also occurs between excitons of neighboring SWNTs of varying diameters, within a bundle, after energy exchange to phonons.’
This EET event after ‘e-ph’ interaction (“phonon assisted exciton energy transfer”) must be observable in every Raman RBM spectra.
One of the major drawbacks of observing EET using resonance Raman spectroscopy is that unlike PL method, which involves clear separation between excitation energies of both donor ($E_{xD}$) and acceptor ($E_{xA}$) (as seen in Figure 2.1 (b)), Raman methods involve excitation of both donor and acceptor with same excitation energy (as seen in Figure 2.2 (b), where excitation, $\lambda_i$ is same for both the SWNTs). In such a scenario, observing EET using a single Raman RBM spectrum becomes difficult. We can overcome this by comparing various Raman RBM spectra from the same sample by varying another parameter which may affect the EET efficiency to varying degrees. Using Raman spectroscopy for observing EET has its advantages too. EET has not been directly observed for metallic SWNTs using PL methods. As one can observe metallic SWNTs using Raman spectroscopy, one can also potentially observe EET occurring in metallic SWNTs. One can also ask interesting questions such as, does EET happen between only metallic SWNTs (i.e. EET between smaller diameter, metallic, donor SWNT to larger diameter, metallic, acceptor SWNT) and can EET occur between metallic and semi-conducting SWNTs?

2.2 Experimental Section

2.2.1 Materials

Pristine SWNTs synthesized via high-pressure carbon monoxide method (HiPco®), obtained commercially from Nanointegris were used. These pristine SWNTs were suspended in deionized water and sonicated for 2 minutes in water bath of a Branson 1510 system. These SWNTs suspensions were aliquoted and drop-casted on a clean silicon substrate and were allowed to dry overnight in desiccator. These dry samples form a mat/film/sheet of SWNT bundles on silicon substrate. These samples were then used for Raman spectroscopy and scanning electron microscopy (SEM) characterization.
2.2.2 Raman Spectroscopy

Raman spectra for all the SWNT samples were obtained on Horiba Jobin Yvon LabRAM HR, using $E_{Laser} = 1.96\text{eV (} \lambda_{\text{Excitation}} = 632.8 \text{ nm})$ (He/Ne Laser) at varying laser powers of 0.2, 1.7, 4.2 and 8.5 mW and $E_{Laser} = 2.33\text{eV (} \lambda_{\text{Excitation}} = 532 \text{ nm})$ (Nd: YAG Laser) at 0.04, 0.4, 1.1 and 2.2 mW laser powers. For both the lasers and all the measurements static grating of 1800 mm was used. All the spectra were recorded for 10 seconds and averaged 3 times each. The final Raman spectrum for each of the conditions is an averaged spectrum obtained from 6 different spots on the SWNT mat sample. The laser spot size (diameter) for all the measurement conditions is 1 μm. All the spectra are normalized to their respective G-band intensities unless specifically mentioned.

2.2.3 Electron Microscopy

SEM micrographs (courtesy: Vishal Desai) were obtained on Hitachi S-4800 using SE-2 detector at 2 kV acceleration voltage and at a magnification of 50 kX. TEM micrographs were obtained on JEOL-2010 LaB$_6$ STEM at 200 kV acceleration voltage. The sample from TEM were prepared from SWNT suspension sample. 2 minute sonication of the SWNT suspension is followed by drop-casting aliquots of the sample and drying them overnight in desiccator on holey carbon grid.

2.3 Results and Discussion

Exciton energy transfer (EET) occurs when distance between the donor SWNT and the acceptor SWNT are in close proximity (< 10 nm). Such a scenario exists when SWNTs are in dry bundled form. Scanning electron microscopy (SEM) is used to observe the morphological characteristics of SWNT mat on which the final Raman analysis is done. Figure 2.4 shows a typical scanning electron micrograph of such a SWNT film made out of pristine HiPco SWNTs on silicon substrate.
As seen in Figure 2.4, the bundling is SWNTs of various sizes and it occurs due to van der Waals attractions between the neighboring SWNTs\textsuperscript{27}. TEM imaging was done on SWNTs on the dried samples to confirm the bundling effect in SWNTs. Figure 2.5, shows the typical bundling effect seen in dried SWNT samples. The SEM and TEM micrographs allow us to confirm that we indeed observe bundling in SWNTs and the distance between SWNTs in a bundle is < 10 nm and usually to the order of graphitic wall to wall stacking as explained by Lefebvre, J. et al\textsuperscript{10}. This fulfills the distance criteria required for EET to occur.

**Figure 2.4**: SEM micrograph of pristine HiPco SWNTs in dry SWNT film form on silicon substrate. SWNTs here are seen to form bundles.
As mentioned in the last paragraph of section 2.1.3, the excitation energies for donor and acceptor are same for SWNT bundles when using resonance Raman spectroscopy. This makes observing

Figure 2.5: TEM micrograph showing typical bundling of SWNTs observed in all the dried SWNT mats/films. The SWNT bundles in the above TEM micrograph are seen to crisscross each other on the holey carbon grid. In SWNT bundles, the inter-tube distance between neighboring SWNTs is less than 10 nm. This makes exciton energy transfer (EET) a possibility in these bundles.

As mentioned in the last paragraph of section 2.1.3, the excitation energies for donor and acceptor
EET in a single Raman RBM plot, difficult. One way to observe EET using resonance Raman spectroscopy is by comparing the Raman RBM plots of the same SWNT mat/film by varying a parameter which may affect the EET efficiency to varying degrees. This may result in changes in the Raman RBM profile of the sample while varying the parameter, which can be compared to one another to identify changes in the Raman spectra due to EET.

Here, the parameter we chose to vary while comparing Raman RBM plots was laser power. The rationale for using varying laser power is based on works by Chen, R. J. et al$^{28}$ and Yang-Yang Hsu. et al$^{29}$. Chen, R. J. et al$^{28}$ demonstrated strong molecular photodesorption dependence on wavelength of incident, excitation light for SWNT samples. In ambient conditions, we find air and vapor interact with SWNT film sample. The molecules in the ambient environment adsorb on to the SWNT surface. This surface adsorption may result in reducing the inter-nanotube interaction, which may lead to reduced efficiency of EET between neighboring SWNTs. Light-SWNT sample interaction leads to desorption of these adsorbed molecules (photodesorption), resulting in increased EET efficiency due to better inter-nanotube interactions and reduced energy losses to adsorbed molecules. While, Chen, R. J. et al$^{28}$ demonstrated wavelength dependency for photodesorption and not laser power dependency, it allows us to appreciate the potential changes that may occur in the extent of photodesorption due to changing photon flux (changing laser power). To this end, Yang-Yang Hsu. et al$^{29}$, demonstrated the laser (light source) power also plays an important part in the desorption kinetics for a carbon nanotube related material, graphene. Therefore, by varying the laser power we can vary the degree of molecular photodesorption leading to varying extents of EET on the same SWNT sample.

**Figure 2.6** is a schematic representation of our Raman RBM spectral measurement approach for studying EET.
It is necessary to explore other explanations offered for Raman RBM spectral dependence on laser power for SWNT bundles. The most commonly cited work on laser power dependency on resonance Raman spectra for SWNT bundles is by Fantini, C. et al\textsuperscript{30}. Figure 2.7 (a) shows the typical Kataura plot showing SWNT diameter-$E_{ii}$ relationship and Figure 2.7 (b) shows the Raman RBM spectra for SWNTs bundles, at a laser excitation of 1.72 eV, at various powers, for HiPco SWNTs as published by Fantini, C. et al\textsuperscript{30}.

The black dotted box in Figure 2.7 (a) is the typical SWNT diameter range usually found for HiPco nanotubes. The smallest SWNT diameters which are possible for HiPco-type are 0.7 nm \textsuperscript{31} and the average diameter range is approximately around 1.00 nm \textsuperscript{32}. According to Fantini, C. et
All the SWNTs observed at 1.72 eV as shown in Figure 2.7 (b) are semi-conducting in nature. These semi-conducting SWNTs are of two types:

a) Semi-conducting, S1 type \[((2n+m)\mod 3 = 1\): (9,1), (8,3), (7,5), (10,2), (9,4), (8,6)

b) Semi-conducting, S2 type \[((2n+m)\mod 3 = 2\): (8,7), (11,4)

Figure 2.7: (a) Typical Kataura plot showing \(E_{ii}\) vs SWNT diameter relationship. The black dotted box shows the usual diameter range of HiPco SWNTs. The red horizontal line at 1.72 eV illustrates the laser excitation energy used for Raman shift measurements in Figure 2.7 (b). The red dotted box approximately encloses all the peaks that are shown in Figure 2.7 (b) which are all, from \(E_{22}\) optical transition level. Figure 2.7 (b) is Raman RBM spectra at different laser powers, as illustrated by corresponding red circles with increasing intensities (from top to bottom). (Reprinted with permission from Fantini, C. et al, Physical Review Letters, 93, 147406 (2004). © 2004 The American Physical Society).

According to Fantini, C. et al\(^30\), Raman RBM peak intensities for semi-conducting, S1 type SWNTs reduces with increasing laser power whereas Raman RBM peak intensities for semi-conducting, S2 type SWNTs increases with increasing laser power as seen in Figure 2.7 (b). Fantini, C. et al\(^30\) also determined the optical transition energies \(E_{ii}\) for each of the eight above mentioned SWNTs (from Figure 2.7 (b)), as a function of laser power density by using the
resonance window obtained for each of the eight RBM peaks, experimentally. This $E_{ii}$ (denoted as $E^8$ in Figure 2.8) vs power density plot obtained by Fantini, C. et al$^{30}$ is shown in Figure 2.8.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure28.png}
\caption{Figure 2.8: $E^8$ vs laser power density plot for the SWNTs in Figure 2.7 (b). (Reprinted with permission from Fantini, C. et al, Physical Review Letters, 93, 147406 (2004). © 2004 The American Physical Society).}
\end{figure}

In Figure 2.8, the dotted lines represent the semi-conducting, S1 type SWNTs from Figure 2.7 (b), whereas, S2 type SWNTs are represented by solid black lines. This red shift (down shift of energy) of S1 type and blue shift (up shift) of S2 type, with increasing laser power is given as an explanation for differing changes in RBM intensities for S1 (reducing intensity) and S2 type (increasing intensity), semi-conducting SWNTs (as seen in Figure 2.7 (b)). While Figure 2.8 shows clear trends, there may be some potential issues with this approach to explain the laser power dependency on Raman RBM spectra in Figure 2.7 (b). These potential issues with this explanation are:
a) According to Fantini, C. et al\textsuperscript{30}, in Figure 2.7 (b), (8,3) and (7,5), which are semi-conducting, S\textbf{1} type $[(2n+m)\mod 3 = 1]$ should have their Raman RBM intensity reduced with increasing laser power. But closer inspection of Figure 2.7 (b) shows that Raman RBM intensities of (8,3) and (7,5) is increasing. There is no signal for (8,3) at lower laser power of 18 μW. But its signal starts emerging at 0.3 mW and keeping increasing at 3.0 mW. Similarly, for (7,5) no discernible peak is seen at low power (18 μW). With increasing laser power, the Raman RBM intensity for (7,5) keeps increasing. These observation directly contradict the explanation offered in the same paper.

b) It completely disregards trends for Raman RBM intensities that may emerge for metallic $[(2n+m)\mod 3 = 0]$ SWNTs with changing laser power. It does not show why or what trends may be seen for Raman RBM intensities for metallic SWNTs, with changing laser power.

Our first objective was to see whether we find any trends in Raman RBM intensities for metallic SWNTs with changing laser power. Here, we used SWNTs of the same type (HiPco) as used by Fantini, C. et al\textsuperscript{30}. To study trends in Raman RBM intensities for metallic SWNT bundles, we used higher excitation energies (1.96 eV and 2.33 eV), which allows for observation of metallic SWNTs ($E_{11}^M$ (or $M_{11}$) optical transition level is in resonance at these energies) along with $S_{22}$ (at 1.96 eV) and $S_{33}$ (at 2.33 eV) levels of the semi-conducting SWNTs. Figure 2.9, shows our Raman data for HiPco SWNTs at increasing laser powers at 1.96 eV. Chiral indexing $(n,m)$ for the SWNTs were made using the method introduced by Maultzsch, J. et al\textsuperscript{33}. Our chiral indexing for HiPco SWNTs (at 1.96 eV) matches with other published works\textsuperscript{34}. The general trends in the Raman RBM signal intensity for the $S_{22}$ optical transitions showed reduction with increasing laser power whereas, the signal intensities for metallic, $M_{11}$ optical transitions increased in general with increasing laser
power. From Figure 2.9 (b), based on their chiral indices (7,5) and (11,1) are S1 type SWNTs whereas (10,3) is S2 type. Unlike in Figure 2.7 (b) (Fantini, C. et al\textsuperscript{30}) we noticed Raman RBM intensity for (7,5) reduce with increasing excitation laser power. More importantly, we also observed changes in Raman RBM intensity signal for metallic, M\textsubscript{11} optical transitions. Figure

**Figure 2.9**: (a) Kataura plot with a red horizontal line (at 1.96 eV) representing the excitation laser energy used to obtain the Raman RBM spectra (shown in Figure 2.9 (b)). The black dotted box represents the usual SWNT diameters one gets to observe for HiPco nanotubes. The red dotted box shows the potential $E_{ii}$ values of SWNTs that are in resonance for HiPco SWNTs (as shown in Figure 2.9 (b)). Figure 2.9: (b) shows Raman RBM spectra for pristine HiPco SWNT bundles (at 1.96 eV) at increasing laser power (from top to bottom). The chiral indices $(n,m)$ for the SWNTs observed are also labelled. Peaks within the blue zone represents the metallic, M\textsubscript{11} optical transitions whereas peaks in the red region represents the semi-conducting S\textsubscript{22} transition. 

![Kataura plot and Raman RBM spectra](image)
2.10, shows the Raman RBM signal intensity dependence on laser excitation power for HiPco SWNT bundles, at 2.33 eV. We observed (from Figure 2.10 (b)), that not only we see trends in changes in the Raman RBM peak intensity in metallic, M_{11} optical transitions, we noticed that same type [(2n+m)mod 3 = 0] of SWNTs showing opposite trends in Raman RBM signal intensity.

Figure 2.10: (a) Typical Kataura plot with a green horizontal line (at 2.33 eV) representing the excitation laser energy used to obtain the Raman RBM spectra (shown in Figure 2.10 (b)). The black dotted box represents the SWNT diameters usually observed for HiPco nanotubes. The green dotted box shows the potential $E_{ii}$ values of SWNTs that may be in resonance for HiPco SWNTs (as shown in Figure 2.10 (b)). Figure 2.10: (b) shows Raman RBM spectra for pristine HiPco SWNT bundles (at 2.33 eV) at increasing laser power (from top to bottom). The chiral indices $(n,m)$ for the SWNTs observed are also labelled. Peaks within the blue box represents the M_{11} optical transition whereas those in the red box represents the semi-conducting S_{33} transition.
To elaborate, all the peaks in the blue region of the Figure 2.10 (b), belong to metallic SWNTs. All these peaks in the blue region also belong to \((2n+m)\mod 3 = 0\), i.e. M0 type. Also, SWNTs belonging to the same \((2n+m)\) family show opposing trends. For example, from Figure 2.10 (b), both (9,3) and (8,5) belong to the same \((2n+m)\) family \((2n+m) = 21\) for both (9,3) and (8,5)). But the Raman RBM signal intensity for (9,3) reduces with increasing laser power and whereas, it increases for (8,5).

To summarize, we found that there is not consistency in the Raman RBM intensity changes even for the same SWNT. This can be seen by comparing (7,5) from Figure 2.7 (b)\(^{30}\) (at 1.72 eV) and from Figure 2.9 (b) (at 1.96 eV). The (7,5) peak intensity increases with increase in laser power in Figure 2.7 (b), whereas it reduces in Figure 2.9 (b). We see changes in Raman RBM peak intensities for metallic SWNTs too (Figure 2.10 (b)). Also, there are no consistent trends in changes in Raman RBM peak intensities within same \((2n+m)\) families as seen for (9,3) and (8,5) in Figure 2.10 (b)). All this indicates that the proposed hypothesis by Fantini, C. et al\(^{30}\) does not completely explain the changes in the Raman RBM spectra with changing laser excitation power. There is a need to explore other alternative hypothesis to explain these changes in the Raman RBM spectra.

The only consistent, common observation in all the three plots (at 1.72, 1.96 and 2.33 eV), shown in Figures 2.7 (b)\(^{30}\), 2.9 (b) and 2.10 (b) respectively is reduction in the Raman RBM intensities for any peak that has the higher Raman shift and increase in Raman RBM intensities for any peak that has lower Raman shift, with increasing laser excitation power. There is an inverse relation between SWNT diameter and Raman shift\(^ {35}\), i.e. larger the SWNT diameter smaller is the Raman Shift. Therefore, the above mentioned observation can be rephrased as, ‘with increasing laser excitation power, the Raman RBM intensity increases for larger diameter SWNTs and reduces for
Similar observations have been made for SWNT bundles using PL spectroscopy where intensity of smaller diameter SWNTs reduced and intensities for larger diameters increased\textsuperscript{8}. These PL based observations have been explained using ‘exciton energy transfer’ (EET) picture, where energy is transferred from smaller diameter donor SWNT to larger diameter acceptor SWNT\textsuperscript{7-8, 10, 12, 19, 23}. We can explain these events (increase in Raman RBM intensity for larger diameter SWNTs and reduction for smaller diameter SWNTs, with increasing laser excitation power) happening in Figure 2.7 (b)\textsuperscript{30}, 2.9 (b) and 2.10 (b) by considering inter-tube interactions via phonon assisted exciton transfer (EET) as discussed in section 2.1.3 and as illustrated in Figure 2.11 (b).

**Figure 2.11**: (a) Illustrates resonance Raman spectroscopy (RRS) in SWNT bundles without considering EET. Figure 2.11: (b) is a schematic of the proposed ‘phonon assisted’ EET pathway, showing RRS while considering EET from small diameter, donor (SWNT-1) to larger diameter, acceptor (SWNT-2) after the excitons lose some energy (Raman Stokes) to phonons (therefore, ‘phonon assisted’).

Most of the resonance Raman spectroscopy works on SWNT bundles have thus far have not considered potential interactions between neighboring SWNTs in terms of EET. This approach is illustrated in Figure 2.11 (a). If one considers EET in the overarching picture of RRS for SWNT bundles (Figure 2.11 (b)), we may realize the potential reason for changes in the Raman RBM
spectra of SWNTs with changing laser power. As mentioned earlier in this section, when light is incident on the SWNTs, it results in photodesorption of adsorbed molecules from SWNT surface\textsuperscript{28}.

Figure 2.12: (a) and (b) are Raman RBM spectra showing increasing extents of EET with increasing excitation laser power (at 1.96 eV-Figure (a)) and (at 2.33 eV-Figure (b)). The black arrows in both the figures show EET events happening from smaller diameter, donor SWNTs to larger diameter, acceptor SWNTs. These EET events are seen for both metallic and semi-conducting SWNTs. Increasing laser power leads increased molecular photodesorption allowing improvement in inter-tube interaction. As a consequence, we see reduction in Raman RBM intensities of smaller diameter SWNTs and increase in Raman RBM intensities of large diameter SWNTs.

This results in better inter-tube interaction, effectively increasing EET. This can be seen by
comparing Raman RBM spectra at varying laser excitation powers (Figure 2.12 (a) and (b)). With this approach we can also address the previous issues arising for comparison of Figure 2.7 (b) and 2.9 (b), where the same nanotube (7,5) showed reverse trends of increasing RBM signal and reducing RBM signal, respectively with increasing laser power. In Figure 2.7 (b)$^{30}$ (at 1.72 eV), there are two more SWNTs ((9,1) and (8,3)) with smaller diameters than (7,5). With increasing laser power, due to improved EET, energy is transferred from (9,1) and (8,3) to (7,5) with increasing efficiency. This therefore, results in increase in Raman RBM intensity for (7,5) SWNT. But in Figure 2.9 (b), (7,5) is the smallest diameter in resonance at 1.96 eV. Therefore, the same (7,5) SWNT, at 1.96 eV, starts losing its RBM signal intensity with increasing laser power due to increased EET efficiency due to improved inter-tube interaction at higher laser powers. EET in SWNT bundles, also explains why the Raman RBM intensity variations with laser power does not depend on SWNT’s $(2n+m)$ family groups or $\textbf{S1} \ [(2n+m) \mod 3 = 1]$, $\textbf{S2} \ [(2n+m) \mod 3 = 2]$or $\textbf{M0} \ [(2n+m) \mod 3 = 0]$type. The two parameters that are important to explain changes in the Raman RBM spectra, for SWNT film samples, with changing laser power, within the EET framework are:

a) Diameter of SWNT (it does not matter if the SWNT is metallic or semi-conducting, phonon assisted EET is also observed for metallic SWNTs)

b) Molecules adsorbed to the SWNT surface. Reducing molecular adsorption from SWNT surface improves EET efficiency.

2.4 Summary

To the best of our knowledge, there is no previous report in the literature on observation of phonon-assisted exciton energy transfer (EET) using resonance Raman spectroscopy (RRS) for SWNT
bundles. Here, we explain changes in the Raman RBM spectral intensity with varying laser excitation power by proposing ‘phonon-assisted’ exciton energy transfer (EET) pathway. Based on the non-equilibrium carrier distribution upon light interaction with SWNT bundles\(^1\) and process life time measurements\(^{1-6, 10, 20}\), we propose the possibility of EET after ‘e-ph’ interaction (therefore, ‘phonon-assisted’) (exciton loses some energy to phonons (in a Raman Stokes process)) and before exciton’s radiative relaxation, via dipole-dipole interactions (FRET).

This is also the first report showing EET in metallic SWNTs. To the best of our knowledge, there have been no previous publications on direct observation of EET within metallic SWNTs. EET is not observed is SWNT bundles with only metallic nanotubes\(^8, 10\), using PL methods. This is due to non-radiative relaxation of the excitons in metallic SWNTs (No bandgap, i.e. there are states available for the electron to occupy at each energy between the ground and the excited states). These EET pathways as observed by PL method is different from EET pathway observed here using RRS. With RRS, we get to observe the ‘phonon-assisted’ EET.

Based on Figure 2.3\(^{17, 26}\), which shows that it is possible to observe both PL and Raman events together, we predict potential observation of ‘phonon-assisted’ EET events using PL methods too, by looking for and comparing the changes in the RBM peaks we get to see in the PLE measurements at varying excitation laser power.

It is necessary to appreciate the potential possibility of different pathways for the occurrence of exciton energy transfer (EET) in SWNT bundles. EET in SWNT bundles can be of classical Förster type\(^8\) or those showing ultra-fast carrier transfer as observed by Lüer, L et al\(^{24}\), which suggested pathways like Dexter charge transfer (but can also be explained using the scheme proposed by O’Reilly, E. J. et al\(^{25}\), which takes the Redfield theory into account) or can be ‘phonon-assisted’ type, as proposed here in this work. All these pathways are possible due to the relatively long ‘e-
h’ recombination (radiative recombination) time, that occurs at nanosecond time scale\(^2\). It means, that the excited electron (or exciton) exists at various excited levels (at \(E_{ii}\) transition level, or at a slightly lower energy than corresponding \(E_{ii}\) transition level due to energy loss to phonons (in case of a Raman Stokes process)). And it remains in such an excited state till the radiative recombination can occur. But as radiative recombination is a slow process, the neighboring excitons belonging to neighboring SWNTs start interacting leading to various exciton energy transfer (EET) pathways occurring in SWNT bundles.

Even while considering resonance Raman spectroscopy of isolated SWNTs, it is said that the Raman signal intensity enhancement is due to the resonance between laser excitation energy and the \(E_{ii}\), optical transition levels of SWNTs\(^3\). The Raman intensity in such cases where phonon energy, \(E_q = \hbar \omega_q\), can be described by Jorio, A. \textit{et al} \(^3\):\(^7\)

\[
I(\omega_q, E_{\text{laser}}) = \sum_f \left| \sum_{m,m'} \frac{M^{op}(k - q, im')M^{ep}(q,m'm)M^{op}(k,mi)}{(E_{\text{laser}} - \Delta E_{mi})(E_{\text{laser}} - \hbar \omega_q - \Delta E_{m'i})} \right|^2 \quad (Eq: 2.2)
\]

\[
\text{where,} \quad \Delta E_{m'i} \equiv (E_{m'i} - E_i) - i\gamma_r \quad (Eq: 2.3)
\]

Where \(i, m, m'\) and \(f\) respectively, denotes the initial ground state, the two intermediate excited states and the final state of an electron, during the complete Raman scattering process. Whereas \(\gamma_r\), represents the resonance broadening factor. Here, \(M^{op}\), \(M^{ep}\) and \(M^{op}\) in the numerator represent the matrix elements for ‘electron-photon’ interaction for initial electron excitation upon light interaction (results in the electron’s transition from initial, \(i\) to excited state \(m\)), ‘electron-phonon’ interaction for phonon scattering event (both Stokes and anti-Stokes) which results in electronic transition from \(m\) to \(m'\) (\(m' < m\) for a Stokes process and > \(m\) for an anti-Stokes process) and another ‘electron-photon’ interaction for final radiative recombination of the electron from \(m'\) to
the final ground state $f (f = i$, final and the initial electron states are same). For detailed description, refer to Jorio, A. et al\textsuperscript{37}.

In Eq: 2.2, the traditional treatment for explaining resonance Raman is such that it does not consider EET. If one were to consider EET, as mentioned earlier, there is a potential chance of excitonic dipole-dipole interaction occurring between the exciton at level $m$ and another exciton after phonon interaction at level $m'$ of the same SWNT. This excitonic dipole-dipole interaction between excitons at $m$ and $m'$, can potentially lead to EET from level $m$ to $m'$, for the same SWNT. This suggests more Raman signal enhancement due to EET between excitons from the same SWNT (in addition to already considered resonance condition). Therefore, this work also highlights the need for further experimental investigation and development of mathematical, theoretical models to incorporate the role of EET within same SWNT and between neighboring SWNTs towards calculating total resonance Raman signal intensity.
2.5 References


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3. Carbon nanotube surface adsorbates and their effects on phonon-assisted exciton energy transfer (EET) in single walled carbon nanotube bundles using resonance Raman spectroscopy.

Previously, we explored exciton energy transfer (EET) events in SWNT bundles using resonance Raman spectroscopy. We have shown ‘phonon-assisted’ exciton energy transfer (EET), by comparing Raman RBM spectra of the same sample, with increasing laser excitation power. This allows for corresponding increase in photodesorption of molecular adsorbates on the SWNT surface, resulting in increased EET efficiency. In this chapter, we demonstrate how cleaning up the SWNT surface allows for enhanced EET events.

3.1 Introduction

3.1.1 Applications of exciton energy transfer (EET)

EET plays major role in many physical and chemical processes cutting across the fields of materials science, chemistry and biology. Excitation transfer is a very commonly occurring natural phenomena, ubiquitous in the light-harvesting proteins present in most plants, as part of photosystem molecules. These help in eventual storage of ever abundant solar energy into energetically rich organic molecules, accompanied by oxygen evolution. It thus plays an integral part in the very basis of life on earth. Exciton energy transfer (EET) pathways have been seen among light harvesting proteins of purple bacteria\(^1\) and also in reaction centers of various other oxygenic
photosynthesis process too\(^1\). Light harvesting complex II (LHC-II) is one of the most abundant proteins on Earth and makes our planet green\(^2\). These complexes function or work like antennae to harvest solar energy and EET pathways are central to most of the photosynthetic processes\(^3\).

Taking cues from nature, we can develop rationale for designing molecules for light harvesting and also develop strategies to optimize light harvesting systems. Because, in principle, the total amount of sunlight reaching Earth’s surface in one day, if completely captured, is sufficient to support our activities for long durations, like a few years\(^4\). Traditionally, EET is seen as a non-radiative energy transfer pathway occurring from a donor to acceptor molecule. EET can also be made to occur via an intermediary to over slightly longer distances and energies. These EET systems can be donor-bridge-acceptor (D-B-A) type\(^5\). We can potentially develop these D-B-A type EET systems from controlled, aligned SWNT bundle films. Aligned, SWNT bundles are also been considered as antenna and energy concentrators for light harvesting applications\(^6\). EET events is also a major player in detection methodologies. FRET microscopy\(^7\) is one the best example to illustrate the use of EET as a detection procedure. EET in SWNT bundles is also been considered for potential use as IR probes\(^8\). To summarize, since the first observations of EET in semiconducting SWNT bundles\(^9\) and identification of potential FRET based mechanisms\(^10\) as one of the major EET pathway for SWNT bundles, there has been a drive for identifying and testing various potential applications of EET in SWNT bundles\(^6,8\). High EET efficiency is desired for any EET based application. In this chapter, we explore the role of SWNT bundle surroundings on ‘phonon-assisted’ EET, to improve EET efficiency.

3.1.2 Rationale for change in EET with change in SWNT bundle surroundings

As discussed in the previous chapter, EET can be observed using resonance Raman spectroscopy by comparing Raman RBM spectra of the same SWNT bundle sample by varying excitation laser
power. We attribute this increase in EET efficiency, with increasing laser power to increasing photodesorption. Here, we make use of already demonstrated event of molecular desorption due to light-SWNT interaction, from SWNT surface\textsuperscript{11}. We can rephrase the same as ‘upon light interaction with the SWNT surface, the adsorbate concentration reduces on the SWNT surface due to photodesorption’. EET therefore increases due to better inter-tube interaction due to reduced adsorbate interference. By extending the same logic we can hypothesize that, ‘removing adsorbates from SWNT bundle surface via mild chemical cleaning, improves EET efficiency’.

Figure 3.1: Schematic showing SWNT bundles with adsorbates sticking to its surface along with the corresponding weak EET (red dotted line) occurring between smaller diameter, donor SWNT and larger diameter, acceptor and its corresponding Raman RBM spectra. After removing adsorbates from SWNT bundle surface (fewer grey dots - adsorbates) results in improved EET between the donor and acceptor SWNT as represented by thick red line and corresponding increased Raman RBM signal for larger diameter, acceptor SWNT, compared to Raman RBM signal of the same large diameter, acceptor before adsorbate removal.

Figure 3.1, is a schematic of the hypothesis. In the previous chapter, the molecular adsorbates discussed can be released from the SWNT surface via photodesorption\textsuperscript{11}. But in this chapter, we will first consider those adsorbates that cannot undergo photodesorption. It is known that pristine
SWNTs, after growth have different impurities\textsuperscript{12} like catalytic impurities such as Fe, or Co and Mo, along with other impurities\textsuperscript{13} such as amorphous carbon, graphite, etc\textsuperscript{14}. Catalytic impurities can be removed by various approaches including different chemical treatment methods\textsuperscript{15}. In this chapter, we look at improvement in the EET in SWNT bundles as we remove amorphous carbon from the pristine SWNT sample via mild chemical treatment methods along with photodesorption of adsorbates. It has already be shown that amorphous carbon impurities can be removed via chemical treatment methods\textsuperscript{16}. The rationale for using milder chemical treatment methods is to minimize SWNT structure damage but at the same time improve EET efficiency by removing adsorbates on the SWNT bundle surface.

3.2 Experimental Section

3.2.1 Materials

Pristine SWNTs (HiPco\textsuperscript{®}), obtained commercially from Nanointegris were used. For oxidizing these pristine SWNTs, hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) used, was obtained commercially from Sigma Aldrich.

Various concentrations of hydrogen peroxide solutions were freshly prepared in deionized water. 1 mg of pristine SWNTs were weighed and added to test tubes containing 5 ml of (a) deionized water, (b) 1M H\textsubscript{2}O\textsubscript{2}, (c) 2M H\textsubscript{2}O\textsubscript{2}, (d) 9M H\textsubscript{2}O\textsubscript{2} solutions. Oxidation of these SWNT suspensions by H\textsubscript{2}O\textsubscript{2} were conducted in the absence of light to prevent peroxide decomposition, for 30 days, by gently mixing using Rotospin – rotary test tube mixer. The suspensions were aliquoted after 30 days and drop-casted on clean silicon substrate and allowed to dry to form a SWNT film/mat. These dried SWNT films on silicon substrate were used for obtaining scanning electron
micrographs (SEM images), X-ray photoelectron spectroscopy (XPS) and resonance Raman spectroscopy based characterization.

3.2.2 Electron Microscopy

SEM micrographs (courtesy: Vishal Desai) were obtained on Hitachi S-4800 using SE-2 detector at an acceleration voltage of 2 kV and a magnification of 50 kX. TEM micrographs were obtained on JEOL-2010 LaB₆ STEM at an acceleration voltage of 200 kV. The samples for TEM imaging were prepared from SWNT suspension samples. These suspension samples were subjected to 2 minute sonication and this is followed by drop-casting aliquots of the sample on to the holey carbon grid. The holey carbon grid with the samples were left overnight in desiccator.

3.2.3 X-ray Photoemission Spectroscopy

The samples were analyzed on Thermo VG Scientific Theta Probe for obtaining X-ray photoelectron spectra. Survey scans were made at a detector pass energy of 300 eV, with a step size of 1.00 eV, dwell time of 50 ms and averaged over 7 scans. The spectra obtained were analyzed using Thermo Scientific’s Avantage software. The spectra obtained from SWNT film is compared to that obtained from pristine highly ordered pyrolytic graphite (HOPG). XPS spectra of pristine HOPG was obtained by exfoliation of HOPG in-situ (inside the XPS load-lock) using scotch-tape method, in argon atmosphere (to avoid HOPG surface exposure to any air, to prevent any HOPG surface oxidation).

3.2.4 Resonance Raman Spectroscopy

Raman spectra for all the carbon nanotube samples were obtained on Horiba Jobin Yvon LabRAM HR, using $E_{\text{laser}} = 1.96 \text{ eV} (\lambda = 632.8 \text{ nm})$ (He/Ne laser), at 1.7mW laser power and static grating
of 1800 mm. Each spectra was recorded for 10 s and averaged 3 times. The final Raman spectra for each sample is an averaged spectra of 26 different spots on the sample. All the respective Raman peaks were normalized to its corresponding G-band of the same spectra unless specifically mentioned.

Other variations to the Raman measurement approaches are mentioned as required in the results and discussion section.

3.2.5 SWNT Density of states (DOS) simulation

Density of states (DOS) for SWNTs with different diameters and indices \((n, m)\) were obtained using the method used by Yang, L. et al	extsuperscript{17}, with C-C spacing taken at 0.142 nm and Tight Binding Energy \((\gamma_0)\) at 3.0 eV.

3.3 Results and Discussion

Just as discussed in the previous chapter where Raman RBM spectra of SWNT bundles with increasing laser power shows increasing EET efficiency, here in this chapter we observe same event of increasing extent of EET but after treatment with increasing concentrations of \(\text{H}_2\text{O}_2\) (as shown in Figure 3.2). Previously, (in Chapter-2) the EET improvement as observed by comparing Raman RBM spectra, was due to increasing extents of photodesorption of molecular adsorbates with increasing laser excitation power. Here, as shown in Figure 3.2, the improvement in EET as observed is due to cleaning of SWNT bundles, by removing the adsorbed amorphous carbon by SWNT sample treatment with increasing concentrations of \(\text{H}_2\text{O}_2\), resulting in improved nanotube-nanotube interactions. It is now necessary to demonstrate, that these changes in the Raman RBM spectra of SWNT bundles with increasing amounts of \(\text{H}_2\text{O}_2\) treatment is indeed due to changes in
EET efficiency. With improving EET, the Raman signal for smaller diameter, donor SWNT reduces further and a corresponding increase in Raman RBM signal for acceptors is observed.

Firstly, it is important to determine if the conditions for EET are fulfilled, i.e. there should be no physical degradation or breakdown of SWNTs upon H$_2$O$_2$ treatment and bundling of SWNTs must

Figure 3.2: On the left is the Raman RBM spectra of SWNT bundles with increasing H$_2$O$_2$ treatment (from bottom to top), at 1.96 eV and measured at a laser power of 1.7 mW. Increasing H$_2$O$_2$ treatment results in corresponding improvement of EET from smaller diameter, donor SWNTs to larger diameter, acceptors. The schematic on the right illustrates improvement of EET as observed by Raman RBM spectra, due to removal of adsorbed amorphous carbon (grey dots) from SWNT surface, with H$_2$O$_2$ treatment. This results in improved inter-tube interactions leading to improved EET.
still be observable after hydrogen peroxide treatment. **Figure 3.3** shows the SEM micrograph of SWNT film/mat after 9M H$_2$O$_2$ treatment. It shows typical tube like formations characteristic of SWNT bundles. However, **Figure 3.3** does not conclusively prove bundling in SWNTs. To confirm tubular nature (no complete degradation of SWNTs) and bundling of SWNTs TEM imaging was done. TEM micrograph, as shown in **Figure 3.4**, confirmed the bundling nature of SWNTs even after 9M hydrogen peroxide treatment of HiPco SWNTs. It also showed that the SWNTs were not broken down and still retained its tubular structure.

Figure 3.3: SEM micrograph of 9M H$_2$O$_2$ treated HiPco SWNTs in dry film form on silicon substrate. SWNTs here can be seen to form bundles. SWNT degradation upon hydrogen peroxide is not observed.
We now need to establish that total amorphous carbon in the system has reduced with hydrogen peroxide treatment leading to improved inter-tube interaction. XPS was used to determine reduction in the total carbon (Figure 3.5).
Figure 3.5: (a) XPS survey scan for ‘in-situ’-cleaved (exfoliated inside argon filled XPS load lock to prevent HOPG oxidation) HOPG, showing a clean carbon (C-$sp^2$) peak. Figure (b) is the survey scan for pristine untreated SWNT film showing catalytic iron peak, along with small oxygen (O-1s) peak indicating some oxidation with a strong carbon peak. This can be compared to Figure (c), which is the survey scan for the 9M H$_2$O$_2$ treated SWNT film showing a relatively stronger oxygen peak and comparatively weaker carbon peak. Catalytic iron is also seen in Figure (c).

XPS survey scan for freshly cleaved (exfoliation) HOPG (Figure 3.5 (a)) shows how the spectra should look like if there was no oxidation to be found for a pure carbon ($sp^2$ hybridized) (like defect free graphene and SWNTs) system. XPS for both pristine and 9M hydrogen peroxide treated SWNTs were made using very thick SWNT film samples on silicon substrates. No silicon peaks
were found in any of the XPS spectra indicating complete and continuous SWNT film (the XPS signal was only from the SWNT film and not from the substrate). By comparing Figure 3.5 (b), XPS survey for pristine SWNT film and Figure 3.5 (c), XPS survey for 9M H$_2$O$_2$ treated SWNT film, we can demonstrate that the total carbon in the SWNT bundle system has reduced and there has also been a corresponding increase in SWNT oxidation due to hydrogen peroxide treatment. Though, this still does not prove that there has been a reduction in the amorphous carbon content in the system. One can also attribute the relative carbon signal loss to breakdown of the carbon from SWNTs itself. If the carbon from the SWNTs are involved, then it should result in a significant rise in the extent of defects in the SWNT walls. The defects in the SWNT walls can be monitored by studying changes in the Raman D-band/G-band intensity ratio. Defect introduction into the SWNT sidewalls results in increase of D-band/G-band intensity ratio.

![Figure 3.6: The $I_D/I_G$, Raman intensity ratio of D-band to G-band helps monitor defects in the SWNT film. $I_D/I_G$ reduced with H$_2$O$_2$ treatment.](image)
Figure 3.6, shows no defects introduction into the SWNT walls upon peroxide treatment and that 9M H$_2$O$_2$ treatment does not breakdown SWNTs. But from the XPS data we can summarize that total carbon in the SWNT film system has reduced upon H$_2$O$_2$ treatment but this treatment has not introduced many defects into the SWNTs. This implies that the carbon loss is from the amorphous carbon sticking on to the SWNT surface and not from SWNTs themselves.

Further confirmation of improvement of inter-tube interaction, upon chemical treatment is made by comparing the changes in Raman RBM spectra with changes in the laser excitation power for pristine SWNTs bundles and 9M H$_2$O$_2$ treated SWNTs. This comparison, brings forth the difference in the extent of EET occurring in the pristine SWNTs verses peroxide treated SWNTs, under similar laser power conditions. Figure 3.7, shows such comparison. From the Raman RBM spectra, in both Figure 3.7 (a) and (b), we see exciton energy transfer (EET) to varying extents with change in laser excitation power (indicated by black curvy arrows hopping from peak to peak). In Figure 3.7 (b), for each of the Raman RBM spectra we see an improvement in the extent of EET when compared to its corresponding RBM spectra for pristine SWNTs. This can be seen as the Raman RBM peak intensity reduction of smaller diameter, donor SWNTs and corresponding increase in the Raman RBM signal intensity for larger diameter, acceptor SWNTs. The blue downward arrow cutting across the Figure 3.7 (b) indicates increasing reduction in Raman RBM spectra for smaller diameter, donor SWNTs and red arrow going upward indicates corresponding increase in Raman RBM spectra for larger diameter, acceptor SWNTs. It is also important to point out that in Figure 3.7, we see improvement of EET due to both molecular photodesorption from SWNT bundle surface, with increasing laser power and also due to the chemical treatment of the SWNTs improving inter-tube interaction. For Figure 3.7, Raman RBM measurements were made at 6 different spots on the SWNT film and an average Raman spectra is plotted.
A variant in Raman RBM measurement approach was tried to negate the role of molecular photodesorption with change in laser power and to help us determine the role of peroxide cleaning in improvement of ‘phonon-assisted’ EET in SWNT bundles. In Figure 3.7, we observe the changes in Raman RBM spectra, due to both molecular photodesorption and peroxide cleaning. To understand the role of peroxide cleaning on changes in Raman spectra we have to negate the
role of molecular photodesorption. Here, to negate the role of molecular photodesorption from SWNT surface towards changes in Raman RBM spectra with increasing laser power, due to increasing extents of EET, is by exposing the exact spot where the Raman measurements are to be made, with a very high power laser (17 mW) for one minute and immediately follow it up by collecting Raman data from the exact spots at lower laser powers (8.5, 4.2 and 0.2 mW). Each such spectrum is an averaged plot obtained from Raman measurements made at six different spots on the SWNT film sample. By exposing the SWNT film for one minute with higher power laser, we ensure that role of molecular photodesorption levels are same for all the eventual Raman measurements at various lower laser powers. Now the changes we observe in the Raman spectra is primarily due to the chemical cleaning of SWNT bundles. It is very important to understand that it is not possible to completely negate the effects of molecular desorption from the SWNT surface from with changing laser power.

Figure 3.8, is Raman measurement, for both pristine (Figure 3.8 (a)) and 9M H₂O₂ treated SWNTs (Figure 3.8 (b)) following the method mentioned in the previous paragraph. A comparison between Figure 3.7(a) and 3.8(a) shows the difference in Raman spectra due to initial over exposure (1 minute) to high power laser (17 mW) for pristine SWNT sample. In Figure 3.8 (a), when compared to 3.7 (a), we notice an increase in the Raman RBM intensities for smaller diameter SWNTs too. This is an important observation, as it demonstrates that due to the presence of amorphous carbon/other non-photo-desorbing molecules, there is weaker inter-tube interaction. This results in weak EET. But due higher molecular photodesorption, results in better light-SWNT interaction that yields better Raman scattering. To summarize, in Figure 3.8 (a), we see improved Raman scattering, resulting in relatively higher Raman signal for smaller diameter SWNTs (in the red region), when compared to Figure 3.7 (a), because of increased molecular photodesorption
due to initial exposure to higher power laser. Now, while comparing Figure 3.8 (a) to 3.8 (b), the Raman RBM intensities for smaller diameter SWNTs (in the red zone) in the 3.8 (b) is not as high as compared to those in 3.8 (a), whereas there is huge signal enhancement for Raman signal for larger diameter SWNTs (in the blue zone). This is due to improved EET in 3.8 (b), due to improved inter-tube interaction after 9M hydrogen peroxide treatment. Another variant to Raman measurement approach as mentioned in Figure 3.8, is made to further probe the nature of photodesorption dynamics and its effects on Raman RBM signal. Here (Figure 3.9), Raman
measurements were made for both pristine (3.9(a)) and 9M H₂O₂ treated (3.9(b)) SWNTs, at (relatively lower) 8.5 mW laser power, for every 15 minutes, for 150 minutes after initial high power laser exposure at 17 mW.

Figure 3.9: Raman RBM spectra for pristine SWNTs (Fig: (a)) and 9M H₂O₂ treated SWNTs (Fig: (b)) measured at 8.5 mW, at 15 minutes time interval for 150 minutes, immediately after 1 minute high power (at 17 mW) laser exposure at the same spot where the measurements are to be made. In Fig: (a), due to weaker inter-tube interaction, we observe EET only after normalizing intensity to (11,1) peak (as shown in in-set and the contour plot in the right). The contour plot for Fig: (a) shows Raman intensity changes with time for (9,9) and (12,3) SWNTs. The reduction of (9,9) and increase in signal for (12,3) (at 220 cm⁻¹) shows reduction of EET with time. For the un-normalized plot, we observe drop in Raman intensities due to increasing molecular readsorption with time. In Fig: (b), after peroxide treatment, due to improved inter-tube interaction due to removal of amorphous carbon/ molecules that do not photo-desorb, we observed improved EET. The reduction of EET with time is observable in both the un-normalized and normalized (to (11,1)) plot. The contour plot for Fig: (b), shows changes in Raman intensities for all the SWNTs with time. The reduction of intensity of (9,9) (at ~195 cm⁻¹) and the corresponding increase in signal for other peaks is due to reducing EET with time due molecular readsorption.
Figure 3.9, shows the difference in changes in Raman RBM signal intensity with time for pristine (Figure 3.9 (a)) and for 9M peroxide treated SWNTs (Figure 3.9 (b)). With time, after initial high power laser exposure (which leads to excessive molecular desorption from SWNT surface), the molecules start to re-adsorb on to the SWNT surface. This effectively reduces the inter-tube interaction with time, leading to reducing EET with time (as illustrated in Figure 3.10).

Figure 3.10: Illustrates how high power laser exposure leads to increased molecular desorption. With time, however, molecule re-adsorb on the SWNT surface, leading to reduced inter-tube interaction, resulting in reducing EET. This can be observed by reduction in Raman RBM peak intensities for larger diameter SWNTs and corresponding increase in the signal intensities for smaller diameter SWNTs with time (as seen in Figure 3.9 (a) and (b))
Another major difference to be noted from the inset images of Figure 3.9 (a) and (b), are that, for Figure 3.9: (a) the Raman RBM intensities are relatively higher for (11,1) when compared (11,1) peak intensities in inset for Figure 3.9: (b). This suggests that molecular photodesorption leads to improved Raman scattering from SWNTs. This is because, after molecular photodesorption, the laser light-SWNT interaction improves. This leads to improved Raman scattering from SWNT surface. This can be seen in both Figure 3.9: (a) and (b). Molecular photodesorption also effects EET. But only to a smaller extent for pristine SWNTs (Figure 3.9: (a)) (due to the presence of excess amorphous carbon). This means, though Raman signal improves with improved photodesorption with high power laser exposure, but because of presence of amorphous carbon, the extent of EET occurring is lowered, thus allowing the smaller diameter SWNTs to retain their Raman signal. But as seen in the inset for Figure 3.9: (b), Raman spectra for peroxide cleaned sample, shows that smaller diameter SWNTs fail to retain their Raman RBM signal, as its energy is transferred to larger diameter SWNTs via EET pathways, due to improved inter-tube interaction.

The next question is to understand if the spike in the Raman RBM signal is indeed due to molecular photodesorption. Here, we used a third variation to our Raman measurement method. Raman RBM measurements (at 8.5 mW) were made on the SWNT sample, at different spots in a straight line, after every 0.5 μm (from spot position ‘-2.0 μm’ through ‘0.0 μm’ to ‘2.0 μm’). Then at spot position 0.0 μm, high power laser exposure (at 17 mW) was made for 1 minute and post-high power laser exposure the Raman RBM measurements were again made at the same spot positions at 8.5 mW. These measurements were made for both pristine SWNT film samples (Figure 3.11) and 9M peroxide treated SWNT film (Figure 3.12). From both the measurements it is clear that post high power laser exposure measurements, demonstrate enhanced EET, due to increased inter-tube interaction.
Figure 3.11: The second column images, illustrates the 3 steps involved in the Raman measurement method. First the Raman measurements (at 8.5 mW, 1.96 eV) were made at different spots on the pristine SWNT film sample, in a straight line. The corresponding Raman spectra obtained is shown in the left and as a contour plot in the right. There are no major variations in the spectra at various spots on the SWNT film. All the Raman peaks are normalized to (11,1) peak (at ~255 cm$^{-1}$), indicated by a horizontal red dotted line. Step – 2 shows high power laser exposure (at 17 mW), at spot position 0.0 μm, for 1 minute. The third step is same as the first where Raman RBM measurements were again made at different spots, in a line, at 8.5 mW. From the spectra obtained it is clear that only, at the spot 0.0 μm, we notice enhanced EET (as indicated by upward facing red arrow, ↑ for largest diameter tube (9,9) due to increase in its Raman signal and Raman signal loss for (12,3), as indicated by downward facing red arrow, ↓). From the contour plot at the bottom right, it is clear that EET is enhanced only at the spot 0.0 μm, due to high power laser exposure, which leads to increased molecular desorption at that spot than its surroundings.
Figure 3.12: The Raman measurement approach here is similar to as explained for Figure 3.11. Here, the experiment is repeated for 9M peroxide treated SWNT film. Here, for the post high power (17 mW) laser exposure Raman RBM measurements, we observe a much stronger EET event at spot position 0.0 μm, than as seen in Figure 3.11 for pristine SWNT film sample. This is due to improved inter-tube interaction for 9M peroxide cleaned SWNTs. This leads to more efficient EET.

Consequently, from Figure 3.11 and 3.12, we can determine that for 9M peroxide cleaned SWNT samples, we see enhanced EET. And EET for both pristine and 9M peroxide treated SWNT samples, is enhanced only at the spot which was subjected to initial 1 minute high power laser
exposure (at spot position 0.0 μm) than its surroundings. This indicates that EET enhancements for both the cases is due to increased photodesorption at the spot position subjected to high power laser exposure. This Raman measurement approach (as shown in Figure 3.11 and 3.12) in conjunction with the Raman measurement method discussed earlier (as discussed in Figure 3.8, 3.9 and 3.10) can be used to studied molecular adsorption kinetics on SWNT surface.

Similar changes in the Raman RBM spectra for chemically or enzymatically treated SWNTs can be attributed to differential oxidation of SWNTs with differing diameters and metallicities. It is also important to make sure that the changes we observe in the Raman measurements is not due differential oxidation of different SWNTs in the mixed SWNT film. As Raman signal depends on various ‘electron-phonon’ and ‘electron-photon’ interactions (From Eq: 2.2). Raman signal is sensitive to both density of states available for the electron to occupy and electron loss during SWNT oxidation. It is important to rule out the changes we observed here is not due to differential oxidation of SWNTs or differential signal sensitivity to electron loss/oxidation due to differences in the DOS of different SWNTs.

A redox potential based approach has been proposed to explain what electron (from which energy sub-band/van Hove singularity (vHs)) can be removed (oxidized) from the SWNTs by using a chemical of a certain concentration (with a certain redox potential value)\(^{18}\). It states that any chemical (or enzyme as proposed by Chiu, C. F. \textit{et al}\(^{19}\)), whose electrochemical potential is greater than a certain SWNT sub-band, then that chemical (or enzyme) can potentially oxidize that sub-band (capable of removing electrons from that sub-band).

Kim, K. K. \textit{et al}\(^{18}\) and Hirana, Y. \textit{et al}\(^{20}\), gave the relation between the electrochemical potentials of corresponding vHs/sub-bands of SWNTs to its diameter. The following equation gives the relation\(^{18}\).
\[ E^{\text{swnt}}_{\text{(SHE)}}(V) = \frac{a}{d_t (\text{nm})} + b \]  
\text{(Eq: 3.1)}

\( E_{\text{(SHE)}} \) is the electrochemical potential (units = V) of a given vHs of a given SWNT with diameter, \( d_t \) and ‘a’ and ‘b’ are the fitting parameter. This gives an inverse relation between diameter, \( d_t \) of the SWNT and its electrochemical potential for a given vHs. Using the values given by Kim, K. K. et al\textsuperscript{18}, for the fitting parameters, we plotted the electrochemical potential, \( E^{\text{swnt}}_{\text{(SHE)}}(V) \) vs \( d_t \) plot for SWNTs (Figure 3.13).

Figure 3.13: Electrochemical potentials of occupied vHs (V1s, V2s and V1m) and unoccupied vHs (C1s, C2s and C1m), along with Fermi energies for both semiconducting (red dotted line) and metallic (blue dotted line) as a function of SWNT diameter. Blue lines for metallic vHs levels and red for semi-conducting. Also labelled are the SWNTs (n,m) tested in this work (black squares). It shows that it is easy to oxidize larger diameter SWNTs than smaller diameter SWNTs. It also shows ease of oxidation trends (V1s>V2s>V1m).
Now, consider changes in Raman RBM spectra for SWNTs for different peroxide treatments (Figure 3.2: (a)), in purview of the redox potential picture presented in Figure 3.13. We notice that the trends proposed in Figure 3.13 do not match the data shown in Figure 3.2. According to the redox potential picture, SWNT treatment with increasing peroxide concentration should lead to increasing levels of SWNT oxidation. Also, this oxidation should be more for semi-conducting S_{22} level and to a lesser extent for smaller diameter metallic SWNTs from the M_{11} level. We do observe this trend in Figure 3.2: (a). But within M_{11} and S_{22} levels, according to the redox potential theory, larger diameters must oxidize faster, leading to drop in their Raman RBM signal. But we observe a reverse trend within M_{11} and S_{22} levels (from Figure 3.2: (a)). We observe that the Raman RBM signal for the larger diameter SWNTs within M_{11} ((9,9)) and S_{22} ((10,3)) levels remain strong whereas the signal for the smaller diameter SWNTs reduces. These observations from Figure 3.2: (a), allows us to rule out the possibility of changes in Raman RBM spectra with peroxide treatment for differential oxidation of SWNTs.

Another possibility to consider that may lead to changes in the Raman RBM signal of SWNTs when treated with increasing concentrations of peroxide is due to varying density of states (DOS) available for the electron to occupy at that vHs level. If there are more DOS, for a certain SWNT at a certain vHs level, then the electron loss/oxidation from that level, does not drastically change the Raman signal for that level. In other words, Raman signal sensitivity depends on the DOS of the SWNT. More the DOS, less sensitive the Raman signal is to SWNT oxidation.

To this end, we calculated the DOS for the all the HiPco SWNTs we observed at 1.96 eV. Figure 3.14, shows the Energy vs DOS plots for the metallic and semi-conducting SWNTs. The upper plot in Figure 3.14, is for metallic and the bottom plot is for the semi-conducting SWNTs. It is
clear that DOS is very similar and comparable for semi-conducting SWNTs. For metallic (9,9) has the highest DOS, followed by (12,3) whereas (13,4) has the least DOS of the three.

Figure 3.14: Energy vs DOS plot for metallic SWNTs (top) and semi-conducting SWNTs (bottom), that were observed at 1.96 eV, for HiPco SWNTs. States available are comparable for semi-conducting SWNTs, but for metallic (9,9) has the most, followed by (12,3), whereas (13,4) has the least of the three SWNTs compared.
From Figure 3.2: (a), we can observe that the Raman signal changes are most drastic for (9,9), when compared to the rest of the SWNTs in the spectra. This suggests that the varying Raman signal sensitivity dependent on DOS is not the reason for the Raman signal change that we have observed in Figure 3.2: (a). To sum up the discussions for Figure 3.13 and 3.14, is that, we have tested out two of the other hypothesis, to explain the changes in Raman RBM spectra of SWNTs with increasing peroxide treatment. We can say that our observations are not primarily due to SWNT oxidation, or changes in the Raman signal sensitivity due to varying DOS for each of the SWNTs with oxidation.

### 3.4 Summary

To the best of our knowledge, there is no previous reported literature on the environmental effects (role of molecular photodesorption and mild chemical cleaning to remove molecules that do not photo-desorb) on ‘phonon-assisted’ exciton energy transfer (EET) for SWNTs, as observed by studying the RBM modes by resonance Raman spectroscopy.

Here, we show:

1) Mild chemical cleaning of SWNTs, can remove amorphous carbon (and other debris, that does not photo-desorb) from the SWNT surface, resulting in improved EET, due to improved inter-tube interaction.

2) Improvement in ‘phonon-assisted’ EET, upon exposure to high power laser and followed by Raman measurements at lower power. This is due to increased molecular photodesorption, resulting in improved inter-tube interaction, yielding better EET.

3) Simultaneous observation of improvement in EET due to increased photodesorption and due to chemical cleaning.
4) Re-adsorption of molecules on to SWNT surface reduces inter-tube interaction resulting in reduced EET (Figure 3.9). Raman RBM spectra, for chemically cleaned SWNT film shows greater sensitivity to molecular re-adsorption. This cleaned SWNT film can be a good surface to probe and study molecular adsorption kinetics.

As pointed out by Heller, D. A. *et al*\(^{21}\), while studying SWNT degradation or separation, in various forms of SWNT aggregates, usage of changes in Raman RBM peak intensities to show specificity and selectivity of certain types of SWNTs has to be done very carefully. In addition to caveats highlighted by Heller, D. A. *et al*, it is also important to understand the role of change in inter-tube interactions due to bundling, cleaning, heating, light interaction etc. This leads to changes in the Raman RBM peak intensities due to changes in the efficiency of ‘phonon-assisted’ EET and this can potentially be misinterpreted as selection or degradation of certain SWNTs.

Another important observation, is that upon 9M peroxide treatment of SWNTs, as shown in Figure 3.6, the Raman D-band/G-band intensity ratio reduced when compared to that of pristine SWNTs. This can be misinterpreted as removal of defects from the SWNT side-wall. Based on our data presented in this chapter, we can say that is reduction in the Raman D-band/G-band intensity ratio can be due to improved first order Raman scattering (increase in G-band intensity), when compared to D-band. This can be due to removal of amorphous carbon/other material debris upon peroxide treatment, leading to better light-SWNT interaction. Similar observations have been made by Feng, Y. *et al*\(^{22}\), for hydrogen peroxide treated few-walled carbon nanotube samples. This is further discussed in the next chapter (Chapter-4).
3.5 References


4. Effects of changes in inter-tube interaction on Raman G-band of SWNT bundles, upon molecular photodesorption and chemical treatment of SWNTs

Chapters 2 and 3 were dedicated to studying ‘phonon-assisted’ exciton energy transfer (EET) in SWNT bundles and the role of nanotube surface adsorbates in affecting the efficiency of EET, using Raman radial breathing mode (RBM) spectra. In this chapter, we demonstrate improved thermal conduction in SWNT bundled film sample, resulting in reduced heat-induced Raman G-band frequency shift due to improved inter-tube interaction upon laser induced molecular photodesorption from SWNT surface. We also demonstrate changes in Raman G-band line shape upon cleaning SWNT bundles via mild chemical treatment and G-band line shape changes due to laser induced molecular photodesorption from SWNT surface.

4.1 Introduction

4.1.1 Thermal conductivity of SWNTs and applications

According to Berber, S. et al., the theoretical thermal conductivity for an isolated SWNTs (specifically (10,10)), is very high (at ~6600 W/mK). This value is comparable to theoretical thermal conductivity of isolated graphene and diamond. Such high theoretical thermal conductivity values were attributed to very large phonon mean free paths in \(sp^2\) systems\(^1\)-\(^2\). This, alongwith high thermal\(^3\) and mechanical stability, and high current carrying capacity\(^4\), make SWNTs very interesting material to research for VLSI interconnects applicability for the future\(^5\).
With the progressive shrinking of the device dimensions, there has been a big push for thermal management at the device design level itself. As scaling progressed to ULSI circuits, its performance became increasingly sensitive to very small changes in the temperature. Diamond and SWNTs alongwith graphene have been identified as potential materials for thermal management for such circuits, owing to their high thermal conductivity. Carbon nanotubes are also being explored as potential filler material in a matrix of other materials to improve thermal stability of the matrix. Biercuk, M. J. *et al* tested SWNTs mixed with industrial epoxy to improve the thermal conductivity of the epoxy matrix.

The measured thermal conductivity values for SWNTs and multi-walled carbon nanotubes (MWNTs) is found to have a linear relation with temperature (increasing thermal conductivity with increasing temperatures). For SWNTs the tested temperature range was from 8 - 350 K. The temperature range tested for studying thermal conductivity relation to temperature for MWNTs was from 10 – 300 K. Hone, J. *et al* also suggested comparable thermal conductivity of SWNTs to that of diamond and *in-plane* graphite, at room temperature. In another work, Hone, J. *et al* suggested thermal conductivity of aligned SWNTs to be 200 W/mK. For individual MWNTs, Kim, P. *et al*, found the thermal conductivity to be at 3000 W/mK, which is 2 orders of magnitude more than other reported measurements for bundled MWNTs. In the same work, the thermal conductivity of the individual MWNTs peaks at 320 K, after which it reduces due to umklapp phonon scattering. For aligned SWNT bundles, thermal conductivity of ~ >200 W/mK was measured and the linearity relation between temperature and thermal conductivity ends at a low temperature limit of 40 K, beyond which the 1 D quantization effects of SWNTs. The reported thermal conductivity values of SWNTs and MWNTs in various forms and at various temperatures have varied from 20 – 3000 W/mK, showing wide range and applicability.
4.1.2 Temperature effects on the Raman G-band spectra of SWNTs

As introduced in the background chapter (Chapter 1), G band is signature multi-peak Raman feature, characteristic of all the sp\textsuperscript{2} carbon systems including graphite, graphene, nanotube families, etc. It occurs at \(\sim 1585 \text{ cm}^{-1}\). For carbon nanotubes (both SWNTs and MWNTs), uniaxial stretching leads to splitting of the G band into G\textsuperscript{+} and G\textsuperscript{-} bands. G\textsuperscript{+} band is due to the C-C vibrational modes that are along the nanotube axis (along the length). Whereas, the G\textsuperscript{-} band is for the C-C vibrations along the tube width (diameter). Where, \(\omega_{G^{-}} < \omega_{G^{+}}\).

Jorio, A. \textit{et al}\textsuperscript{15}, is a good source to understand the temperature and doping effects on the Raman G band. Here, the temperature effects are explained by connecting G band (vibrations) properties to electron-phonon (‘e- ph’) coupling. These effects are studied within the ‘non-adiabatic’ approximation of time-dependent perturbation theory. Here, due to \(\Gamma_{6}^{+} (E_{2g})\) lattice distortions (perturbation), the electron momenta does not have enough time to relax; to follow the instantaneous ground state (GS). As a consequence, in the absence of scattering, the Fermi surface remains same as was at the unperturbed state, leading to the softening of the \(\Gamma_{6}^{+} (E_{2g})\) phonons of the C-C bond\textsuperscript{16}. In other words, increasing temperature leads to softening of the modulus (of the phonons) of C-C bond, leading to reduction in the Raman shift\textsuperscript{17}. The non-adiabatic scheme within the time-dependent perturbation theory works here because it is known that the atomic motion for the G band is 22 fs\textsuperscript{15,18}. Whereas, the measured electron momenta relaxation times in is the order of few hundred femtoseconds\textsuperscript{19}. There are also other groups\textsuperscript{20}, which propose anharmonic contribution due to thermal expansion, for the Raman frequency downshift with increasing temperature, for SWNTs\textsuperscript{21} based on the classic work done by Postmus, C. \textit{et al}\textsuperscript{22}. The G band frequency dependency on temperature for different \(sp^{2}\) nano-carbon species can be measured and represented by:
\[ \omega_G = \omega_G^0 + \chi T \]  

(Eq: 4.1)

Where, \( \omega_G^0 \) is the G band frequency (Raman shift) when limit \( T \to 0 \) (\( T \) is temperature) and \( \chi \) is the temperature coefficient of the frequency of C-C bond stretching mode (can also be used to study changes in SWNT radial breathing modes (RBM)). Many groups have independently obtained \( \chi \) values for G band and RBM for SWNTs. The values are ~ -0.013 cm\(^{-1}\)/K, for G band and ~ -0.038 cm\(^{-1}\)/K for RBM\(^{23}\).

As used by Li, H. D. et al\(^{23}\), Raman temperature dependency studies are usually conducted by making Raman measurements at varying laser power (laser induced heating effects).

### 4.1.3 Rationale

As mentioned at the end of the previous section, it is known that using different laser powers for making Raman measurements leads to varying levels of heating effects (more the laser power, more the induced heating effects) on the substrate. Based on results obtained and discussed in Chapters 2, 3 and from the work done by Chen, R. J. et al\(^{24}\), we know that light interaction with the SWNTs also leads to molecular photodesorption from the SWNT surface in addition to heating effects mentioned in the previous section (Section 4.1.2). From the results discussed in chapter 3, we also know that both mild chemical cleaning (peroxide treatment) of SWNTs and laser induced molecular photodesorption leads to improved inter-tube interaction.

Imagine illuminating high power laser on to the SWNT sample, which has poor inter-nanotube interaction due to the presence of amorphous carbon and other surface adsorbed molecules. In such a case, due to poor inter-nanotube interaction, the heating effect caused by laser would take longer to dissipate. This means, the Raman G band shifts can potentially be more pronounced for such SWNT samples. Now, if we can clean up the SWNT sample by removing amorphous carbon (say
via chemical treatment methods), it would improve the inter-nanotube interaction. If we repeat the same experiment of illuminating high power laser on to the surface cleaned SWNT, due to improved inter-nanotube interaction. The heat dissipates faster (due to better inter-tube interaction and high thermal conductivity (as discussed in section 4.1.1)) and the observed Raman G band shift due to heat may not be as pronounced. Such an experiment with similar observations has already been made by Terekhov, S. V. et al.\textsuperscript{25} In this work, Terekhov, S. V. et al\textsuperscript{25}, used Raman approach to estimate carbon nanotube purity by laser heating method. It shows (Figure 4.1), progressive reduction in the G band shift (‘flattening’ of the trend) due to laser induced heating, with progressive purification.

![Figure 4.1: I and II are as grown raw SWNT samples with Fe and Ni as their respective catalysts. For these (I and II), there is a steep increase in change in position of the G band (y-axis), with increasing laser induced heating. But with progressive cleaning steps (III is a sample taken from an intermediate chromatographic cleaning step of sample II, whereas IV is after partial chemical purification of sample II. V is a highly purified Smalley’s bucky-paper sample with 95% SWNTs) the change in the G band position with increasing temperature reduces. This indicates removal of adsorbates from the SWNT surface upon cleaning (improving inter-tube interaction) leading to faster heat dissipation. (Reprinted with permission from Terekhov, S. V. et al. Applied Physics A, 74, 393-396 (2002). © Springer-Verlag 2002)
Here (in Figure 4.1\textsuperscript{25}), we see improved heat dissipation (therefore, lesser change in the G band position due to laser induced heating) after purifying the SWNTs. Purification removes amorphous carbon and other adsorbates, improving the inter-tube interaction. From, chapter 3, we know photodesorption also improves inter-tube interaction. Therefore, upon molecular photodesorption from SWNT surface when illuminated with light, should also resulting in similar reduction in the G band frequency change. Other works so far have not discussed the role of molecular photodesorption on the changes in G band position change with increasing laser power.

We hypothesize that, ‘\textit{Molecular photodesorption from SWNT surface improves thermal conduction between the SWNTs, resulting in reduced change (‘flattening’ of the trend) in G band position with increasing laser induced heating.’

4.2 Experimental Section

4.2.1 Materials

The materials and methods are similar to those in the previous chapter (Chapter 3). Same samples (as used in chapter 3) were used for all the measurement in this chapter. Pristine SWNTs (HiPco\textsuperscript{®}), obtained commercially from Nanointegris were used. For oxidizing these pristine SWNTs, hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) used, was obtained commercially from Sigma Aldrich.

Various concentrations of H\textsubscript{2}O\textsubscript{2} solutions were freshly prepared in deionized water. 1 mg of pristine HiPco SWNTs were weighed and added to test tubes containing 5 ml of (a) deionized water, (b) 1M H\textsubscript{2}O\textsubscript{2}, (c) 2M H\textsubscript{2}O\textsubscript{2}, (d) 9M H\textsubscript{2}O\textsubscript{2} solutions. Oxidation of these SWNT suspensions by H\textsubscript{2}O\textsubscript{2} were conducted in the absence of light to improve peroxide lifetime, for 30 days, by gently mixing using Rotospin – rotary test tube mixer. The suspensions were aliquoted after 30
days and drop-casted on clean silicon substrate and allowed to dry to form a SWNT film/mat. These dried SWNT films on silicon substrate were used for obtaining X-ray photoelectron spectroscopy (XPS) and resonance Raman spectroscopy based characterization results.

4.2.2 X-ray Photoemission Spectroscopy

The samples were analyzed on Thermo VG Scientific Theta Probe for obtaining X-ray photoelectron spectra. All the C1s peaks were analyzed at a detector pass energy of 50 eV, with a step size of 0.1 eV, dwell time of 50 ms and averaged over 20 scans. The spectra obtained were analyzed using Thermo Scientific’s Avantage software. The spectra obtained from SWNT film is compared to that obtained from pristine highly ordered pyrolytic graphite (HOPG). XPS spectra of pristine HOPG was obtained by exfoliation of HOPG in-situ (inside the XPS load-lock) using scotch-tape method, in argon atmosphere (to avoid HOPG surface exposure to any air, to prevent any HOPG surface oxidation). This was done (XPS analysis of HOPG) to obtain the standard $sp^2$ C1s peak. The fitting parameter obtained from $sp^2$ C1s HOPG were used to fit the $sp^2$ C1s for all the SWNT samples.

4.2.3 Resonance Raman Spectroscopy

Raman spectra for all the SWNT samples were obtained on Horiba Jobin Yvon LabRAM HR, using $E_{laser} = 1.96$ eV (He/Ne laser) at a static grating of 1800 mm, with a laser spot size of 1 μm. All the spectra are normalized to their respective G band intensities. The spectra obtained is an averaged spectrum from 6 different spots on the SWNT film sample. Discussed in the chapter, are the spectral G band changes with changing laser power (at 50%, 25%, 10% and 1% of 17mW laser power) for both pristine and 9M H$_2$O$_2$ treated SWNTs. These are compared to Raman measurements, with changing laser power (at 50%, 25%, 10% and 1% of 17mW laser power) made
on the same samples immediately after 1 minute of high power laser exposure (at 17 mW). Other variations to the Raman measurement approaches are mentioned as required in the results and discussion section.

### 4.3 Results and Discussion

**Figure 4.2.** shows the changes in the Raman G band position, at different laser powers, for pristine SWNTs. The laser powers at which the Raman measurements were made are 1% (~0.2 mW), 10% (1.7 mW), 25% (4.2 mW) and 50% (8.5 mW), using filters for a 1.96 eV laser whose power is 17 mW.

![](image)

**Figure 4.2:** Shows the changes in the Raman G band frequency with change in laser power for pristine SWNTs. The data is same for both the plots (left and right). The general trend observed is reduction in the frequency of G band position with increasing laser power. In left panel the data is fit linearly and on the right panel the same data is fit using non-linear logistic fit.

The changes in the Raman G band frequency with changes in the laser power (or at different temperatures), are traditionally fit linearly\textsuperscript{23, 25-26}, as also shown in the left panel of **Figure 4.2.** The linear fit here, was not perfect. Consequently, a non-linear logistic fit was used to fit the data. As discussed earlier in the previous sections and as shown by other groups\textsuperscript{23, 25-26}, even here, (in **Figure 4.2**) we observe increasing reduction in Raman G band frequency with increasing heating
effects due to increasing laser power. These plots are now to be compared to another variation to the Raman measurement, on the same pristine SWNT sample (as shown in Figure 4.3). In Figure 4.3, we do the same Raman measurements on the pristine SWNT sample as done in Figure 4.2 at 1%, 10%, 25% and 50% of 17 mW, but immediately after 1 minute exposure to high power laser at 17 mW.

Figure 4.3: Shows the changes in the Raman G band frequency with change in laser power for pristine SWNTs, immediately after 1 minute high power laser exposure at 17 mW. The data is same for both the panels. The general trend observed is reduction in the frequency of G band position with increasing laser power. In the left panel the data is fit linearly and on the right panel the same data is fit using non-linear logistic fit. The green arrows indicate the relative change with respect to data from Figure 4.2. Here, we observe ‘flattening’ or reduced reduction (or change) in G band frequency.

In Figure 4.3, we observe ‘flattening’ of the change in Raman G band frequency (not much change with changing laser power, as observed in Figure 4.2). This is improves heat dissipation, due to improved inter-tube interaction, resulting from increased molecular photodesorption. A comparison between Figure 4.2 and 4.3 shows that at Raman measurements at low power are similar for both without (Figure 4.2) and with (Figure 4.3) initial high power laser exposure. But for Raman G band measurements at higher powers, we notice deviations (shown by the green
arrows in Figure 4.3). This can be regime at which the molecular photodesorption plays a role in reduction in the Raman G band change with measurements with higher laser power.

Similar work has been done by Mialichi, J. R. et al\textsuperscript{27}, where Raman G band measurements were as the sample was subjected to cyclic ‘heat’, ‘cool’ and again ‘heat’ steps, via changing laser power (similar to Raman measurement approaches used by our group, in Chapter 3 (as discussed in Figure 3.8 and 3.9) for RBM bands, instead). They observe that once a spot on the sample is subjected to a ‘heating’ cycle, no further change in G band is observed, upon any subsequent irradiation, indicating a ‘saturation effect’. This is attributed to elimination of amorphous material from the SWNT surface. On a side note, another important observation made by Mialichi, J. R. et al\textsuperscript{27}, made in this work is that the primary mode of heat dissipation is not radiation, but thermal conduction.

Unlike, Mialichi, J. R. et al\textsuperscript{27}, we also consider molecular photodesorption, for ‘flattening’ of the G band frequency with changing laser power (or ‘saturation effect’ as described by Mialichi, J. R. et al\textsuperscript{27}). We attribute this ‘flattening’ to molecular photodesorption based on the data presented in Chapter 3, where we see changes in the Raman RBM spectra with changing inter-tube interaction level upon both chemical cleaning (removal of amorphous material from the SWNT surface) and molecular photodesorption. To understand, if amorphous materials plays any role in change in Raman G band frequency with changing laser power, we have to compare the results obtained from pristine SWNTs (Figure 4.2 and 4.3), to those of 9M peroxide cleaned SWNTs.

Before we explore the data for 9M peroxide treated SWNTs, we need to study the XPS data for HOPG, pristine SWNTs and 9M peroxide treated SWNTs, to understand each of the states (pristine and 9M peroxide treated SWNTs), chemically. This XPS data is shown in Figure 4.4.
From Chapter 3 (Figure 3.5), we show that upon 9M peroxide treatment, the total carbon (carbon from SWNT walls and from amorphous carbon sticking on the SWNTs) reduces and from Figure 3.6 (reduction in the $I_D/I_G$ ratio, after 9M peroxide treatment), we observe that SWNT walls do not breakdown. This implies that the relative loss of carbon signal in the XPS data upon 9M peroxide treatment is due to removal of amorphous carbon. From Figure 4.4, we also observe that upon 9M peroxide treatment leads to oxidation of the carbon. This oxidation can lead to chemical doping of the SWNTs. The hallmark of mild chemical doping is upshift of Raman G band frequency.$^{15}$
**Figure 4.5** shows the changes in the Raman G band frequency with change in laser power (at 1%, 10%, 25% and 50% of 17 Mw), for 9M peroxide treated SWNTs (showing both linear and logistic fit).

![Figure 4.5](image)

In **Figure 4.5**, one major difference observed, when compared to other published works\(^25\) is that there is no ‘flattening effect’. Upon progressive purification (as seen in **Figure 4.1**\(^25\)), the change in the Raman G band frequency with increasing laser power reduces (flattening of the trend). But with 9M peroxide treatment (from **Figure 4.5**), we observe no such ‘flattening’ of the trends, as compared to untreated SWNTs (**Figure 4.2**). One possible explanation is that 9M peroxide treatment is a mild treatment which can only partially remove amorphous carbon. This partial removal is not strong enough to elicit ‘flattening’ of the trends in the G band frequency change.
with changing laser power. Another possibility is the potential difference in sensitivity range of G band frequency change to amorphous carbon. As an example, in Figure 4.1, the power densities at which the Raman G band measurements were made is in the range of 0 – 65 mW/cm², whereas the power densities at which our measurements were made are 27, 54, 135 and 270 kW/cm². Our measurements are made at a higher range than those made by Terekhov, S.V. et al. It is possible that changes in Raman G band frequency to changing laser power as a function of amorphous carbon/impurities is observable at lower power densities. Whereas, molecular photodesorption plays a greater role in effecting the changes in the G band frequency with changing laser power at higher power densities (as observed in Figures 4.3 and 4.6). For such a sample (9M peroxide treated SWNT) as shown in Figure 4.5, if Raman G band measurements are made at 1%, 10%, 25% and 50% of 17 mW, immediately after 1 minute exposure to high power laser (17 mW), we observe trends as shown in Figure 4.6.

Figure 4.6: Shows the changes in the Raman G band frequency with change in laser power for 9M peroxide treated SWNTs, immediately after 1 minute high power laser exposure at 17 mW. The data is same for both the panels (left panel: linear fit, right panel: logistic fit). The green arrows indicate the relative change with respect to data from Figures 4.2 and 4.5. Here, we observe ‘flattening’ or reduced reduction (or change) in G band frequency compared to Figure 4.5, just as observed in Figure 4.3.
We observe (in Figure 4.6) ‘flattening’ of the trends for changes in Raman G band with changing laser power, upon prior exposure to high power laser for 9M peroxide treated SWNTs (just as observed for untreated SWNTs, Figure 4.3). As it is already known (from results in Chapter 3 and works by Chen, R. J. et al and Hsu, Y.-Y. et al) that high power laser exposure leads to increased molecular photodesorption, leads to improved inter-nanotube interactions. This leads to improved heat dissipation via thermal conduction between the SWNTs, resulting in reduced (‘flattening’ trends) changes in the Raman G band measured at increasing laser power.

For Figures 4.2, 4.3, 4.5 and 4.6 we fitted the data both in traditional fashion (linear fit) and also using logistic fit. Within the given range we see that logistic function fits the data better. We are seeing logistic fit because, two competing events are pushing the trends in two opposite directions (as seen in Figure 4.2 and 4.5): (Note: Thermal conduction is the most important pathway for heat dissipation in SWNTs)

a. Raman measurements at low laser power, leads to lesser levels of heating effect, which is efficiently dissipated. Inter-nanotube interaction does not play a major role in this regime. Efficient dissipation means change in Raman G band frequency due to heating is low.

b. Raman measurements at higher laser powers, leads to higher thermal load. In such cases, fast dissipation needs better inter-nanotube interaction. If the inter-nanotube interaction is poor, it leads to poor heat dissipation. This results in heating up the SWNTs. Therefore causing greater change in Raman G band frequency.

This is why, prior high power laser exposure results in more efficient heat dissipation (via thermal conduction between SWNTs). Prior high power laser exposure leads to higher molecular photodesorption from the SWNT surface leads to improve inter-nanotube interaction. Thus, resulting in the ‘flattening’ of the treads in G band frequency change with increasing laser power.
Another important observation to be made for Raman G band, with increased photodesorption is G band line shape. G band shape for Figures 4.2, 4.3, 4.5 and 4.6 is shown in Figure 4.7.

Figure 4.7: The top left (without prior high power laser exposure) and top right (after initial high power laser exposure) for untreated SWNTs. The bottom left (without prior high power laser exposure) and bottom right (after initial high power laser exposure) for 9M peroxide treated SWNTs. For the top and bottom right plots we notice sharpening of G band (black arrow), after high power laser exposure. When comparing top plots to the bottom plots, we observe increase in the width of G band (red arrow) after 9M peroxide treatment. There is also an enhancement of G band intensity, due to removal of amorphous carbon after 9M peroxide treatment. This manifests as reduction in D band intensity upon normalization (green arrow).
In Figure 4.7, we observe sharpening of the G⁻ band for measurements made after 1 minute exposure to high power laser (at 17 mW). This is due to increased molecular photodesorption. Here, all the Raman spectra are normalized to the G band intensity, the intensity enhancement of G⁺ band manifests itself as reduction of $I_D/I_G$ ratio (Figure 4.8), in other words, the relative intensity of the D-band (~1320 cm⁻¹) reduces in comparison to first order Raman G band intensity, after 9M peroxide treatment (shown by green arrow in Figure 4.7). Raman spectra of carbon is dominated by $sp^2$ in the visible range due to resonance with the $\pi$ states. Thus, even the presence of very large $sp^3$ (amorphous carbon) only yields very small D band (not as sensitive as G band).

Figure 4.8: Shows improvement (reduction) of $I_D/I_G$ upon 9M H₂O₂ treatment of SWNTs (bottom plots) when compared to those of untreated SWNTs (top plots). This is an indication of improvement of first order Raman scattering (G band intensity) upon 9M peroxide treatment, when compared to the D band intensity. It also indicates no breakdown of amorphous carbon with exposure to high power laser.
Upon 1 minute high power laser exposure, the G\textsuperscript{-} band line shape became stabilized (indicated by the overlap of majority of G\textsuperscript{-} band peaks in top and bottom right plots in Figure 4.7). Also, important to note is the change in the G\textsuperscript{-} band line shape for untreated versus the 9M H\textsubscript{2}O\textsubscript{2} treated SWNTs (as shown by the red arrows Figure 4.7). There is an increase in the line width for 9M peroxide treated SWNTs when compared to untreated pristine SWNTs. Similar observations were made by Yu, Z. \textit{et al}\textsuperscript{30} (Figure 4.9). Yu, Z. \textit{et al}, compared changes in the G band line shapes for (a) HNO\textsubscript{3} treated, (b) H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2} treated and (c) thermally treated SWNTs, first measured Raman spectra at low power (3.3 kW/cm\textsuperscript{2}), then at higher power (340 kW/cm\textsuperscript{2}) and finally at lower power (at 3.3 kW/cm\textsuperscript{2}). For the thermally treated the measurements were made at 6 kW/cm\textsuperscript{2}.

Yu, Z. \textit{et al}, suggest that these changes are a consequence of charge transfer between the interactions of SWNT surface with oxidizing adsorbates upon degassing (photodesorption with high power laser) the acid treated samples, leading to irreversible Raman changes.

Figure 4.9: Raman G band spectra for (a) HNO\textsubscript{3} treated, (b) H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2} treated and (c) thermally treated SWNTs. It shows that no change in the Raman G band line shape after exposure to high power laser (340 kW/cm\textsuperscript{2}) and the final measurements later at 3.3 kW/cm\textsuperscript{2}. Similar effect is seen for thermally treated SWNT sample. Upon thermal treatment, the G\textsuperscript{-} band intensity increases. (Reprinted with permission from Yu, Z. \textit{et al}. J. Phys. Chem. A, Vol. 104, No. 47 (2000). © (2000) The American Chemical Society)
Based on results from Chapter 3, we know that degassing (molecular photodesorption) is reversible (with time we observe readsorption). Alternatively, we propose that G band line shape to be a reflection of corresponding RBM spectra at a given laser power and energy (Figure 4.10).

Figure 4.10: Top left shows the peak fitted G band spectra of untreated SWNTs at 1.96 eV and 1.7 mW and bottom left is its corresponding Raman RBM spectra. Top right is the peak fitted G band of the 9M peroxide treated SWNT sample at the same 1.96 eV and 1.7 mW, power. The bottom right is the corresponding RBM spectra for the 9M peroxide treated SWNTs. The arrows indicate the relative changes in the RBM spectra of the 9M peroxide treated sample to the RBM spectra of the untreated SWNT sample. As seen, due to EET, the corresponding RBM signal for large diameter metallic M11 improves. This translates to improvement in the G- band intensity (increased area under the asymmetric BWF fit) for the 9M peroxide treated SWNTs (top right) compared to G band for untreated SWNTs (top left).

In Figure 4.10, the G band peak fitting was done as shown by Shen, X. et al. The G- band intensity improves and the asymmetric Breit-Wigner-Fano (BWF) lineshape, characteristic of
metallic SWNTs also increases (this change is more pronounced in G band line shape in Figure 4.9) in Figure 4.10. As seen in Chapter 3, with increasing peroxide treatment, we observe improved EET from smaller diameter, donor SWNTs to larger diameter, acceptor SWNTs. At 1.96 eV, for the HiPco SWNTs we used, upon peroxide treatment the EET improves and the corresponding Raman RBM signal changes in such a way that the signal for larger diameter, SWNTs (metallic SWNTs, \( M_{11} \) optical transition) increases and for the smaller diameter semiconducting SWNTs reduces (as seen in Figure 4.10, bottom right plot as compared to bottom left plot). Because the energy transfer is resulting in increase in the resonance Raman signal for metallic SWNTs, we must also observe a corresponding increase in the characteristic BWF line shape indicative of metallic SWNTs in the sample must also increase.

4.4 Summary

In this chapter, we have shown the role of photodesorption in improving heat dissipation in the SWNT bundles. This was observed by studying the changes in the Raman G band frequency with increasing laser power. The Raman G band frequency change is dramatic when heat dissipation is not efficient. Increased heating caused increased downshift of Raman G band frequency. Upon exposure to initial high power laser and subsequent Raman G band measurement at lower laser powers shows (‘flattening’ of the trends) reduced reduction (downshift) in Raman G band frequency. Here we show that logistic function fits the trends in the changes in the Raman G band frequency with increasing laser power, better than the linear fit.

The \( I_D/I_G \) ratios improve (reduce), upon 9M peroxide treatment of the SWNTs. This improvement is a consequence of improved Raman scattering upon removal of amorphous carbon from the SWNT surface. This results in signal enhancement of first order Raman G band than the
corresponding D band. This is because, the G band sensitivity is higher (due to resonance of $\pi$ states), in the visible regime than the D band$^{29}$. It is also important to point out that there is no $I_D/I_G$ ratios improvement (reduction), upon 1 minute exposure to high power (17mW) laser, for untreated SWNTs. This is a clear indication that 1 minute high power laser exposure does not remove amorphous carbon.

Two types of G band line shape changes have been observed:

a) Sharpening of the $G^-$ band is observed for both untreated and 9M peroxide treated SWNTs for Raman measurements after high power laser exposure for 1 minute (black arrows in Figure 4.7 indicate this event). This is due to improved Raman scattering after molecular photodesorption.

b) The change in G band line shape seen in Figure 4.7 as increase in BWF asymmetric fit indicates increased metallic SWNT characteristics, upon 9M peroxide treatment. This is due to increased EET upon 9M peroxide treatment. The energy transfer results in increase of peaks in the $M_{11}$ transition (from the RBM spectra for 9M peroxide treated SWNTs in Figure 4.7), indicating energy transfer to large diameter metallic SWNTs, this manifests as increase in BWF line shape for the $G^-$ band upon improved EET, after 9M peroxide treatment.
4.5 References


5. A comparative study of enzymatic and chemical degradation of single walled carbon nanotubes

Here, we show enzymatic degradation of single walled carbon nanotubes (SWNTs) using horseradish peroxidase (HRP) in the presence of H$_2$O$_2$, after a 30 day period. For faster degradation of SWNTs, chemical (H$_2$SO$_4$/HNO$_3$) and physical (sonication) approaches were studied. It was observed that simultaneous acid treatment (H$_2$SO$_4$/HNO$_3$) and sonication resulted in the fastest SWNT degradation for all the tested degradation methods studied in this work.

5.1 Introduction

5.1.1 Chemical and biological approaches to SWNT degradation

Pristine SWNTs due to weak van der Waals interactions tend to bundle up$^2$. Chemical functionalization is necessary to give charge to the SWNT side walls and prevent them from the bundling effect. These chemical modifications$^3$ make SWNTs more soluble$^4$ than the pristine SWNTs. Debundling of SWNTs is necessary for obtaining individual SWNTs, necessary for various applications such as SWNT based electronic devices$^5$, biosensor$^6$ and drug delivery$^7$. However, some of the chemical modification methods lead to creation of carboxylic acid$^8$ groups on the SWNT surface via oxidation. These oxidative methods lead to introduction of defects$^9$ into the SWNTs, shortening of the nanotubes$^{10}$ and eventually can also lead to degradation of SWNTs. While some researchers pursued purification of SWNTs without inducing any major damage to the SWNTs$^{11}$ (considering methods involving chemical treatments leading to covalent modifications), others tried to studied methods of completely SWNT breakdown as a sorting (large
diameter from small diameter SWNTs\textsuperscript{12} or removal of metallic from semi-conducting SWNTs\textsuperscript{13}) method.

On the other hand, biotechnological and natural degradation pathways are also been considered for degradation of carbon nanotubes. One of the first works involving enzymatic degradation of SWNTs was shown using horseradish peroxidase (HRP) in the presence of hydrogen peroxide\textsuperscript{14}. Whereas, Allen, B. L. \textit{et al}\textsuperscript{15}, state that only carboxylated SWNTs (C=O, COO\textsuperscript{-} functionalized SWNTs, via oxidation process) (and not pristine SWNTs) can be degraded using HRP, as the negative charge on the carboxylated SWNT allows for better interaction with the enzyme via the positively charged arginine residues near the enzyme’s active site (\textit{heme} core). A complete drug payload delivery method based on enzymatic uncorking of the drug, from nanotube cups is also been explored\textsuperscript{16}. HRP has since also been used for biodegradation of multi-walled carbon nanotubes too\textsuperscript{17}. Apart from HRP, other peroxidases, like myeloperoxidase (MPO) have also been explored to study potential biodegradation approaches inside human cells. It has been observed that carbon nanotubes degraded by neutrophil MPO, induces less pulmonary inflammation\textsuperscript{18}. Hypochlorite has been identified as a major oxidant capable of \textit{in vivo} degradation of SWNTs\textsuperscript{19}, via peroxidase pathways. Kagan, V. E. \textit{et al}, have also explored SWNT degradation via more persistent macrophages and how they ‘digest’ SWNTs using a superoxide/peroxynitrite oxidative pathway\textsuperscript{20}. Eosinophil peroxidase is another major oxidant-producing enzyme, involved during the inflammatory states in the human lung which has been used to degrade SWNTs\textsuperscript{21}. Kotchey, G. P. \textit{et al}\textsuperscript{22} is a good source for all the \textit{in vivo} and \textit{in vitro} methods for biodegradation of SWNTs.

The catalytic peroxidase pathway, involves the cyclic changes occurring that the enzyme’s \textit{heme} site. The \textit{heme} site, is Fe (III) protoporphyrin IX group. When the enzyme is the inactive state, the \textit{heme} group is in a resting state (ferric). In the presence of hydrogen peroxide, the enzyme is
activated, when the \textit{heme} group converts to a state called ‘Compound I’, where it exists as a ferryl oxo iron (Fe$^{4+}$=O) porphyrin π cation radical. This ‘Compound I’ can immediately oxidize the substrate (SWNTs in this case) and it reduces to another intermediary, ‘Compound II’ state, before completely returning to its resting ‘ferric’ state after oxidizing the substrate again, when in its ‘Compound II’ state. Under acidic conditions and in the presence of chloride ions, ‘Compound I’ of the MPO, uses up 2 electrons from the chloride ions to yield hypochlorous acid (HOCl), as it returns directly to resting ‘ferric’ state. \textbf{Figure 5.1}, shows the binding poses of the two peroxidases, \textbf{Figure 5.1(a)} for HRP and \textbf{Figure 5.1(b)} for MPO, with the carboxylated SWNTs. \textbf{Figure 5.1(c)} shows the catalytic peroxidase cycle for HRP and MPO (under acidic conditions in red).
Here, we explore the potential degradation of SWNTs using HRP. In addition, we also explore the degradation of same set of SWNTs to achieve fastest chemical degradation of SWNTs.

Chemical degradation methods using very strong acid mixes have already been explored\textsuperscript{13}. Sonication approaches have been used to improve the dispersion of SWNTs in suspensions\textsuperscript{23}. Sonication in conjunction with surfactants\textsuperscript{24} have been used to improve dispersion of SWNTs\textsuperscript{25}. Agitation of the suspension, by sonication, reduces the nanotube-nanotube interaction (via van der

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.1.png}
\caption{Binding poses of (a) HRP, (b) MPO with carboxylated SWNTs. Fig: (c) is the peroxidase cycle for HRP and MPO (red pathway in acidic conditions in presence of Cl\textsuperscript{-} ions for MPO). Fig: (c) is adapted from Veitch, N. C.\textsuperscript{1}. (Figures a, b and c are reprinted with permission from Kotchey, G. P. \textit{et al.} Accounts of Chemical Research, 1770-178 (2012) Vol. 45, No. 10. © (2012) The American Chemical Society) }
\end{figure}

5.1.2 Rationale

Here, we explore the potential degradation of SWNTs using HRP. In addition, we also explore the degradation of same set of SWNTs to achieve fastest chemical degradation of SWNTs.
Waal interactions) and allows for better interaction of the surfactant with the SWNTs. Following the same approach, SWNT degradation can be made faster by combining acid treatment and sonication.

We hypothesize that, ‘Sonication (physical) in conjunction with oxidative acid mixture (chemical) can breakdown the SWNTs more effectively.’

5.2 Experimental Section

5.2.1 Materials

For the enzymatic degradation, carboxylated CoMoCAT® SWNTs (from Sigma Aldrich, USA) were weighed and suspended in 1X PBS at pH 7.4 and sonicated (Branson 1510, frequency 40 kHz) for 1 hour. To the first set, 0.09 mg/ml of HRP along with 40 μM H₂O₂ (H₂O₂ was added once every 24 hours) were added. To the second sample set only 0.09 mg/ml of HRP was added (no peroxide). To the third, only 40 μM H₂O₂ was added every 24 hours. Volumes for all the samples were up to 5 ml, with DI water. All the experiments were made in the absence of light to avoid degradation of peroxide. The samples were constantly mixed using Rotospin. Experiment design is shown in table 5.1. Samples were aliquoted from these suspensions for later analysis.
For chemical degradation, commercially available carboxylated CoMoCAT® SWNTs (from Sigma Aldrich, USA) (same set of SWNTs were used for both enzymatic and chemical degradation approaches) were used. Three samples were made.

a) SWNTs were weighed and suspended in DI water and were only sonicated ((Branson 1510, frequency 40 kHz). Samples were aliquoted from these suspensions for analysis.

b) Weighed SWNTs were subjected to only acid treatment, sulfuric acid and nitric acid mix (3:1 ratio). Aliquots were taken for analysis. These aliquots were filtered to collect degraded SWNTs and wash away the acid mix. These degraded samples were resuspended in DI water and were used for later analysis.

c) These SWNTs were weighed and added to nitration mixture of sulfuric (H\textsubscript{2}SO\textsubscript{4}) and nitric acid (HNO\textsubscript{3}), in 3:1 ratio. In conjunction, these samples were also subjected to sonication. Aliquots were taken for analysis. These aliquots were filtered to collect degraded SWNTs and wash away the acid mix. These degraded samples were resuspended in DI water and were used for later analysis.

The suspensions were aliquoted (for both enzymatic and chemical degradation experiments) and drop-casted on clean silicon substrate and allowed to dry to form a SWNT film/mat. These dried SWNT films on silicon substrate were used for obtaining scanning electron micrographs, X-ray

<table>
<thead>
<tr>
<th>Enzyme + Peroxide</th>
<th>HRP(Enzyme)</th>
<th>Peroxide</th>
<th>CNTs in water</th>
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<tr>
<td>+</td>
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<tr>
<td>Enzyme + Water</td>
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**Table 5.1: Experiment design for understanding the role of HRP and peroxide for the biodegradation of SWNTs.**

For chemical degradation, commercially available carboxylated CoMoCAT® SWNTs (from Sigma Aldrich, USA) (same set of SWNTs were used for both enzymatic and chemical degradation approaches) were used. Three samples were made.  

a) SWNTs were weighed and suspended in DI water and were only sonicated ((Branson 1510, frequency 40 kHz). Samples were aliquoted from these suspensions for analysis. 

b) Weighed SWNTs were subjected to only acid treatment, sulfuric acid and nitric acid mix (3:1 ratio). Aliquots were taken for analysis. These aliquots were filtered to collect degraded SWNTs and wash away the acid mix. These degraded samples were resuspended in DI water and were used for later analysis. 

c) These SWNTs were weighed and added to nitration mixture of sulfuric (H\textsubscript{2}SO\textsubscript{4}) and nitric acid (HNO\textsubscript{3}), in 3:1 ratio. In conjunction, these samples were also subjected to sonication. Aliquots were taken for analysis. These aliquots were filtered to collect degraded SWNTs and wash away the acid mix. These degraded samples were resuspended in DI water and were used for later analysis. 

The suspensions were aliquoted (for both enzymatic and chemical degradation experiments) and drop-casted on clean silicon substrate and allowed to dry to form a SWNT film/mat. These dried SWNT films on silicon substrate were used for obtaining scanning electron micrographs, X-ray
photoelectron spectroscopy (XPS) (XPS was used only for the analysis of chemical degradation experiment samples) and resonance Raman spectroscopy based characterization results.

5.2.2 X-ray Photoemission Spectroscopy

The samples were analyzed on Thermo VG Scientific Theta Probe for obtaining X-ray photoelectron spectra. Survey scans were made at a detector pass energy of 300 eV, with a step size of 1.00 eV, dwell time of 50 ms and averaged over 5 scans. The spectra obtained were analyzed using Thermo Scientific’s Avantage software.

5.2.3 Resonance Raman Spectroscopy

Raman spectra for all the SWNT samples were obtained on Horiba Jobin Yvon LabRAM HR, using $E_{\text{laser}} = 2.33$ eV, at a static grating of 1800 mm, with a laser spot size of 1 μm, at a laser power of 0.4 mW. All the spectra are normalized to their respective G band intensities. Each of the spectrum obtained was recorded for 10 seconds and averaged 3 times each. The final Raman measurement shown is as an averaged spectrum from 6 different spots on the SWNT film sample.

5.2.4 Electron Microscopy

SEM micrographs were obtained on Zeiss LEO 1550, using In-lens detector at 0.5 kV acceleration voltage. TEM micrographs were obtained on JEOL-2010 LaB₆ STEM at 200 kV acceleration voltage. The sample from TEM were prepared from SWNT suspension sample. 2 minute sonication of the SWNT suspension is followed by drop-casting aliquots of the sample and drying them overnight in desiccator on holey carbon grid.
5.3 Results and Discussion

**Figure 5.2**, upon optical inspection (left panel) after enzymatic treatment after 30 days, we observe clearance in the SWNT suspension solution of HRP with hydrogen peroxide, as against the other controls. The absorbance spectra confirms this clearing of the HRP + peroxide solution (in blue) by reduction in the absorbance when compared to those of the controls. The black color is due to the SWNTs in the suspension. SWNT breakdown leads to clearing of the suspension solution.

![Image](image.png)

**Figure 5.2**: Optical image (left) shows degradation of SWNTs in the HRP + H\textsubscript{2}O\textsubscript{2} SWNT suspension (in the red box) after 30 day period. The absorbance spectra to the right also shows corresponding drop in the absorbance value for HRP + H\textsubscript{2}O\textsubscript{2} SWNT suspension (blue) when compared to the controls, due to SWNT degradation. The absorbance spectra was also taken after 30 day period.

SEM images for all the enzymatic degradation experiments were taken after 30 day period (**Figure 5.3**). SEM image for HRP + peroxide shows SWNT breakdown, where most of the SWNTs are ~
300 nm in length, whereas for the control samples, the typical long tubular structure of SWNTs is retained.

**Figure 5.3:** SEM micrographs showing degradation of SWNTs in HRP + H$_2$O$_2$ (top), when compared to controls (HRP + water) and (H$_2$O$_2$ + H$_2$O). The scale bar for all the SEM micrographs is 300 nm.
Raman spectroscopy results are shown in Figure 5.4.

Figure 5.4: The G-band intensity has drops for HRP + H₂O₂ sample compared to control samples. The un-normalized intensity plot (Top inset), shows dramatic drop in intensity for HRP + H₂O₂ sample, indicating SWNT degradation. Bottom left shows the changes in Raman G peak position indicating progressive doping from HRP + water (green) to water + H₂O₂ (red) to HRP + H₂O₂ (blue). Bottom right shows (I_D/I_G) plot) reduction in defects for HRP + H₂O₂, when compared to water + H₂O₂. This is because, HRP is known to attack carboxylated sites introduced by H₂O₂.
From Figure 5.4, the Raman $G$ line shape change observed for HRP + H$_2$O$_2$ sample, indicates more semi-conducting property than for the un-degraded controls. The reduction intensity for HRP + H$_2$O$_2$ sample in the un-normalized inset, also indicates degradation of SWNT. It is known that the $G$ peak frequency (bottom left panel), upshift with increased level of doping (for both ‘p’ and ‘n’ type doping)$^{26}$. The bottom right panel shows the $I_D/I_G$ plots, which follows the trends as proposed by Allen, B. L. et al$^{15}$. It is proposed that HRP is not efficient in breaking down pristine SWNTs. Here, peroxide introduces both the defects into the SWNTs by oxidizing the SWNTs and simultaneously activating the enzyme. Therefore, for water + H$_2$O$_2$ sample we observe highest $I_D/I_G$ ratio. HRP binds to these defect/carboxylated sited introduced by the peroxide and degrade them, thus reducing the total defect levels and thereby improving (reducing) the $I_D/I_G$ ratio.

It is very important to observe that enzymatic degradation of SWNTs is never a complete process and it needs a prior step of chemical oxidation of SWNTs. From our Raman data, we see a very decent $I_D/I_G$ ratio even for HRP + H$_2$O$_2$ treated samples. This indicates an overall ‘good’ SWNT side wall integrity. The $I_D/I_G$ ratio has to be drastically high (~1) to indicate degradation. This shows that though it is possible to degrade carbon nanotubes enzymatically, it is not a very efficient process. If the objective is to study fast and complete degradation very strong oxidative degradation methods are to be used. To this end, we then studied degradation of same type of carboxylated SWNTs (as used for the enzymatic degradation), via only sonication (physical degradation approach), only acid treatment (chemical oxidation approach) and sonication along with acid treatment of SWNTs (physical plus chemical degradation approach). This approach has not been studied much.

Figure 5.5, shows SEM images of sonication only, acid treated only and acid treated + sonication, after 24 hours. We observed SWNT degradation in the acid treated + sonication SWNTs.
Figure 5.5: SEM micrographs showing SWNT degradation in acid treated + sonication (third image) sample after 24 hours. The SWNTs are not visible in the SEM micrograph. The scale bar for all the three images is 300 nm.
From **Figure 5.5**, it is evident that acid treatment + sonication is best of the degradation approaches tested here. We observe compete degradation of SWNTs, for the acid treatment + sonication. The SWNTs were not observed via SEM techniques. It is important to point out that the degradation of SWNTs (shortening of the length) for acid treated + sonication sample was evident from 4 hours onwards. As shown in **Figure 5.6**, we started observing SWNT losing their ‘tubular’ morphology to become more ‘needle’ like morphology from time point 4 hours onwards (**Figure 5.6:(a)**).

![Acid treated + sonication](image)

**Figure 5.6:** SWNT degradation via acid treatment + sonication at different time points (a) at 4 hours, SWNT length shortens and the morphology changes to more ‘needle’ like. Figure (b) is at 8 hours, the needle like morphology start becoming more prominent. No nanotube was found to be more than ~300 nm in length. Figure (c) after 12 hours, SWNT ‘needles’ were observed alongwith increasing amorphous carbon debris. Figure (d) at 16 hours, the SWNT ‘needle’ length were < ~ 200 nm. Here, the debris was more prominent.
Another interesting feature observed for 24 hour acid treated + sonication sample is that when sample was aliquoted on to the silicon substrate for SEM imaging and Raman analysis, it forms ‘ring’ patterns upon deposition. This is due to the slip-stick capillary effect leading to ring like pattern upon evaporation of material on a substrate, commonly known as the ‘coffee ring effect’\(^{27}\).

This is shown is Figure 5.7.

![Figure 5.7: The SEM micrographs show the ‘ring’ formation effect of the degraded (24 hour acid treated + sonication sample) SWNT, upon deposition on the silicon substrate. The scale bar on the left micrograph is 100 μm and is 30 μm for the right micrograph.](image)

TEM analysis for the same samples was also done. Figure 5.8, shows the TEM imaging for SWNTs samples after 24 hour sonication only. Here, we get to observe bundling of SWNTs. This occurs due to the evaporation process during the drying step to prepare SWNTs. Also, interesting to notice is that there is not much amorphous carbon sticking on to the SWNT surface. Amorphous carbon was seen, but on the holey carbon. The central panels are from are from the same area on the TEM grid. The central left panel was imaged using the CCD whereas the right imaged was developed from a negative. Each image gives us important information. While the right image did not any amorphous carbon that was present, it was very sharp and was ideal for measuring inter-tube distance. Here, we observe ‘the tubular’ nature of the SWNTs.
Figure 5.8: TEM micrographs of SWNT sonication only samples after 24 hours. The scale bars for top left is 5 nm and top right is 20 nm, whereas middle left is 100 nm and middle right (developed from a negative) is 50 nm. The orange boxes in the middle images are the exact area magnified in bottom left image (scale bar = 20 nm). The red dotted box in bottom left image is the same as the bottom right image (scale bar = 5 nm).

Figure 5.9, shows the TEM images for SWNTs subjected to 24 hours of only acid treatment.
Figure 5.9: TEM micrographs of SWNTs subjected only to acid treatment for 24 hours. The scale bars for top left is 5 nm and top right is 20 nm. Both show plenty of amorphous carbon sticking on the SWNT bundles. Middle left and right are taken at the same spot (right image was taken minutes after the left image). Electron beam damage can be seen on the sample on the middle right image in the red dotted circle area. The damaged area is the amorphous carbon sticking on to the SWNT bundles. Scale bar is 20 nm for the middle images. The bottom right image was taken within minutes after the left image. The scale bar is 5 nm for both the bottom images. The black dotted line indicates the change from the bottom left image. This is due to sample (amorphous carbon) damage.
In Figure 5.9, we observed great amounts of amorphous carbon, because here, the acid treatment can oxidize the SWNTs, thus leading to potentially more number of defect introduction in the SWNT side walls. Without sonication this amorphous carbon is not removed from the sidewalls. Despite breakdown, we still see SWNTs with ‘tubular’ morphology. Closer observation of SWNTs in these samples also reveal bundling. In Figure 5.10, we observe bundling within the amorphous carbon blob.

![Figure 5.10: SWNT bundling as observed within a blob of amorphous carbon, for 24 hours acid treated sample.](image)

SWNT samples for which the SEM images showed complete breakdown, are the acid treated + sonication samples, after 24 hour time point. In Figure 5.11, we see the TEM images for these samples.
Figure 5.11: TEM micrographs of acid treated + sonication samples after 24 hours. The SWNTs observed were small (< ~50 nm). The amorphous seen in the only acid treated is not seen here. The scale bar for the top left image is 20 nm, whereas it is 100 nm for the top right. The middle left is a low magnification image (scale bar = 100 nm) of the image on the middle right (scale bar = 20 nm). The scale bar for the bottom images is 20 nm. Bundling can be seen in these images too.
From Figure 5.11, we can observe that the amorphous carbon is not seen as much. This is because the simultaneous sonication step for these samples. Sonication removes all the excessive amorphous carbon that is formed during the oxidative degradation of SWNTs in an acid mix. Sonication also breaks the weak kinks in the SWNT side wall and make them more susceptible to oxidative acid action. Thus leading to cutting of the SWNTs leading to the formation of small ‘needle’ like morphology as observed in the SEM and TEM. The length of the SWNTs observed here are not less than ~ 50 nm. The TEM images in Figure 5.11 are much cleaner than the TEM images for sonication only samples. This is because of the removal of the amorphous carbon.

Figure 5.12, shows the XPS spectra, the survey scans of all the three samples. For all the three samples, it can be seen that after 24 hour time point measurement when compared to its initial after 30 minute treatments, we observed increase in O1s/C1s after each of the treatments. This indicates oxidation. But by observing the relative heights of C1s and O1s peaks, it can also be said that the extent of oxidation is higher for acid treated only and acid treated + sonication, than only sonication samples. This is due to strong oxidative action of the acid mix.
Figure 5.12: XPS spectra for sonication only (top left – after 30 min, top right – after 24 hour), only acid treated (middle left – after 30 min, middle right – after 24 hour) and for acid treatment in conjunction with sonication (bottom left – after 30 min, bottom right – after 24 hour).
Raman G band line shapes also show that degradation is best for samples which were acid treated in conjunction with sonication, when compared to other controls (Figure 5.12).

From Figure 5.12, it is interesting to notice the changes occurring in the $I_D/I_G$ ratios. To this end we plotted the $I_D/I_G$ ratios for all this samples (Figure 5.13).

![Figure 5.13: The Raman G band line shape does not change significantly for the untreated, sonication only and acid only samples. We observe a drastic change in the G band shape for acid treated + sonication sample indicating degradation.](image-url)
Figure 5.13 shows that degradation is most efficient in the acid treated + sonication sample. The next best method is the acid treated only sample.

**5.4 Summary**

We demonstrated the HRP based enzymatic degradation of SWNTs. We also demonstrated that acid treatment in conjunction with sonication is a faster and better method for degradation of SWNTs.
5.5 References


