

Spectroscopic Studies of Diameter Dependent Properties, Defects and Defect Engineering in Single-Walled and Multi-Walled Carbon Nanotubes

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by

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Dedicated to my Eya
(Grandmother)





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STATEMENT

The work contained in the thesis entitled “**Spectroscopic Studies of Diameter Dependent Properties, Defects and Defect Engineering in Single-walled and Multi-walled Carbon Nanotubes**” has been carried out by me under joint supervision of Dr. P. K. Giri, Associate Professor, Department of Physics and Dr. P. K. Iyer, Associate Professor, Department of Chemistry, Indian Institute of Technology Guwahati. This work has not been submitted elsewhere for the award of any degree.

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CERTIFICATE

It is certified that the work contained in the thesis entitled “*Spectroscopic Studies of Diameter Dependent Properties, Defects and Defect Engineering in Single-walled and Multi-walled Carbon Nanotubes*”, by **Mr. Dilip Kumar Singh**, has been carried out under our supervision and this work has not been submitted elsewhere for a degree.

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SYNOPSIS

Carbon nanotubes (CNTs) are unique one-dimensional nanostructures with remarkable electronic, optical, mechanical and thermal properties. Since its discovery in 1991, CNTs have caught widespread attention of researchers worldwide for studies of fundamental properties as well as device applications. Carbon nanotubes were first thought of as perfect seamless cylindrical graphene sheets- a defect-free structure. However, with time and as more studies have been undertaken, it has emerged that nanotubes are not necessarily that perfect i.e. it may contains various kinds of topological defects. The issue is further complicated by the fact that the quality of a nanotube sample depends very much on the growth method such as commonly used chemical vapor deposition (CVD). As-grown nanotubes containing various forms of carbon and other impurities can be purified by various methods. However, often defects are created on the tube walls during growth as well as in the process of purification. Several exotic properties of single walled carbon nanotubes (SWCNTs) predicted by theory have been verified experimentally to a reasonable extent. However, presence and role of defects in the nanotube properties are yet to be understood properly. Detrimental effects of defects in CNTs have been recognized from studies of nanoelectronic devices fabricated from CNTs that often have very short lifetime and high failure rates. Defective nanotubes are known to be highly electron emitting and lifetime of these devices are too short for commercial applications. Defect induced enhanced conductivity and defect-enhanced dispersion of carbon nanotube in DNA solutions have been reported recently for multiwalled carbon nanotubes (MWCNTs). Thus, defects are expected to play a significant role in determining various functionalities of carbon nanotube based devices. A controlled introduction of defects and nondestructive evaluation of defects in nanotubes are of immense significance for their potential applications in various devices. Understanding the influence of specific type of defects in the nanotube structure on the electronic and optical properties is of particular interest.

During the growth of carbon nanotubes, the number and nature of defects is decided by various factors like temperature of growth, carbon source feeding rate, carrier gas flow rate, nature of carbon source being used etc. The identification of various kinds of defects and their methods of characterization is not established for carbon nanotubes using traditional methods like Raman spectroscopy, electron spin resonance (ESR), photoluminescence (PL)

spectroscopy, positron annihilation lifetime spectroscopy etc. Use of the sophisticated techniques like ultrahigh vacuum scanning tunneling microscopy (UHV-STM), high resolution transmission microscopy (HRTEM) for monitoring structural defects in CNTs are often time consuming and can not be used for the bulk characterization. In the literature, UHV-STM and aberration corrected low voltage HRTEM have been used recently to obtain evidence of defects and defect dynamics in nanotubes. However, nondestructive techniques like Raman spectroscopy, PL spectroscopy and ESR spectroscopy are not explored in the literature to study the presence and influence of structural defects in the structural and optical properties of carbon nanotubes.

This thesis focuses on the spectroscopic studies of diameter dependent structural properties, defects and defect engineering in SWCNTs and MWCNTs. Defect engineering of carbon nanotubes through controlled introduction of defects by low energy ion irradiation at different doses and defect removal by vacuum annealing is achieved. Further, application of defects in CNTs as an efficient quencher of fluorescence from several common fluorescent dyes is demonstrated. A large number of samples of SWCNTs and MWCNTs of very wide range of diameters (5 nm-100 nm) grown by CVD method have been studied systematically. Some samples were grown in-house with a home-built CVD setup and some of the samples studied were procured commercially. The pristine and processed (e.g. vacuum annealed, laser annealed and ion irradiated) nanotubes were studied systematically to understand the spectroscopic signature of various structural defects and the influence of defects, interlayer interactions, strain/curvature in the microstructure and optical properties of the nanotubes. Microstructure of the nanotubes is investigated by powder X-ray diffraction (XRD), HRTEM, scanning electron microscopy (SEM) and atomic force microscopy (AFM), while the thermal stability and oxidation kinetics of the nanotubes as a function of nanotube diameter are studied by Thermogravimetry analysis (TGA). Electron paramagnetic resonance (EPR) studies in conjunction with vibrating sample magnetometer measurements are performed to study residual magnetic impurities and paramagnetic defects in the as-grown and processed nanotubes. Raman spectroscopy is extensively used in this work to obtain spectroscopic fingerprint of different types of defects in CNTs, for the first time. Optical absorption and photoluminescence studies enabled us to identify defect related absorption and emission bands in carbon nanotubes. Covalent functionalization of the nanotubes yields absorption and

emission in the visible range of wavelength, as compared to the near-infrared emission expected from defect-free nanotubes. Defect mediated efficient quenching of fluorescence from several common dyes using carbon nanotubes is demonstrated. Controlled introduction of defects and dynamic annealing of defects for improvement in the structure of the nanotubes are studied by low energy ion-irradiations at various doses with different ions.

Several significant new results have been reported in this thesis through different chapters of the thesis. Firstly, diameter dependence of interlayer separation, strain/curvature effects have been probed systematically by spectroscopic studies and results are corroborated by HRTEM analysis. Diameter dependence of the oxidation kinetics of as-grown and vacuum annealed nanotubes have been observed and explained on the basis of defects and strain in the nanotubes. Secondly, Raman active modes due to structural defect in the pristine and processed nanotubes are probed by Raman studies. Several new Raman active modes due to modification of the phonon density of states induced by defects are observed and are believed to be fingerprints of well known structural defects such as pentagon/heptagon rings, Stones-Wales defects in nanotube walls. Thirdly, defect related visible photoluminescence emission from as-grown and functionalized carbon nanotubes have been observed for the first time and the role of defects is elucidated through excitation and emission spectroscopy studies. Further, defect engineering of carbon nanotubes through vacuum annealing and low energy ion irradiation at various doses has been demonstrated. In particular, defect removal by thermal annealing, controlled introduction of defects by low dose ion-irradiation, irradiation induced reconstruction and structural improvement of nanotubes, and evolution of nanotube structure to novel carbon nanospring like structures with higher ion doses have been presented in this thesis. On the basis of these studies, difference in mechanism of defect formation in single walled and multiwalled nanotubes is elucidated. Finally, the application of surface defects on the efficient quenching of fluorescence by SWCNTs and MWCNTs for common fluorophores has been demonstrated.

The work has been presented in *eight chapters*. The first two Chapters of the thesis provide introduction, review of literature, motivation for the present work and details of the experimental techniques developed in house and used for the growth as well as characterization of defects in nanotubes. Chapters 3, 4, 5 discuss results of various microscopic and spectroscopic studies of diameter dependent properties with a focus on

structural defects in the pristine and different processed nanotubes of wide range of diameters. In Chapter 6 and Chapter 7, different aspects of defect engineering in CNTs are presented. Finally, Chapter 8 summarizes salient conclusions of the work and presents an outlook for future works. In what follows, we summarize contents of each chapter.

Chapter 1 provides introduction to structure and optical properties of carbon nanotubes, review of literature on defect studies on nanotubes and motivation for the present work.

Chapter 2 gives brief account of the experimental techniques adopted for this work and their working principles. This chapter also includes details of the design and in-house development of a laser Raman setup used for the present study. Further, the design and development of a home-made thermal CVD system used for synthesis of carbon nanotubes are discussed in details. Details of the samples of SWCNTs and MWCNTs grown in-house and commercially procured for the present study are provided in this chapter. It also includes the details of the processing conditions for vacuum annealing, chemical functionalization, laser irradiation and ion irradiation on different nanotubes samples.

Chapter 3 provides results of microstructure analysis of CNTs using HRTEM and XRD. HRTEM studies on SWCNTs (diameter <2 nm) and MWCNTs (diameter: 5-100 nm, length: 5-15 μm) show direct evidence of topological defects in the as-grown (acid purified) samples. HRTEM analysis of MWCNTs of various diameter ranges (6 different samples) clearly show that as the diameter of the MWCNTs increases the interplanar d-spacing between different concentric walls decreases. Some of the large diameter MWCNTs shows d-spacing smaller than that of turbostratic graphite due to interlayer interactions and defects, as evidenced by HRTEM imaging.

Peak intensity and the line profile analysis of the XRD pattern shows diameter dependent lines shape profiles for (002), (100) and (101) peaks of MWCNTs. Interplanar spacing d_{002} shows exponential decrease with increasing diameter of MWCNTs consistent with the HRTEM observations and it is attributed to the interwall interactions. On the other hand, FWHM shows inverse diameter dependence as a result of lower strain/curvature of the larger diameter tubes. With the help of XRD studies, we detected additional peak at $\sim 12.7^\circ$

due to non-hexagonal carbon rings. These results demonstrate the power of XRD in estimating diameter of MWCNTs, similar to the presently used Raman spectroscopy for diameter estimation of SWCNTs. Study of curvature effects of various diameter multiwalled carbon nanotubes (MWCNTs) on Raman spectral parameters shows diameter dependence. Deconvolution of the Raman spectra for different diameter MWCNTs show gradual decrease of G band frequency with increasing diameter, this has been explained on the basis of nanotubes curvature and atomic vibrations involving interaction among the walls in MWCNTs. This can be used as an experimental tool to quantify the diameter of the MWCNTs. Probing of interlayer interaction and curvature effects on the structure of MWCNTs have been possible through nondestructive techniques such as XRD and Raman spectroscopy and results are corroborated by HRTEM analysis.

Oxidation kinetics and thermal stability studies of the nanotubes show definite signature and influence of defects as studied by thermogravimetric analysis (TGA). We have shown diameter dependence of the oxidative stability of MWCNTs of very wide diameter range (7-100 nm). Reverse sigmoidal function was found to fit better to the experimental TGA data as compared to the commonly used Gaussian fitting for estimating amount of different carbon phases. It was found that the oxidative stability of lower diameter MWCNTs is primarily controlled by lattice strain, while that of large diameter MWCNT is decided by the defects in the nanotube wall. Multiple component in the TGA spectra of different diameter MWCNTs as revealed from spectral deconvolution (using reverse Sigmoidal function) indicates that multiple phases of carbons are present in the samples. Lower diameter MWCNTs shows lower oxidation temperature due to high lattice strain. Higher diameter MWCNTs showing relatively high oxidation temperature have lesser defects or better crystalline. Vacuum annealing at 300, 500, 700 and 1000 °C are performed to investigate structural improvement of the nanotubes. TGA spectra of the annealed samples show higher oxidation temperature for the 700 °C annealed SWCNTs and 1000 °C annealed MWCNTs, as a result of defect removal.

VSM studies performed on various diameter MWCNTs show clear hysteresis loop in the M-H plot depending on the catalyst impurity content. Saturation magnetization (emu/gm) being proportional to the amount of metallic impurities present in the sample, M-H loop gives more precise estimate of the metallic impurity content in the CNTs as compared to the TGA

analysis. Some of the sample where TGA studies shows negligible or zero residual metallic content, VSM gives a finite value of the metallic content as estimated from saturation magnetization value. Due to higher sensitivity of VSM as compared to TGA, VSM proved to be a powerful tool for studies of metal impurity content. This study also helped understanding the relative contributions of defects and impurities in the oxidative stability of CNTs.

Chapter 4 is devoted to the Raman scattering and photoluminescence studies of SWCNTs and MWCNTs in the as-grown and processed conditions. In the Raman spectrum, besides the commonly observed radial breathing modes, D-band, G-band and G' band, a number of additional Raman active modes appear in the intermediate frequency (IFM) range ($500\text{--}1200\text{ cm}^{-1}$) and between G and G' band due to structural defects in the nanotubes. These IFM modes become more prominent with 632 nm laser excitation as compared to the modes observed with 488 nm excitation. These IFM modes show laser power dependent intensity for various bands. We have also experimentally observed Raman characteristic peaks of pentagon defects on the pristine nanotube structures, as predicted theoretically recently. These defect induced features were observed at 1725 cm^{-1} , 1984 cm^{-1} and 2332 cm^{-1} . New IFM modes observed in the Raman spectra that are different from the combination mode were correlated with various structural defects observed in HRTEM. Raman spectroscopy studies of vacuum annealed samples shows structural improvement through defect annihilation.

Room temperature PL measurements with 488 nm laser excitation show two broad PL emission bands in the visible range for both SWCNTs and MWCNTs. Two broad PL peaks are common to both samples and are independent of impurity contents in CNTs. The visible PL peaks are centered at 2.33 eV and 2.05 eV with full width at half maxima (FWHM) of about 0.22 eV and 0.40 eV, respectively for SWCNTs, and at 2.34 eV and 2.05 eV with FWHM of 0.25 eV and 0.25 eV, respectively for the MWCNTs. It is argued that these visible emission bands arise from defect induced local change in band structure in the CNTs, as defect-free nanotubes have emission only in the near-infrared region. Various kinds of defects that are observed with HRTEM can be correlated with the visible PL bands and the intermediate frequency Raman modes.

Functionalization of carbon nanotubes with Aniline shows strong visible PL peaks at 561 nm and 600 nm for SWCNTs and at 565 nm and 611 nm for MWCNTs respectively, at room temperature. A broader emission band with additional peak is observed with lower excitation wavelength. PL lifetime measurements shows different decay life times in case of SWCNTs and MWCNTs functionalized with Aniline. PL decay curves on functionalized SWCNTs show double exponential decay with time constants of 0.21 ns and 1.42 ns, while in case of MWCNTs it shows a single exponential decay with time constant of 1.91 ns for 565 nm emission band in each case. These results are understood in terms of surface defects created by aniline treatment during reflux reaction, as supported by HRTEM analysis. Aniline is expected to be form a noncovalent bond at the defects sites of CNTs and due to modified electronic structure, visible PL is observed from the functionalized SWCNTs and MWCNTs.

In **Chapter 5**, results of electron spin resonance (ESR) and vibrating sample magnetometer (VSM) measurements are discussed. EPR measurements were carried out with the intention to get information on the presence and local structure of paramagnetic centers. ESR spectra of as-grown samples show broad resonance absorption band due to combined effect of the ferromagnetic resonance (FM) from residual metallic catalyst and conduction electron spin resonance (CESR) from nanotubes. The observed line shapes were asymmetric in nature. The asymmetric Dysonian line shape results from the CESR of nanotubes. In MWCNTs with extremely low metallic impurity content (as confirmed from TGA, EDX and VSM measurements), a sharp peak at $g = 2.0013$ close to that of free electron g -value was observed. This sharp peak disappears after vacuum annealing confirming its origin as structural defects, not due to magnetic impurities. Line width of ESR spectra in MWCNTs is higher than of the SWCNTs, despite a lower metallic content in MWCNTs. The ' g ' value in the range 2.01-2.02 is assigned to the interaction between the conducting electrons in the nanotubes trapped at defects or magnetic ions site. A higher deviation from the free electron ' g ' value indicates higher localization by defects. ESR spectra of MWCNTs of six samples in the diameter range 5–100 nm, were deconvoluted using combination of derivative of Dysonian and Gaussian line shapes using Matlab. The line shape parameters were extracted for estimating the contributions from ferromagnetic resonance, conduction electron of carbon nanotubes and the structural defects. Interestingly smaller g -value was observed for samples

having higher metal content. The FWHM of this FM peak is lower for the samples containing lesser metallic impurities. ESR peak originating due to conduction electrons shows higher g-value for higher diameter tubes, likely to be caused by interaction among electron from concentric tubes. ESR measurements are carried out at room temperature and low temperatures (down to 153.3 K) to explore further the nature of defects and metallic density of states.

Chapter 6 discusses the results of controlled introduction of defects by low energy ion irradiation. We show that the structure and properties of carbon nanotubes can be engineered through introduction of defects and reconstruction of carbon network by energy deposition through ion irradiation. Significant new results have been achieved that enable us to isolate the Raman spectral features specifically assigned to structural defects in CNTs created by ion irradiation. Different ion species of H^+ , C^+ , N^+ and Ar^+ ion irradiations were carried out at 30 keV energy at three doses 10^{12} , 10^{13} and 10^{14} ions/cm² on SWCNTs and MWCNTs. Various microscopic and spectroscopic studies including X-ray photoelectron spectroscopy (XPS) have been performed before and after ion irradiation on SWCNTs and MWCNTs for different ions. No doping of nitrogen was found in CNTs with N^+ ion irradiation.

HRTEM studies on ion-irradiated SWCNTs show formation of vacancy type defects in SWCNTs at low dose. With increasing ion dose, it results into curved graphitic structures, protrusions on the wall and formation of MWCNTs from coalescence of SWCNTs. Raman studies show that intensity of IFM modes at 804, 868 and 926 cm⁻¹ scale with irradiation dose/ defect density confirming the fact that IFM modes originate from structural defects in CNTs contrary to the belief that IFM modes originates from combination modes only. Some of RBM features in SWCNTs disappear after irradiation due to conversion from SWCNTs to MWCNTs, in agreement with the HRTEM analysis. Raman studies further reveal peaks at ~ 1135, 1162 and 1184 cm⁻¹ due to Stones-Wales defects in SWCNTs and MWCNTs. We find that substantial amount of point defects are created at 10^{12} ions/cm² dose, while at a dose of 10^{13} Ar^+ ions/cm² the structure of the nanotubes improves as evidenced by increase in intensity ratio of G⁻ to D-band. It is due to the dynamic annealing of defects and reconstruction of carbon network that an improved structure is obtained for intermediate dose. Similar improvement is observed in case of N^+ ion irradiation at 10^{13} ions/cm² dose. Higher dose (10^{14} N^+ ions/cm²) irradiation shows formation of large protrusions on nanotube walls and amorphous carbon in HRTEM images. In some regions of the CNT network, we

observed re-nucleation and growth of novel carbon nanospring structures with single wall structure having a width of ~30 nm and length of ~500 nm. Such nanosprings may find important applications in nanomechanical system. In case of MWCNTs, formation of curved graphitic structure was observed upon irradiation. These curved carbon structures gets converted to fullerene like carbon with increasing dose, as observed in HRTEM images. HRTEM studies show that SWCNTs and MWCNTs behave differently under ion irradiation. Nature and type of defects produced in these two types of nanotubes are different due to structural differences.

XPS C1s core spectra of SWCNTs before irradiation shows peaks at 284.21 eV, 284.89 eV and 286.12 eV originating from sp^2 carbon, sp^3 carbon and structural defects, respectively. In case of SWCNTs, before irradiation sp^3 tetrahedral bonded carbon peak was observed to be shifted by 0.61 eV from standard peak reported in the literature and it is observed at 285.5 eV after irradiation. An estimate of the sp^3 hybridization in each of these samples was estimated from the ratio of the corresponding area of the sp^3 peak to the total area of C_{1s} peak. Relative content of sp^2 carbon was found to improve and sp^3 content was drastically reduced after 10^{13} ions/cm² irradiation as compared to the 10^{12} ions/cm² irradiated sample. This is consistent with the Raman results. Thus, a tuning of relative contents of sp^3 , sp^2 and defects in CNTs is achieved through controlled introduction of defects by ion irradiation at different doses.

EPR studies on N⁺ ion irradiated MWCNTs show new EPR active centers at g=2.462, 2.068, 2.074, 1.986, 1.9882 and 1.913 at different doses due to paramagnetic defects introduced as a result of ion irradiation.

In **Chapter 7**, one specific application of defects in SWCNTs and MWCNT as efficient quenchers of fluorescence in common fluorescent dyes is demonstrated. Experiments performed on three well known fluorophores, namely, fluorescein, rhodamine 6G and quinine sulphate show that carbon nanotubes with structural defects acts as an efficient fluorescence quencher for all three fluorophores in the visible region. In each case, the Stern-Volmer plot was found to be highly non-linear indicating involvement of combined static and dynamic quenching processes. Possible involvement of impurities like metal nanoparticles, amorphous carbon, graphite etc in the nanotubes was studied systematically and their contribution to

quenching was ruled out. The involvement of structural defects in the nanotube surface for the fluorescence quenching was elucidated through careful analysis of UV-Vis absorption and steady state PL results. With increasing concentration of carbon nanotubes in fluorescein, the relative change in intensity of absorption in fluorescein was monitored at 490 nm. The intensity of the characteristic emission band of fluorescein decreases with increasing concentration of carbon nanotubes, indicating a possible surface adsorption. However, surface adsorption alone can not explain the non-linear behavior of Stern-Volmer plot. It accounts for the static quenching part of the combined static and dynamic quenching process as observed experimentally. PL quenching effect was found to be dominant even in the cases where adsorption was very low. Our studies on vacuum annealed CNTs confirm that structural defects are primarily responsible for the quenching of fluorescence from fluorescein. Adsorption isotherm has been studied using Langmuir and Freundlich models. Freundlich model was found to represent better the process of adsorption of fluorophores on carbon nanotubes surface. Confocal laser fluorescence microscopy on glass slide coated with fluorescein solution mixed with carbon nanotubes shows very dark regions near the nanotubes confirming the efficient quenching by CNTs. Quenching experiment was repeated with graphite powder to study comparative surface adsorption, ball milled graphite powders to study effect of defect as binding sites and activated charcoal where complete surface adsorption is expected. Stern-volmer plot for graphite shows a linear plot, whereas SWCNTs clearly showed a non-linear characteristic. This strongly supports the idea that besides the surface adsorption, defects in CNTs act as an efficient site for quenching of fluorescence. A small number of holes and electrons in the nanotube may quench the excited states of fluorophores through a non-radiative Auger recombination mechanism. Annealed SWCNTs show maximum decrease in intensity of the absorption peak with concentration, but it show least quenching of the fluorophore. Since decrease in the absorption peak and static quenching are related, this signifies that dynamic quenching plays a major role in case of SWCNTs. Since density of defects is much more in as-received SWCNTs than annealed SWCNTs, this indicates that defects in the nanotubes are responsible for dynamic quenching. Different fluorophores show different quenching efficiencies and different levels of agreement with the isotherms for adsorption. This is due to different affinities shown by different dyes depending upon the molecular geometry and charge. Time resolved photoluminescence spectroscopy

was performed to estimate the relative contribution of dynamic quenching. SWCNTs were found to be more efficient fluorescence quencher than the MWCNTs.

In **Chapter 8**, summary and conclusions of this work are collected highlighting the new findings on various aspects of defects in carbon nanotubes and their nondestructive evaluation. Several spectroscopic techniques in conjunction with high resolution microscopy have been utilized to obtain fingerprint of defects in SWCNTs and MWCNTs. Finally, defect engineering of CNTs structure have been possible through low energy ion irradiation and vacuum annealing. Without the use of much sophisticated techniques, this work paves the way of detecting and understanding the properties of defects in CNTs by various nondestructive methods. Defect engineering of CNTs is a field of growing interest and this study makes significant contribution towards this direction. Results of this work would enable understanding the role of defects and application of defects in CNT based functional devices that are otherwise extremely difficult to characterize. At the end of this chapter, we suggest directions in which this work could be extended.

Part of this work has been published /communicated in various journals and presented in conferences as listed next.

List of Publications

Carbon Nanotubes (Included in this thesis):

1. Dilip K. Singh, Parameswar K. Iyer, and P. K. Giri, “Diameter dependence of oxidative stability in multiwalled carbon nanotubes: Role of defects and effect of vacuum annealing”, **J. Appl. Phys.** **108**, 084313 (2010).
(Also appeared in *Virtual Jr. of Nanoscale Science & Technology*, November 1, 2010)
2. Dilip K. Singh, Parameswar K. Iyer, and P. K. Giri, “Diameter dependence of interwall separation and strain in multiwalled carbon nanotubes probed by X-ray diffraction and Raman scattering studies”, **Diam. Rel. Mater.** **19**, 1281 (2010).
3. Dilip K. Singh, Parameswar K. Iyer, and P. K. Giri, “Defect evolution and structural improvement in low energy ion irradiated carbon nanotubes: Microscopic and spectroscopic studies”, **Int. J. Nanosci.** (2011). DOI: 10.1142/S0219581X11007661
4. Dilip K. Singh, Parameswar K. Iyer and P. K. Giri “Improved chemical synthesis of graphene using a safer solvothermal route” **Int. J. Nanosci.** (2011). DOI: 10.1142/S0219581X11007636.
5. Dilip K. Singh, Parameswar K. Iyer and P. K. Giri, “Evidence for defect-enhanced photoluminescence quenching of Fluorescein by single-walled carbon nanotubes”, (**Chem. Phys. Lett., Under Review**).
6. P. Goutam, P. K. Iyer, Dilip K Singh, P.K. Giri, “Enhancing the Photo Stability of Poly-(3-Hexylthiophene) by Preparing Composites with Multiwalled Carbon Nanotubes”, (**J. Phy. Chem. B** **115**, 919 (2011)).
7. Dilip K. Singh, Parameswar K. Iyer, and P.K.Giri, “Quantitative analysis of diameter dependent properties of multi-walled carbon nanotubes”, **AIP Conf. Proc., Vol. 1147**, 450 (2009).
8. Dilip K. Singh, P. K. Iyer, and P. K. Giri, “Optical Signature of Structural Defects in Single Walled and Multiwalled Carbon Nanotubes” **J. Nanosci. Nanotechnol.** **9**, 5396 (2009).
9. Dilip K. Singh, Parameswar K. Iyer, and P. K. Giri, “Functionalization of Carbon nanotubes and study of its optical and structural properties” **Nano Trends** **4**, 55 (2008).
10. P. K.Giri and Dilip K. Singh “Possible role of defects in the Visible Photoluminescence from Single Walled and Multiwalled Carbon Nanotubes” **Mater. Res. Soc. Symp. Proc.** **Vol. 1018**, EE07-03 (2007).

11. Dilip K. Singh, Parameswar. K. Iyer, P. K. Giri “*Study of fluorescence quenching effect of Carbon Nanotubes*” **Proc. 52nd DAE Solid State Physics Symposium, Vol. 52, 347 (2007)**. Ed. Amitabh Das, Meenakshi Sunder and Shiv Kumar Gupta.

Others:

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2. Dilip K. Singh, Parameswar K. Iyer, and P. K. Giri, “*Spectroscopic study of low energy N⁺ ion-irradiation induced structural transformations and defects in carbon nanotubes*”.
3. Dilip K. Singh, Parameswar K. Iyer, and P. K. Giri, “*Effect of ion species on the structural modification of low- energy ion-irradiated carbon nanotubes*”.

4. Dilip K. Singh, Parameswar K. Iyer, and P. K. Giri, “*Interaction of carbon nanotubes with fluorophores: Photoluminescence and Adsorption studies*”.

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Bibliography

List of Symbols and Abbreviations

<u>Symbol</u>	<u>Description</u>
AFM	Atomic Force Microscopy
BWF	Breit-Wigner-Fano
CESR	Conduction Electron Spin Resonance
CLSM	Confocal Laser Scanning Microscopy
CNTs	Carbon Nanotubes
DTA	Differential Thermogravimetric Analysis
DV	Double Vacancies
EPR	Electron Paramagnetic Resonance
FMR	Ferromagnetic Resonance
FWHM	Full Width at Half Maxima
HRTEM	High Resolution Transmission Electron Microscopy
IFMs	Intermediate Frequency Modes
IMJs	Inter Molecular Junctions
MWCNTs	Multiwalled Carbon Nanotubes
PL	Photoluminescence
RBM	Radial Breathing Modes
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SPR	Super Paramagnetic Resonance
SV	Single Vacancies
STEM	Scanning Transmission Electron Microscopy
SW	Stone-Wales
SWCNTs	Single Walled Carbon Nanotubes
TGA	Thermo-gravimetric Analysis
TRPL	Time Resolved Photoluminescence
VSM	Vibrating Sample Magnetometer
XRD	X-ray Diffractometry

Chapter 1

Introduction

1.1 Introduction to Carbon Nanotube

Carbon nanotubes (CNTs) are an interesting class of nanostructure that can be thought to arise from the folding of graphene sheet, which is a planar crystalline structure of hexagonal carbon rings. After the first experimental report of CNTs by Iijima in 1991 [1], it has caught wide spread attention of researchers worldwide due its fascinating properties and diverse range of applications. More recently, the parent structure graphene has made massive impact on the scientific community following the Nobel prize for its discovery [2] and some ground breaking experiments on it [3].

The diameter of a CNT is of few nanometers and length in microns. Due to its small diameter, large aspect ratio and unique electronic properties, it has got immense potential applications in electronic and photonic devices. Depending upon its diameter and chirality, it behaves as metallic or semiconductor. The energy gap of semiconducting CNTs can be tuned in the range 0-1 eV by varying the nanotube diameter. In this way, the desired semiconducting properties can be incorporated using only carbon atoms with a specified geometric structure. The basic ideas of the lattice, electronic and phonon structures, magnetic and transport properties, quantum confinement effects in CNTs have been extensively reviewed by M. Dresselhaus and others in several reviews and books [4-7]. The symmetry related properties of CNTs have been reviewed by Eduardo B. Barros [8]. Electronic and transport properties of CNTs are well summarized by Stephen Roche [9]. The unique structure of the CNTs result in numerous superior physical and chemical properties, such as the strongest mechanical strength, the highest thermal conductivity, room-temperature ballistic quantum conductance, electromechanical coupling and super

surface functionality. CNTs derive their unique properties from one dimensional quantum confinement effect along the radial direction giving rise to van Hoon singularities (vHs) in the density of states (DOS).

The large scale synthesis of CNTs by arc discharge was discovered by Ebbesen and Ajayan [10]. The first catalyzed growth of single walled carbon nanotubes (SWCNTs) was reported in 1993 [11]. Presently, there are basically three known methods of synthesis of CNTs: (a) Arc discharge, (b) Pulsed laser deposition, and (c) Chemical vapor deposition (CVD). CVD is a simple process scalable to industry scale production of nanotubes. In this method, one can control the diameter of SWCNTs produced. CVD grown nanotubes are usually MWCNTs often riddled with defects. On the other hand, laser ablation is a costly technique but produced CNTs are relatively defect free. CNTs produced using arc discharge technique tends to be short with random sizes and directions. These basic synthesis processes have undergone a number of modifications to produce defect free high purity CNTs. In case of arc discharge technique, use of pulsed power [12], various catalyst type etc. have been attempted to improve the quality of CNTs. Various carbon sources like gas sources methane, acetylene etc and various catalyst types like bimetallics and different substrates has been experimented with to improve the yield and quality of the CNTs produced. In few experiments, to avoid usually used transition metal catalysts Fe, Co, Mo etc which limits the device applications, noble metals, like gold [13], copper [14] and many others metals [15] have been tried for CNTs growth. To produce very low diameter SWCNTs, templated catalyst preparation methods have been used like Zeolite supported CNTs synthesis from alcohol [16] and MgO impregnated catalyst etc. [17]. For better growth there are few successful attempts with water assisted synthesis [18], use of poly-

hexyl-thiophene [19], helps in avoiding poisoning of the catalyst and results in much longer CNTs growth.

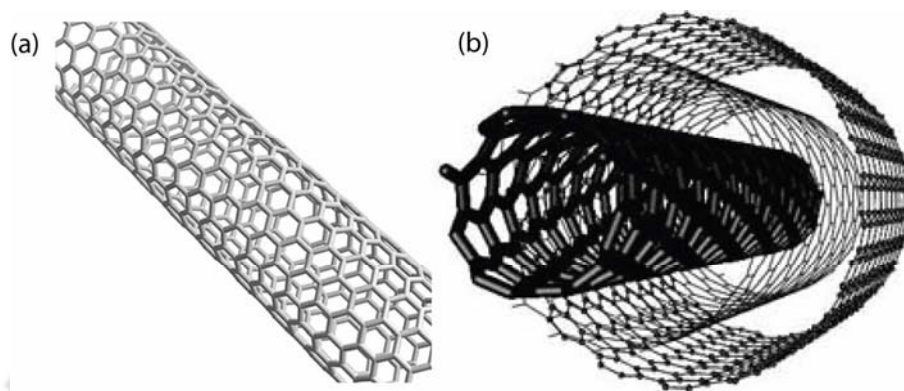


Figure 1-1: Typical structure of a CNTs; (a) a SWCNT and (b) a MWCNT. It consists of rolled hexagonal graphene sheets of carbon atoms.

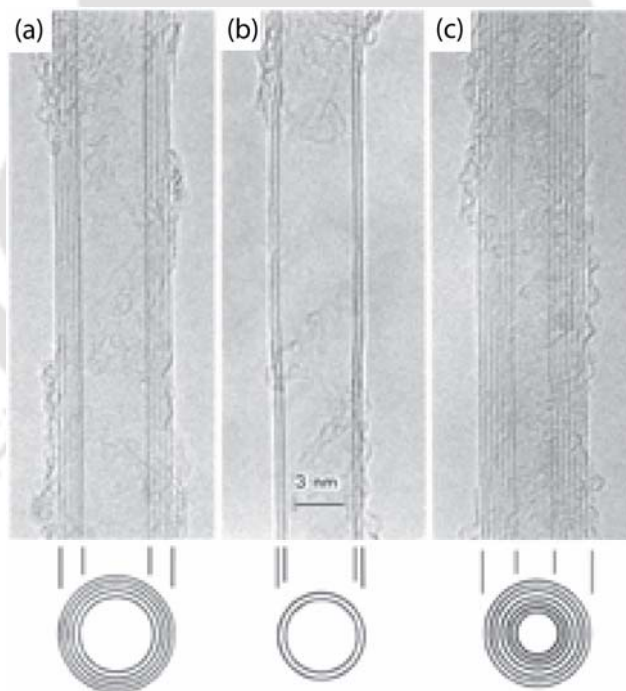


Figure 1-2: HRTEM image of multi-wall coaxial nanotubes with various inner and outer diameters, d_i and d_o and number of shells N : (a) $N=5$, $d_o=67$ Å, (b) $N=2$, $d_o=55$ Å, and (c) $N=7$, $d_o=65$ Å [1].

Depending on number of walls, CNTs are classified under three categories: SWCNTs (Fig. 1.1(a)), Double walled carbon nanotubes (DWCNTs) and Multiwalled Carbon nanotubes (MWCNTs) (Fig. 1(b)). Fig. 1.2 shows high resolution transmission electron micrograph (HRTEM) of multiwall coaxial nanotubes with various inner and outer diameters. Fig. 1.2 (a) shows a MWCNT with outer diameter 67 Å and 5 walled structure. Fig. 1.2 (b) shows DWCNTs consisting two concentric tubules of carbon, having outer diameter 55 Å and Fig. 1.2 (c) MWCNTs having seven walled structure and outer diameter 65 Å.

1.1.1 Single-walled carbon nanotubes (SWCNTs)

The atomic structure of SWCNTs is specified by a single chiral vector $\vec{C}_h$ defined as $\vec{C}_h = n \vec{a}_1 + m \vec{a}_2$, where, $\vec{a}_1$ and $\vec{a}_2$ are unit vectors of the hexagonal honeycomb lattice, while n and m are positive integers. A (n, m) tube is formed by folding the graphene sheet into a cylinder so that equivalent atoms at O and A, or B and B', are connected by $\vec{C}_h$ as shown in Fig. 1-3 for the case of (5,2) nanotube. The “chiral angle”, θ , is defined as the angle between the unit vector $\vec{a}_1$ and the chiral vector $\vec{C}_h$. Two limiting cases exists, i.e, when $m = 0$, or $n=m$, the corresponding chiral angles are $\theta = 0^\circ$ or $\theta = 30^\circ$, respectively. Nanotubes with chiral indices (n, 0) i.e ($\theta = 0^\circ$) are called “Zigzag” tubes, whereas nanotubes with chirality (n, n) i.e ($\theta = 30^\circ$) are called “Armchair” nanotubes. All other tubes with $n \neq m$ are referred as “Chiral tubes”. Armchair and Zigzag nanotubes have higher symmetry and shows mirror symmetry plane containing the tube axis as compared to general “chiral” tubes (n, m; $n \neq m$). The electronic properties of a perfect CNTs can be predicted from their diameter and chirality [20, 21] and it can be

uniquely determine by the chiral vectors (n, m) [22]. If the difference of chirality indexes is a multiple of 3 it behaves as metallic nanotube, otherwise it behaves as semiconducting nanotube [23]. Mathematically if, $n - m = 3q$ (q : integer): metallic otherwise, $n - m \neq 3q$ (q : integer): semiconductor. Semiconducting CNTs have bandgap ~ 0.5 eV. The gap

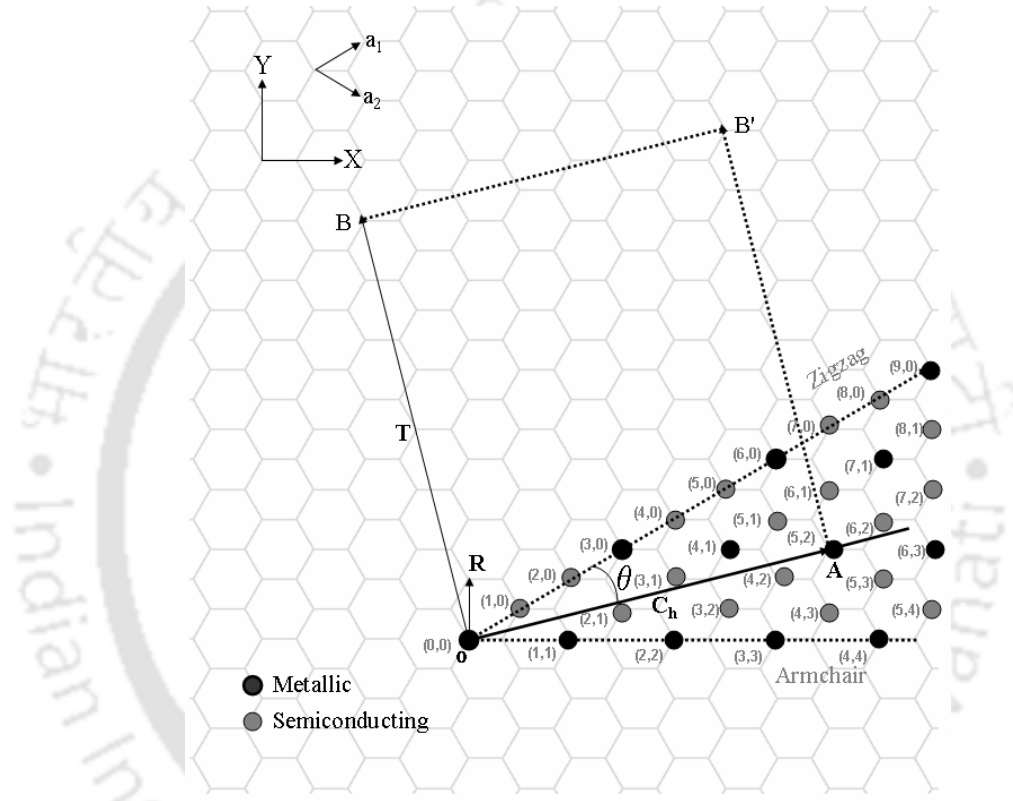


Figure 1-3: Chiral vector $\vec{OA}$ or $C_h = n\vec{a}_1 + m\vec{a}_2$ is chiral vector is defined by unit vectors a_1 and a_2 and chiral angle q with respect to the zigzag axis. Along the zigzag axis, $\theta = 0^\circ$. Nanotube is formed by connecting sites O and A and sites B and B' . $\vec{OA}$ and $\vec{OB}$ define the chiral vector C_h and the translational vector T of the nanotube respectively. The rectangle $OAB'B$ defines the unit cell for the nanotube. The diagram is constructed for $(5, 2)$ nanotube.

energy of the semiconducting CNTs is related to the chirality [24] and is approximately proportional to the inverse of the tube diameter [25]. Armchair nanotubes are always

metallic in behavior, while zigzag nanotubes can be metallic and semiconducting both. Chiral nanotubes are always semiconducting in behavior.

Extended Brillouin zone picture of the chiral nanotube is shown in Fig. 1-4. It shows that for a chiral CNT the unit cell consist of a chain of five hexagonal rings to account for circular boundary condition as shown in Fig. 1-4(a). The top hexagon is

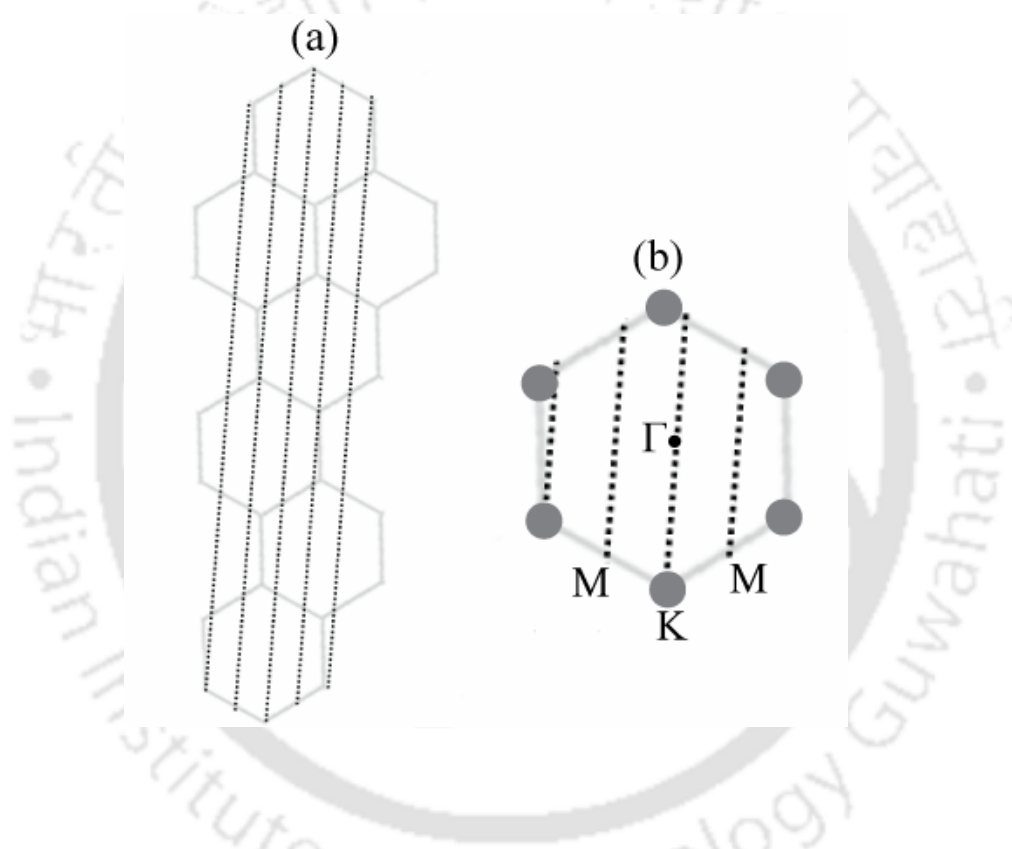


Figure 1-4: (a) Extended Brillouin zone picture showing top hexagon is equivalent to the bottom hexagon. (b) Central Brillouin zone showing the allowed states due to chiral boundary condition imposed. The high symmetry points Γ , K, M are indicated.

equivalent to the bottom hexagon. The central Brillouin zone is shown in Fig. 1-4(b), with high symmetry points Γ , K and M. Calculations shows that at six corners of the hexagon, i.e, the K-points, the valence and conduction band touch each other in a linear dispersion

relation near the Fermi edge [4]. A structural defect in CNT would lead to modification of allowed states and hence it would give rise to characteristic signature of structural defects.

Fig. 1-5 (a) shows the energy band diagram of a typical CNT [26]. It consists of a number of Van-Hove singularity states generated in the valence and conduction band due to cylindrical folding of graphene sheet (cylindrical boundary condition) to form a

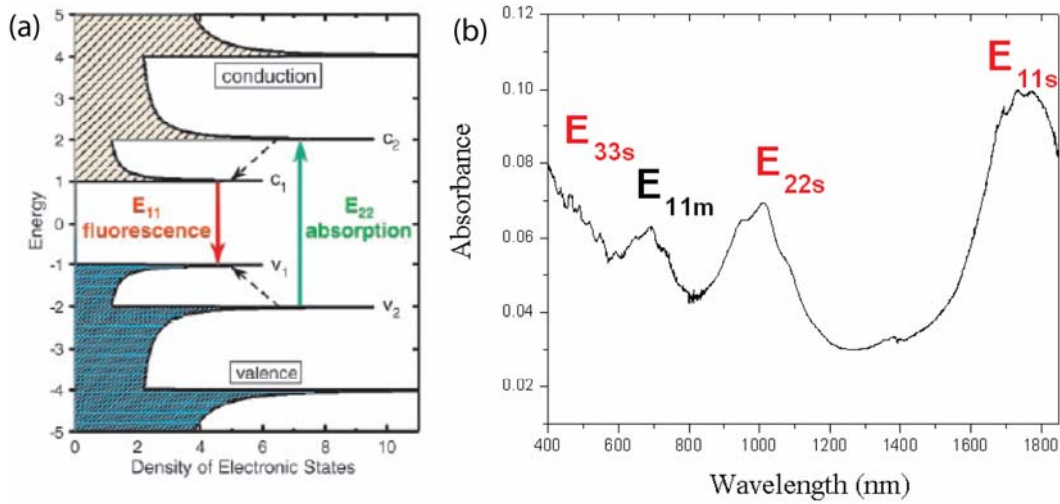


Figure 1-5: (a) Schematic of the electronic transitions between Van-Hove singularity states in a CNT [26]. (b) Typical absorption spectra of SWCNTs corresponding to absorption between various Van-Hove singularity states. Subscripts m and s represents metallic and semiconducting CNTs [27].

nanotube. Fig. 1-5(b) shows typical absorption spectra of SWCNTs containing absorption bands corresponding to various possible transitions between different Van-Hove singularity states [27]. Similarly, the photoluminescence (PL) peaks of SWCNTs are determined by their specific band gaps, depending upon the diameter and chirality of the nanotube. Hence, the electronic structures of CNTs can be detected by PL spectrum. The natural band gap of defect free CNTs lies in the NIR region. Within the simple tight binding (STB) theory which assumes that the electronic band structure arises from a pure

π -orbital at each conjugated carbon atom (s, p) separately, the low energy band gap transitions is expressed as: $S_{11} = 2a\beta / d$, $S_{22} = 4a\beta / d$, $M_{11} = 6a\beta / d$. Where, a is the carbon-carbon bond length (nm), β is the transfer or, resonance integral between the p-orbitals ($\beta = 2.9 \text{ eV}$), and d is the diameter (nm) of the particular semi-conducting or metallic SWCNT. Semi-conducting SWCNTs has been further classified into two sub-categorie, Type-I $[(n-m) \bmod 3 = 1]$ and Type-II $[(n-m) \bmod 3 = 2]$ due to their different behavior depending upon chirality [28]. Presence of structural defect may lead to modifcaiton of chirality and diameter, leading to changes in the band gap.

Protocol and various experimental methods of characterization of SWCNTs have been very well studied [29, 30]. Diameter dependent optical properties of SWCNTs have been extensively studied through a number of spectroscopic techniques like Raman spectroscopy, absorption spectroscopy and PL spectroscopy. Detailed analysis of mean diameter and diameter distribution of SWCNTs has been done from their optical response [29]. Diameter grouping of bulk samples of SWCNTs from optical absorption spectroscopy has been illustrated [31]. Raman spectroscopy has evolved as a powerful tool to probe the properties of CNTs like diameter distribution, chirality, doping, nature like semiconducting or metallic etc [32- 34]. Raman scattering intensity is known to depend on the diameter for SWCNTs [35].

In reality, CNTs are rarely perfect. Different growth conditions under different growth techniques and post growth purification process give rise to various kinds of defects like point defects (vacancy and interstitial defects), strains, adatoms, pentagon-heptagon pairs, pentagon-octagon-pentagon pairs etc in the CNT walls and tips. During the growth of CNTs, the number and nature of defects is decided by various factors like

temperature of growth, carbon source feeding rate, carrier gas flow rate, nature of carbon source being used etc. These defects modifies/alter the band structure in different ways [36] and hence the electronic properties as well. Impurities such as hydrogen and nitrogen have been found to modify the band structure of CNTs [37].

1.1.2 Multiwalled Carbon Nanotubes (MWCNTs)

MWCNTs contain many layers of concentric graphene cylinders as shown in Fig. 1-1(b). MWCNTs of various inner and outer diameter, and number of cylindrical shells have been observed experimentally [1]. MWCNTs offer remarkable electrical, mechanical and chemical properties similar to SWCNTs with lesser production cost and comparatively lesser carbonaceous and metallic impurities. The unique mechanical and electronic properties of MWCNTs are proving to be a rich source of new physics and could also lead to new applications in materials and devices. MWCNTs have got immense applications as molecular composites in organic solar cell [38], as supercapacitor [39], gas sensors [40], infrared detectors [41] and in biological systems. Oscillations of the core of the MWCNTs have been demonstrated as a nanomechanical system of operating frequency of several Gigahertzes [42]. Electron emission from the side wall of individual MWCNTs has been observed [43].

In spite of numerous applications demonstrated using MWCNTs, no protocol exists for characterizing and quantifying the quality of MWCNTs. Most of the optical spectroscopy techniques used for characterization of CNTs can not be directly applied to MWCNTs due to multiple absorption and emission between concentric cylindrical structures. The concentric tube of a MWCNT can be of similar or, of different chirality. This gives rise to resonance effect in between the layers of MWCNT making the situation

more complicated for characterization using spectroscopic techniques. Resonance effects and small penetration depth of visible lasers into nanotubes may limit the use of Raman spectroscopy for quantitative characterization of macroscopic volume of MWCNTs. It has been reported that the spacing between the pair of nanotubes varies with increasing diameter of the MWCNTs upto certain diameter [44].

Besides the Raman spectroscopy, structure of MWCNTs can be probed by X-ray diffractometry (XRD) and HRTEM analysis. However, XRD probes milligram of sample without any specific selection between carbon nanotubes in the sample. Diameter and chirality distribution in CNT samples makes multiple orientations with respect to the X-ray beam leading to a statistical result. Diffraction profile resulting from X-ray scattering has been used to characterize DWCNTs [45] and it has been used for characterization of composition and structure of macroscopic amount of DWCNTs [46]. Different possible structures of MWCNTs like Russian doll and jellyroll type has been distinguished using temperature dependent XRD profiles [47]. It has been shown theoretically that for graphite and turbostratic carbon, increase in the curvature of the graphite sheet leads to increase in the Bragg angle and decrease in the FWHM [48]. XRD profile for CNTs has been used for estimating contribution of particle size broadening and strain broadening resulting from distribution of d-spacing. Interestingly the major contribution to the width of the (001) peak was found to arise from strain rather than finite size effects [49]. Studies on CNTs and nanocapsules using XRD and electron diffraction have shown that the interlayer spacing between layers of CNTs is about 2.6% higher than that of graphite [50]. Structure of CNTs including the nature of disorder has been studied using computed and experimental XRD data [51]. XRD has been used to characterize the degree of alignment in as-grown nanotubes [52]. However, previous to our work no systematic studies were

reported on the diameter dependence of the XRD pattern of MWCNTs. Majority of the reported studies have been carried out on MWCNTs of diameter up to 10-15 nm. We had explored the properties of large diameter nanotubes in the diameter range 10-100 nm.

In the literature, only a few of the studies are dedicated to Raman spectroscopic analysis of MWCNTs. RBM like feature in MWCNTs is reported to originate from innermost wall of MWCNTs and it is found to be inversely proportional to the diameter of the innermost tube [53, 54]. It has been proposed that the inner tubes of a MWCNT contribute to the SWCNT-like feature in the spectra, while the other tubes more closely resembled graphite [55]. Splitting of graphitic mode G-band has been observed in case of MWCNTs [54]. HRTEM has been utilized to find the interlayer d-spacing that showed an increase in the d-spacing with decreasing diameter of MWCNTs having diameter less than 10 nm [44]. However, large diameter MWCNTs with diameter in the range 10-100 nm has not been studied systematically. A recent study has shown influence of diameter of MWCNTs on the Raman shift [56]. However, no detailed analysis was made on the diameter dependence of line width, intensity and splitting of G band in Raman spectra [56].

The oxidative stability of CNTs can be influenced by nanotube diameter and local curvature of CNTs [57]. It is generally accepted that under oxidative conditions, tubular structures are substantially less stable than graphite and most disordered carbon [58]. Smaller diameter nanotubes are believed to oxidize at lower temperature due to higher curvature and strain [59]. Bond curvature has been found to affect the oxidation of SWCNTs [60]. The relation between bond curvatures with the nanotube radius has been expressed in terms of “local curvature radius” defined as an inverse of the “bond curvature” [61]. Smalley et. al. [62] have observed an excellent correlation between

oxidation temperature and Raman spectra in case of SWCNTs of diameter range 0.8-2.0 nm indicating an inverse variation of oxidation rate with tube diameter.

In reality, the situation is more complex because defects and derivatization moiety in nanotube walls can lower the thermal stability [63]. Defects are inherently present in as-grown and acid purified CNTs, and are known to decrease the oxidative stability of CNTs [64]. Various kinds of defects including edges, dangling bonds, vacancies, dislocations, steps, 5,7-membered ring defects, Y-junctions and kinks may be present in CNTs. Defects including five-membered rings are responsible for closing the ends of nanotubes. Most of the defects sites are particularly reactive to oxygen at elevated temperatures. It has been demonstrated that high temperature air oxidation occurs preferably at kink sites [65]. TGA studies by Bom et al have provided evidence for defects playing a significant role in the thermal stability of MWCNTs [63]. For MWCNTs grown by chemical vapor deposition (CVD) technique, catalyst type and synthesis temperature have a measurable impact upon nanotube stability, suggesting differing levels of crystalline perfection in the resulting nanotubes [65]. Defect sites were found to affect the oxidation temperature of MWCNTs.

Through partial oxidation of CNTs, non-CNT carbon impurities can be removed, but it requires exact knowledge of oxidation temperature and role of defects. As the oxidation progresses simultaneously in a competitive manner among various forms of carbon, only those less stable than CNTs may be effectively removed in this manner. Weight loss below 400 °C shows presence of amorphous carbon [66]. An enhancement of oxidative stability has been observed in case of high temperature annealed MWCNTs [63]. Also the degree of crystallinity improves generally with high temperature annealing [67]. HRTEM studies have shown that as the annealing temperature is raised, the interlayer

distance between nanotube walls decreases, suggesting higher orders and diminishing defect density [68]. Annealing at high temperatures may lead to decrease in metallic impurity content and increase of nanotube diameter [69, 70]. Open tips and graphite defects allow a means to escape for the metal and metal oxide vapor [68, 70]. Kinetics of oxidation of various forms of carbon including SWCNTs has been investigated by monitoring calorimetric signals from phase transformations using differential thermogravimetric analysis and two exotherms have been observed corresponding to more than one transformations [71]. More recent study has shown that the oxidation of CNTs need not originate in the nanotube caps, but may originate in the other areas of increased reactivity, such as wall defects [72]. Most of the reported studies have been carried out on either low diameter SWCNTs and MWCNTs or on carbon nanofibres with large diameters. However, no systematic studies on the effect of diameter and the role of defects and strain on the oxidative stability of MWCNTs of intermediate range of diameters, such as 10-100 nm have been reported in the literature.

1.2 Structural Defects in CNTs

Immediately a year after the discovery of CNTs, experimentally it was realized that as grown CNTs contain a number of defects and impurities [73]. At the same time, theoretically the possibility of connecting two tubes was predicted using a pentagon-heptagon pair [74, 75]. Specifically, types of structural defects and the role of sp^3 defect structures were first discussed by Ebbesen [76, 77]. The possible defect structure of CNTs can be classified into three groups: topological defects (introduction of ring types other than hexagons), rehybridization (ability of carbon atom to hybridize between sp^2 and sp^3), and incomplete bonding defects (vacancies, dislocations, etc). Since defective sites of

CNTs are more reactive than the perfect nanotubes [78, 79], controlled introduction of defects can be used for site selective functionalization of CNTs. By introducing a pentagon and a heptagon into the hexagonal carbon lattice, two tube segments with different atomic and electronic structures can be seamlessly fused together to create intramolecular metal-metal, metal-semiconductor, or semiconductor-semiconductor junctions. Metal-semiconductor junction was found to behave like a rectifying diode with nonlinear transport characteristics. Ultimate miniaturization of functional electronic devices has been demonstrated using a pentagon and a heptagon into the hexagonal carbon lattice [80]. Huge potential applications of structural defects of CNTs were immediately realized after experimental realization of possibility of linking CNTs of two different chiralities using pentagon-heptagon pairs.

1.2.1 Point Defects

Point defects in CNTs include a missing carbon atom from its lattice site known as “vacancy” or missing two adjacent atoms “divacancy” and adsorbed non-carbon atoms at the carbon lattice site. Apart from mono-vacancy and divacancy defects, there is finite probability of formation of tri-vacancy and tetra-vacancies. Fig. 1-6 shows schematic of various kinds of point defects. Fig. 1-6(a) shows a typical vacancy (V) and an adsorbed atom (A). Fig. 1-6(b) shows cross linking between different layers of a MWCNT and Fig. 1-6(c) shows linking of a number of SWCNTs in a bundle. It's often difficult to detect these point defects using microscopic and spectroscopic techniques. Atomic resolution scanning tunneling microscopy (STM) is a powerful technique for identifying defects in SWCNTs, but it is too slow and painstaking for statistically relevant material characterization and it can not be performed on insulating gate oxides. Raman

spectroscopy lacks the spatial resolution to directly identify a single defect in otherwise pristine materials [81]. Recently, selective electrochemical deposition has been shown as a

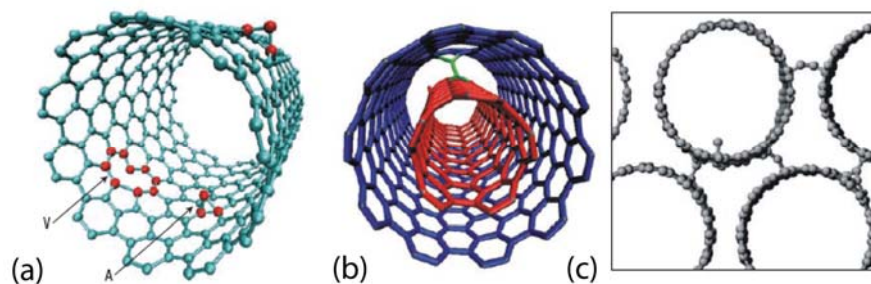


Figure 1-6: Schematic of various kind of point defects like (a) vacancy (V) and adsorbed atom (A), (b) cross-linking between different layers of MWCNTs and (c) linking of various SWCNTs [83].

potential tool to identify and count point defects in CNTs [82]. Structure, formation and influence of various kinds of point defects possible in CNTs are discussed below. Usually point defects are observed as surface voids on the wall under HRTEM / STEM.

(a) Vacancy: Vacancies are the missing atom sites from the hexagonal tubular network of CNTs. Vacancies may be a single atom or cluster of carbon atoms missing from their sites. Unlike metals, where point defects can be easily observed under microscope, CNTs exhibit a strong reconstruction of the atomic network near the vacancy. Self-repairing capability of CNTs under electron beam exposure in the microscope makes observation of point defects too difficult [84]. DFT (density functional theory) and DFT based TB calculations showed that single vacancies (SVs) in the nanotubes are reconstructed by saturating two dangling bonds and forming a pentagon [85]. In case of graphite, SVs reconstruct due to Jahn-Teller distortion [86]. Compared to graphite, nanotube reconstruction is much stronger due to curvature and inherent nanosize of the system. For

nanotubes, it is easier to contract locally and “heal” the hole and thus saturate energetically unfavorable dangling bonds. The curvature gives rise to a shorter bond in the pentagon (as compared to the bond in graphite) and considerable drop in the vacancy formation energy E_{sv} (E_{sv} for graphite ~ 7.5 eV). Artificially vacancies can be created by ion-irradiation. When ion energy barely exceeds the threshold value for displacement of surface atoms, the ion-surface collision can remove one or, at most a few surface atoms, producing mostly point defects on an atomic scale. It has been experimentally found that semiconductor-metal intermolecular junctions can be formed by reconstruction of vacancy clusters through a series of generalized Stone-Wales transformation [87]. Further, through simulation the mechanism of formation of CNT semiconductor-metal intramolecular junctions with specific locations and controlled sizes was suggested with the possibility of application to nanoelectronic devices [88, 89]. Lu and Pan have shown through tight binding calculations that reconstruction of a network around a single vacancy occurs with no constraint. They also found that the formation energy of point defects depends on radius and chirality [85]. Theoretical calculations show the formation energy of vacancies to be 5.82 eV [90]. In situ HRTEM studies at elevated temperatures shows vacancies or, ‘holes’ tend to migrate and coalesce with each other to form larger ones [91].

Calculations show that the vacancies may form semiconductor-metal intramolecular junctions by self-assembly of vacancy defects [88]. In another calculation, it was shown that the process of vacancy Stone-Wales transformations leads to formation of pentagon-heptagon [89]. Theoretically, it has been shown that vacancies can modify the band gap of CNTs [92]. Gómez-Navarro et. al. have shown that even a low concentration of vacancies in SWCNTs can produce a large decrease in their electrical conductance [93]. Calculation of conductance of metallic CNTs with vacancy defects using the Landauer

approach and a tight-binding Green's function technique show dramatic decrease in conductance of small-radius tubes, while tubes with large radii are less affected [94]. It is difficult to identify vacancies under electron microscope, but it is expected to show definite singnature in electron paramagnetic resonance (EPR) [95] and Raman spectroscopy [96].

(b) Di-Vacancy: Di-vacancies represent two missing carbon atoms form hexagonal network. Divacancies are the most important defects that alter the charge transport properties of SWCNTs [97, 98]. A low concentration of about 0.03%, it can change the SWCNT conductance by about 3 orders of magnitude. Divacancy formation energy is smaller than a single vacancy itself [99]. Theoretical studies have shown that 5-8-5 structures are more stable than the 555-777 defect structure [100]. Using DFT calculation, Okada found that the activation barriers for formation and healing of a defect consisting of pair of an ad-atom and vacancy are ~ 10 and 2 eV [101]. This indicates the possibility of defect healing under moderate conditions. Defect was found to introduce two gap states with characteristics strongly dependent on its arrangement. They also observed metal-insulator transition in case of (9,0) nanotube owing to the formation of gap states [101]. Ab initio calculations show that 585 structures are more stable than the 555-777 divacancies.

(c) Ad-atoms: Ad-atoms represent adsorbed atoms in the carbon lattices either at the vacancy sites or in between the carbon lattice. Theoretical calculations have shown that the band gap is sensitive to bromine adsorption at CNTs. DFT calculations have shown the activation energy for formation and healing of pair of ad-atom and vacancy defects to be 10 and 2 eV [101]. A strong relation was found between the density of states at the Fermi

level and the binding strength of the C-Br chemical bond. Oxygen adsorption dramatically influences the electrical resistance, thermoelectric power and local density of states, as determined from Transport measurements [98].

(d) Dislocations: Dislocations represent the displaced atoms from the perfect hexagonal positions. It also includes dislocation of atoms resulting from deformation due to compressive or elongation strain. Fig. 1-7(a) and (b) shows schematic of the dislocations loops formed in graphite due to precipitation of vacancies and interstitials respectively. Similar to graphite case [102], dislocation loops can be present in MWCNTs. These are probably formed due to quenched in point defects. Such dislocations sometimes result in interlayer linkages between concentric tubes. First-principle density functional theory calculation shows that the structure of the dislocation defect with two 5-7 pairs are more stable than a local haeckelite composed of defect units of three pentagons and three heptagons (555-777). Calculations have shown that radial deformation of CNTs perpendicular to the tube axis demonstrate band gap modification such as opening and closure [103, 104]. Through high resolution microscopy, we have attempted to observe dislocations in MWCNTs.

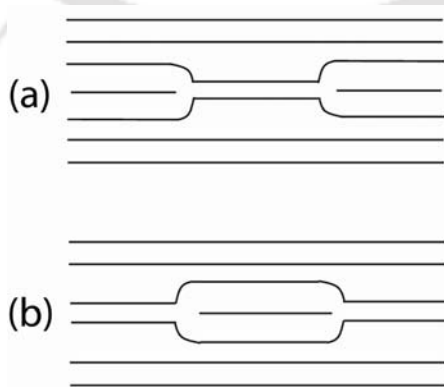


Figure 1-7: (a) Schematic view of dislocation loop due to precipitation of vacancies (b) Schematic view of dislocation loop due to the precipitation of interstitials. [102]

(e) Wigner Defects: An interstitial carbon atom right beside a vacancy is called Wigner defect. Ab initio density functional theory suggests that this defect has low formation energy ~ 7.27 eV, lower than vacancy itself. In case of bundles, this reduces to 5.53 eV. Thus it is predicted to be one of the most important defects that are created after electron or, ion irradiation. However no experimental observation has been reported yet.

(f) Stone-Wales Defects: Stone Wales defects are formed by 90° rotation of two carbon atoms with respect to the midpoint of the bond schematically shown in Fig. 1-8 [87]. By the Stone-Wales transformation, four hexagons are changed into two pentagons and two heptagons. SW defect creates an unoccupied flat band, very close to the conduction band

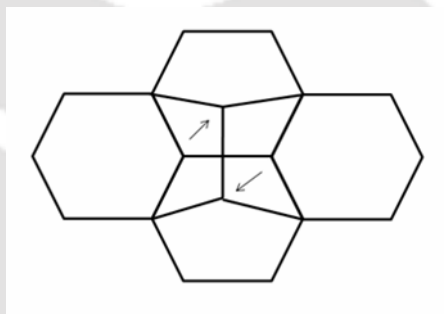


Figure 1-8: Formation of Stone-wales defect by 90° bond rotation, forming two pentagon-heptagon pairs.

minimum (CBM), forming a shallow donor level. A bond rotation defect closes the gap in the large-gap nanotubes, opens gap in small-gap nanotubes, and it increases the density of states in metallic nanotubes [36]. It has been proposed that the coalescence process of fullerenes or CNTs may occur through a sequence of such rearrangements. The defects are thought to be responsible for nanoscale plasticity and the brittle-ductile transitions in CNTs. Stone-wales defects have been predicted to reduce the CNTs emission current [105]. A Stone-Wales defect produces quasibound states and exhibits reduction in the quantized conductance [106]. However experimental observation of this defect have been

extremely difficult due to self-repair process in CNTs. Theory predicts that Stone-Wales defects would give rise to Raman modes at 985 cm^{-1} and 1020 cm^{-1} arising from intermolecular junction and the central bond respectively [107]. In contrast to this J. Dong et. al. theoretically predicts the characteristic frequency of SW defects to lie between 1820 and 1962 cm^{-1} depending upon diameter [108]. Recently, in surface enhance Raman experiment, peaks observed at 1122 and 1173 cm^{-1} in temporal fluctuating spectra have been assigned to SW defects in SWCNTs [109].

1.2.2 Topological Defects

Topological defects in CNTs represent inclusion of ring types other than the hexagonal structure. It is the most commonly observed defect structure in as grown CNTs. Topological defects change the curvature of CNTs. Pentagon, heptagon or pentagon-heptagon (5-7) pairs are the most common type of topological defects. Apart from this, tetragon, octagons, heptagon-triangle pairs, pentagon-octagon-pentagon pairs and polygonal defects have been predicted to exist on the walls of as grown and ion-irradiated CNTs. [77, 83, 100]. The formation mechanism, energy and stability of these types of defects have been a topic of extensive theoretical studies. Compared to other kinds of structural defects, some of the topological defects can be easily identified under HRTEM, because they usually introduce curvature effects. Presence of pentagon rings induce positive curvature ($+60^\circ$ disclination), while the heptagon rings induce negative curvature (-60° disclination) [5]. Different kinds of bent angles require various member rings. Sharp bent is only possible with tetragonal rings or vacancy, whereas low curvature bent nanotubes will consist of pentagon-heptagon pairs with varying separation distance or pentagon-octagon-pentagon pairs. Direct observation of such defects has been reported

using HRTEM and scanning tunneling microscopy (STM) [110-114]. Fig. 1-9 shows schematic of topological defects created by removing carbon atoms. Fig. 1-9(a) shows a SWCNT (8,8) with 5-7 pair couple defect formed after removing 14 carbon atoms indicating a bending, whereas Fig. 1-9(b) shows SWCNT containing 5-7 pair couple defects formed by removing eight atoms indicating a local curvature change. Accumulation of point defects lead to the formation of topological defects.

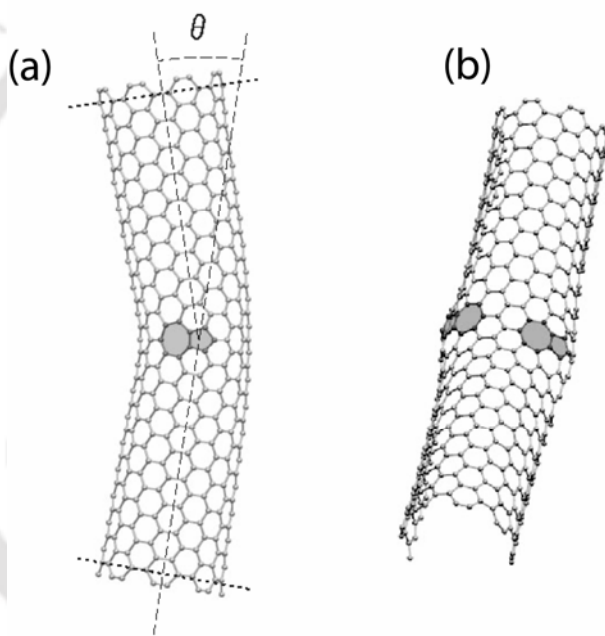


Figure 1-9: (a) SWCNT (8,8) with 5-7 pair couple defect formed after removing 14 carbon atoms shows maximum bending angle of 16.6° . (b) Shows nanotube containing 5-7 pair couple defects formed by removing eight atoms [115].

Fig. 1-10 shows reconstruction of the atomic network of a CNT near point defects leading to formation of 5-8-5 member ring from double vacancy (DV) as schematically shown in Fig. 1-10(a), while a single vacancy (SV) and an adatom forms a metastable Stone-wales (5-7-7-5) defect. Fig. 1-10(b) shows tetra-vacancy collapses into 5-7-7-7 ring structure finally leading to local modification of diameter of CNTs [83].

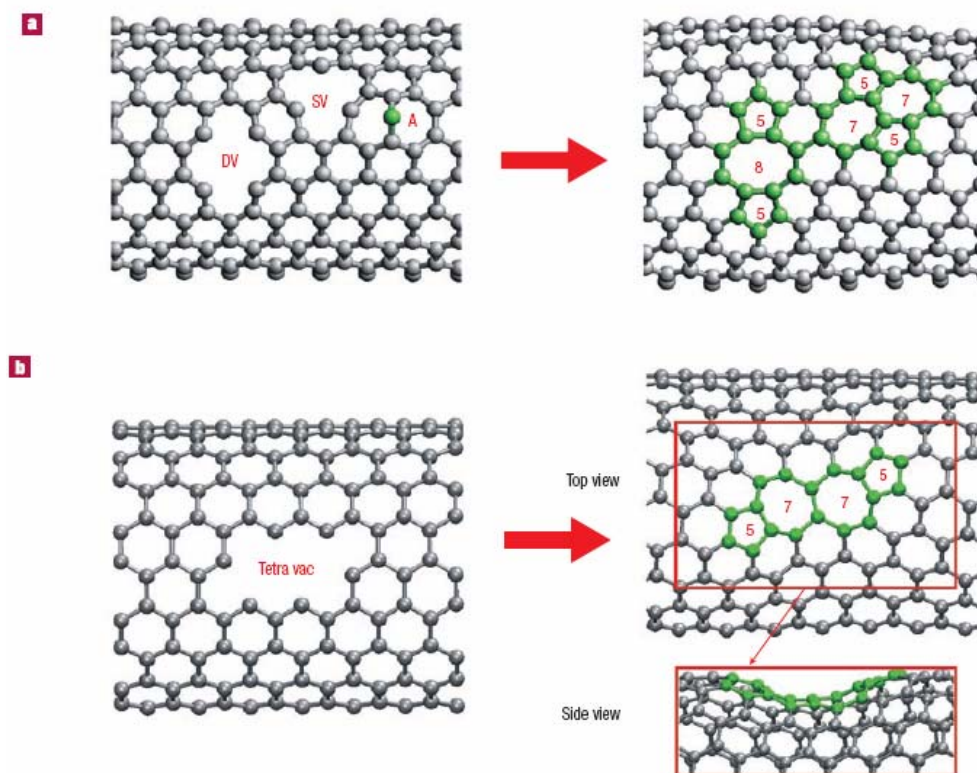


Figure 1-10: Reconstruction of the atomic network of a CNT near point defects (a) represents a double vacancy (DV) transforms to an aggregation of 5-8-5 member ring, while a single vacancy (SV) and an adatom form a metastable Stone-wales (5-7-7-5) defect. (b) Shows tetra-vacancy collapsing into 5-7-7-7 ring structure finally leading to local modification of diameter of CNTs. [83]

(1) Pentagonal Defects: Pentagonal defects represent presence of five membered carbon ring structure. Presence of such ring structure is must for closing the tip of CNTs. The end regions of nanotubes show transformation from the simple cylindrical geometry to conical and polyhedral shapes. The closure of an open cylindrical surface necessarily involves topological defects, at the atomic level that would introduce positive Gaussian curvature. Nanotube lattice consists of a network of six-membered rings and the introduction of positive curvature is achieved by introducing positive wedge disclinations [116, 117] or rings with fewer than six members. The wedge disclinations have been

observed before in surface crystals, [116] such as biological membranes, which show translational periodicity in two dimensions. In CNTs, these defects correspond to pentagonal rings. Pentagonal rings leads to either a strained 2D lattice or a topologically positively curved lattice.

A perfect CNT obeys Euler's theorem given by $V - E + F = 2$, where V is the number of vertices, E is the number of edges and F is the number of faces of a polyhedron. The total number of such defects on any closed surface is determined by Euler's principle stating relation between the number of edges, corners and faces on any regular polyhedron and corresponds to 12 pentagons (a total rotational deficit of 4π) in the hexagonal network. The five fold symmetry due to pentagonal site is destroyed in tube structures by the requirement of helicity. The presence of disclinations relieves strain in a folded graphite sheet, which otherwise would have to be accommodated in the C-C bonds, resulting in a large increase of the energy of the system. The pentagons in the hexagonal lattice can be thought of as defects in a sp^2 -bonding configuration. The solid cone angle produced by transformations due to one pentagon corresponds to $\sim 19^\circ$ [73]. In case of SWCNTs, the pentagon defects are concentrated at the tip of the nanotubes leading to formation of fullerene like caps at the tips. In MWCNTs various morphologies exists for the tip shapes. In general, the morphology of the tips in MWCNTs can be divided into two categories: straight and conical. The exact position of the pentagonal defect determines the actual shape of the tip. Ajayan et. al have shown presence of sharp resonant states near the valence edge in the local density of states due to pentagonal defects through scanning tunneling spectroscopy and tight-binding calculations both [118].

(b) Heptagonal defects: Seven membered rings introduce defects by introducing negative curvature in the hexagonal carbon lattice. These defects were considered by Mackay [119, 120] for the mathematical construction of minimal surfaces that are observed in nature in systems like soap bubbles and lipid bilayers. As the sign of this defect is opposite and the strength exactly equal to a pentagonal defect, the presence of a heptagon nullifies the curvature due to a pentagon. Hence in order to achieve topological closure for any single tube in a tubule, the total number of pentagons (P) and heptagons (S) present should conform to the relation, $P = S + 12$ [5]. This leads to the possibility of having an unlimited number of heptagons and pentagons on any tube till the sum rule is satisfied and to the creation of various complicated morphologies by the combination of pentagons, heptagons and pentagon-heptagon pairs.

(c) Pentagon-Heptagon Pairs (5-7) or, Intermolecular Junctions: There are two processes for the formation of the 5-7 pair defects on nanotubes after growth. (a) Splitting of Stone-Wales (SW) defects proposed by Yakobson [121]. In this process, SW defects formed on a nanotube are divided into two 5-7 pair defects by the rotation of a bond; these two 5-7 pairs are separated by a single row of hexagons. The rotation of another bond drives the 5-7 pairs away from each other (b) Other process of formation of 5-7 pair defects is by the removal of carbon atoms from the wall. When pentagon and heptagon are nucleated in pairs on a tube surface, one possibility is the creation of a stepped surface, with two cylindrical surfaces of different diameters separated by a wedge. This leads to change in diameter of the nanotubes without deforming the graphite network and cylindrical geometry. It is speculated that adjacent pentagon-heptagon pairs can be used as bridges to connect two different types (helicity) of tubules [74]. Introduction of an isolated

pentagon and heptagon is less stable than the introduction of a single 5-7 pair defect (+0.076 eV/atom).

CNTs having different helicities, behaves as one dimensional metal or semiconductor depending upon their chirality [122]. By introducing a pentagon and heptagon into a hexagonal carbon lattice, two tube segments with different atomic and electronic structures can be seamlessly fused together to create intramolecular metal-metal (M-M), metal-semiconductor (M-S), or semiconductor-semiconductor (S-S) junctions. CNT junctions with different band gaps can be used to produce quantum electro-optical devices while, M-S CNT junctions and selectively doped CNTs are proposed to be used for active electrical devices [80, 111, 123, 124]. Experiments have shown that M-S junction behave like a rectifying diode with nonlinear transport characteristics which are asymmetric with respect to bias polarity. In case of M-M junction, the conductance appears to be strongly suppressed and it displays a power-law dependence on temperature and applied voltage, consisting with tunneling between the ends of two Luttinger liquids. Carbon based molecular electronics requires controlled production of intramolecular junctions [80].

Theoretical studies on Zig-zag tubes using TB (tight binding) models have shown that 5-7 pair defects apart from leading to the change in diameter, also governs electronic behavior around the Fermi level. It introduces a sharp peak below and above the Fermi level associated with one 5-7 pair defect [125]. Young Kuk et. al. have resolved the electronic structure of an SS CNT intermolecular junction by scanning tunneling spectroscopy and observed a localized defect state decaying into both sides of the junction and the peaks of the Van-Hove singularities decaying into the opposite side of the tube [126]. Presence of isolated 5-7 defects significantly perturbs the electronic properties of

the hexagonal network [127]. These defect sites shows different reactivity compared with the hexagonal network and act as nucleation sites for chemical attack, such as oxidation. The localized defect states were predicted theoretically [123, 128] and has been observed in case of M-M CNT junctions [111] as well as in SS CNT junctions [126]. Single molecular devices based on intermolecular junctions of CNTs gives solution to several limiting [126] problems arising due to the miniaturization of active electronic components to nanometer scales like accurate patterning, processing of parts, routing of the interconnection wires and the clock frequency. Experimentally AFM induced kinks shows resistance in the range 10 to 100 k Ω , allowing control over conductance of metallic nanotube device [127].

1.2.3 Rehybridization Defects

Rehybridization property of carbon makes it unique among all the elements of periodic table. It can hedybridize between sp , sp^2 and sp^3 thus forming a number of compounds and allotropes. Graphite is perfect sp^2 hybridization, while diamond refers to a perfect sp^3 structure. A carbon atom in a sp^3 hybridization state can only form σ bonds, sp and sp^2 hybridized carbon atoms contains π bonds also. Depending upon the degree of curvature of graphene sheet as folded; it looses its sp^2 character and gains some sp^3 character. This indicates lower diameter CNTs contains higher sp^3 character. Research of various kinds of defects and their effect on the properties of CNTs started with sp^3 defect structures [76, 77]. It has been shown that line defects having sp^3 character are formed preferentially along the symmetry axes of the graphite sheet [76]. In case of CNTs, these re-hybridization effects occure because of the existence of high curvature and plays an important role in determining the electronic properties [128, 129]. Detailed knowledge of sp^2 and sp^3 states

of carbon at sub-nanometer resolution can be obtained from electron energy loss spectroscopy by monitoring carbon K-edge in transmission electron microscope [130]. Near-edge x-ray absorption spectroscopy (NEXAFS) [131] and X-ray photoelectron spectroscopy on core levels [132] can be used for quantitative determination of presence of sp^2 and sp^3 hybridization states separately. Experimentally it has been observed that the ozone exposure to MWCNTs shows threefold increase in CNT conductivity due to cross-shell bridging via sp^3 bonds formation [133].

1.2.4 Scrolled and Other Structures

Apart from various structural defects, MWCNTs exists in various structural forms making the situation complicated. Fig. 1-11 shows various types of possible concentric structures of MWCNTs. Fig. 1-11(a) shows most commonly observed concentric Russian doll type structure. Fig. 1-11(b) shows Scroll (jellyroll type structure), whereas Fig. 1-11(c) shows a more complicated situation of mixed MWCNTs of Russian doll and jellyroll type structures. Fig. 1-11(d) shows other form polyhedral graphitic tubes. The scroll type tubes have been experimentally found in MWCNTs grown by arc discharge [134]. Y. Ando and group have shown that thicker MWCNTs are typically highly defective and may have the jelly roll (scroll) or, defective polygonal structure consisting of flat graphitic domains [46]. Fig. 1-11(e) shows a typical HRTEM image of a bamboo shaped carbon, where internal hollow space is portioned in a number small segment like bamboo. Fig. 1-11(f) shows schematic diagram of a staked cone type nanotube. These staked cone type nanotubes are known as “Herring bone type CNTs”. Sometimes they are also referred as “Carbon nanofibers”. Fig. 1-11(h) shows HRTEM image of a helically coiled nanotube. All these types of nanotubes may be produced during a typical growth process of CNTs.

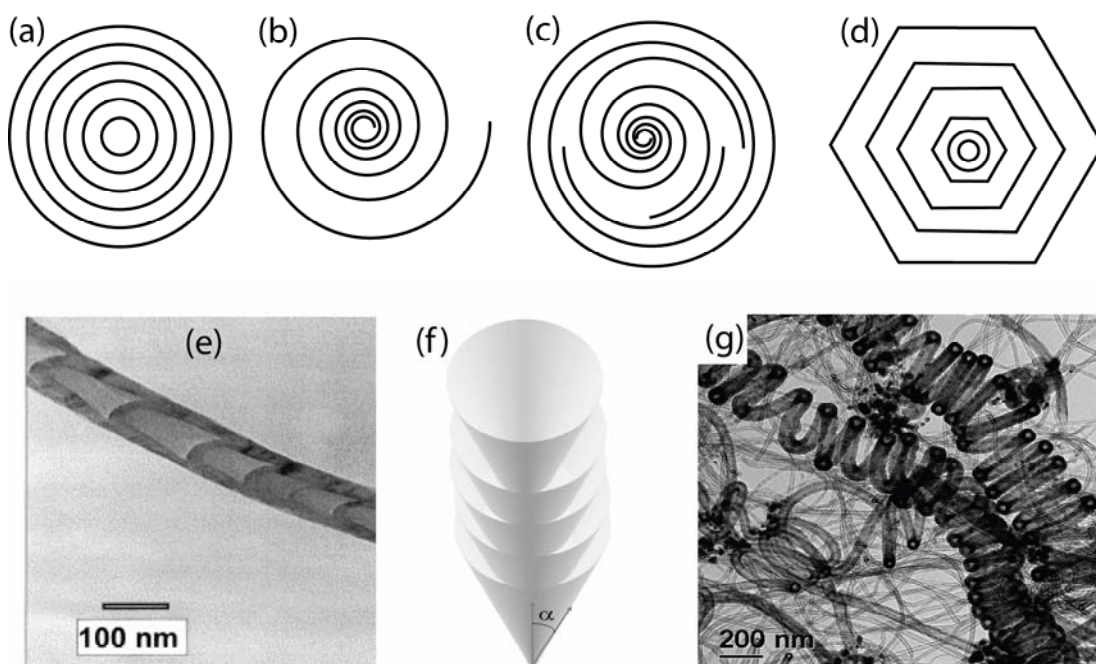


Figure 1-11: Various types of possible concentric structure of MWCNTs (a) Concentric (Russian doll) (b) Scroll (jellyroll type) (c) mixed MWCNTs of Russian doll and jellyroll structures (d) polyhedral tubes. (e) HRTEM image of a bamboo shaped CNT [135] (f) Stacked cone type (herringbone) nanotube. (g) HRTEM image of helically coiled nanotube [136].

1.3 Spectroscopic Signature of Structural Defects

A number of theoretical studies have been devoted to obtain spectroscopic fingerprints of various kinds of structural defects in CNTs. Till date, there are very few experimental reports in this direction either due to the limitation of characterization techniques used or, due to lack of control/manipulation of defects in CNTs. As discussed before structural defects in CNTs greatly control its optical and electronic properties. In CNTs, therefore, establishing the spectroscopic fingerprints of structural defects is of paramount importance for identification, control, manipulation and application of defects in CNTs.

There are very few studies reported on the spectroscopic features of structural defects in CNTs [137, 138]. Use of the techniques like scanning tunneling electron microscopy (STEM), HRTEM, atomic force microscopy (AFM) are time consuming and can not be used for the bulk amount of sample. The information obtained from these techniques is always local in nature. Spectroscopic signature of structural defects using conventional techniques like Raman spectroscopy, electron spin resonance (ESR), photoluminescence (PL), positron annihilation lifetime spectroscopy etc are not established in case of CNTs. The common techniques like Raman spectroscopy, PL and ESR can be used to characterize the structural defects in CNTs.

(a) Raman spectroscopy

Raman spectroscopy is a standard tool for studying defects in materials, especially in carbon based materials [139, 140]. Requirement of phonons only at the centre of the Brillouin zone arises from the translational symmetry related momentum conservation rules. Structural disorders break the translational symmetry, which activates the phonons at the k point of the Brillouin zone. CNTs similar to other sp^2 -hybridized carbon atoms, shows a disorder induced band (D-band) in the range ~ 1250 - 1450 cm^{-1} depending on E_{laser} [141]. Jinming Dong and group have theoretically calculated the Raman characteristic peaks induced by the topological defects of CNTs intermolecular junctions and they found that characteristic frequency of the SW defects lie between 1820 and 1962 cm^{-1} , depending on the local curvature of the tube [108]. Raman modes at 65.5 , 85.7 and 108.4 cm^{-1} in the low frequency region are predicted to arise from junctions in the nanotubes. It was shown that Raman modes caused by the pentagon defects lie out of the highest Raman peak of SWCNTs, regarded as indicator of the pentagon defects. Another calculation by

the same group shows that vibrational frequency due to di-vacancies lie out of the G-band, typically for (18,0) SWCNT, it occurs at 1748 cm^{-1} (for symmetric divacancy) or, at 1761 cm^{-1} (for asymmetric divacancy) [142]. There have been a number of attempt to calculate the effect of bending and deformations on the Raman active modes [143, 144]. Syndqvist and group have studied the Raman signature of pressure induced transition of SWCNTs. There have been very few attempts to experimentally identify the Raman spectroscopic signature of structural defects in CNTs. Very recently, using surface-enhanced Raman spectroscopy evidence of dynamic pentagon-heptagon pairs in SWCNTs has been found at 1139 and 1183 cm^{-1} , consistent with the theoretical predictions of 1122 and 1173 cm^{-1} for STW defects [109]. It is due to the dynamic creation and annihilation of these defects during measurement that makes the detection and identification of these defects extremely difficult.

Besides the characteristic graphitic peaks of nanotubes, namely low frequency radial breathing modes (RBM), Graphitic E_{2g} mode (G band at $\sim 1570\text{ cm}^{-1}$) and second order G' modes ($\sim 2700\text{ cm}^{-1}$), a number of Raman active modes are often observed in the region $300\text{--}1200\text{ cm}^{-1}$ (called as “Intermediate frequency modes (IFMs)”) and $1600\text{--}2400\text{ cm}^{-1}$. The origins of these modes are not well understood in the literature. Some of the reports claim these to be combination and overtone modes [145], while others claim it to originate from structural defects in CNTs [146]. No controlled experiments have been carried out to distinguish the specific features of combination modes and the defect related modes.

Raman spectra contains information of crystal structure, symmetry and interaction of photons with various kinds of excitations like phonons, plasmons, polaritons and magnons. Raman scattering studies has been extensively used to study structural defect in

a wide variety of material including semiconductors, polymers and dielectrics. Raman spectroscopy has been widely used for characterization of carbon based materials [33, 147, 148] and to study their structural defects [149]. Raman spectroscopy using visible laser only probes the phonon at the Brillouin zone centre ($q \approx 0$). This condition arises due to requirement of momentum conservation and hence a requirement of translation symmetry. Structural defects break down the momentum conservation and it activates phonons at the interior K point of the Brillouin zone ($q \neq 0$ phonons). Disorder induced lattice distortions can also lead to a break down of other symmetry-based selection rules, activating $q = 0$, which are otherwise not Raman active in the relaxed lattice structure. This can be graphically understood from Fig. 1-4, where we have shown the picture of extended Brillouin zone for a CNT. Structural defects will modify the position of the high symmetry points in the CNT, thus allowing characteristic defect induced peaks in the Raman spectra. Usually, in crystalline materials disorders / defect result into broadening of the Raman allowed peaks (G-band) [150, 151], new features (D or, D') related to the symmetry forbidden scattering process and observation of phonon density of states like spectra [139].

Although the defects greatly modify the electronic [125, 126] and optical properties [105, 152] of CNTs, there have been very few experimental attempts to explore the defect related spectroscopic signatures in the Raman spectra. In contrast to experimental attempts, there are a number of reports on theoretically expected defect related spectral features of CNTs like effect of bending [144] and deformation [143], fingerprints of presence of vacancies [96] and divacancies [142], stone-wales defects [153], pentagon and heptagon pairs (IMJs) [108] etc.

A brief accounts of various defect related features and defect induced modification of Raman spectra are reviewed below:

(i) Defect Induced Modification of RBM Modes: Structural defects like non-hexagonal carbon rings, vacancies etc. can lead to modification of diameter of SWCNTs and its chirality. SWCNTs are known to have high self-healing capacity in structural modification [83]. Such change may lead to either decrease or, increase of diameter or change in the chirality being reflected in the change in Raman shift of characteristic RBM modes. Such changes are always expected to be accompanied by a change in the intensity due to different electron-phonon interaction in CNTs.

(ii) Origin of IFM an Open Question: Defect Induced Modes or Combination modes?: A number of additional peaks are observed in the frequency range 300 and 1400 cm^{-1} . These band are known as “IFMs” and were first pointed out by Rao [32]. According to group theory, it should be a Raman-silent region for infinitely long tube [154]. There has been many proposal for origin of IFM modes like various types of combination modes, structural defects etc, as summarized in Table 1-1. Saito et. al. showed that the Raman active mode in this region may be due to the symmetry lowering effect from the finite tube size [155]. Excitation energy dependence of the Raman modes in this range (700-1000 cm^{-1}) and their tentative assignments have been reported [156] and their (strong) resonant characteristics have been observed [157]. The frequency of weak peak observed around 860 cm^{-1} is independent of the laser excitation. On the other hand, two series of bands (with one to three bands per series depending on the sample) are observed below and above 860 cm^{-1} and found to up and down-shift, respectively for increasing excitation energy [157].

Table 1-1: Summary of the various IFMs reported in the literature.

Sl.	Raman shift (cm^{-1})	Origin	Reference
1	(a) 789, 810 cm^{-1} , dispersive sharp features. (b) 700, 860 and 1070 cm^{-1} , non-dispersive broad features.	Second-order process, Combination of acoustic and optical phonon.	C. Fantini et. al., 2004 [146]
2	650-720 and ~ 840 -880 cm^{-1} : depends on the diameter (step like dispersion).	Second-order process, Combination of acoustic and optical phonon.	C. Fantini et. al, 2005 [158]
3	765 cm^{-1}	Localized defects in the nanotube lattice	L. Novotny et. al., 2005 [159]
4	740 and 950 cm^{-1} ($\lambda_{\text{ex}} = 2.54$ eV), 720 and 980 cm^{-1} ($\lambda_{\text{ex}} = 2.54$ eV) and 790, 818 and 942 cm^{-1} ($\lambda_{\text{ex}} = 2.18$ eV) 850 cm^{-1} : non-dispersive.	Finite size <i>defects</i> of CNTs	M. Kalbac et. al, 2006. [160]
5	(a) 516 and 682 cm^{-1} (SW defects) (b) 597, 1129, 1180, 1298, 1338 and 1356 cm^{-1} (heptagons)	<i>Defects</i> (Theoretical calculation)	J. Dong et. al, 2006 [108]
6	390-460, 460-510 cm^{-1} : broad and asymmetric peaks	Nanotube related, E_{11}^S and E_{22}^S optical transitions.	S. K. Doorn et. al., 2007 [161]
7	(a) 760, 985, 1275 and 1315 cm^{-1} due to IMJs (b) 1020, 1270 cm^{-1} due to SW defects.	<i>Defects</i> (Theoretical calculation)	P. Lambin et. al., 2007 [107]
8	386-490, 585-635 cm^{-1} (broad features) and 845 cm^{-1} (sharp feature) defects. 670-730, 1000-1100 and a shoulder at 775-980 cm^{-1} from perfect CNTs.	<i>Defects (low energy Ar^+ irradiation)</i>	S. Roth et.al. , 2007 [145]
9	1139 and 1183 cm^{-1} (SERS spectra)	Pentagon/ heptagon defects	K. Kaneko, 2010 [109]
10	669 (from perfect CNTs) and 805, 868, 926 cm^{-1} from defects.	<i>Defects (Low energy N^+ irradiation)</i>	D. Singh et. al., 2010 [162]

It was also proposed that the IFMs are due to the combinational mode of Zone-folded optic and acoustic branches of 2D graphite and that they can only be activated within low chiral-angle tubes (i.e, zigzag) at certain excitation energies **[146]**. Step like dispersive behavior observed experimentally was explained on the basis of a process

involving optical absorption and emission between the E_{44}^S and E_{33}^S states mediated by two E_3 symmetry phonons (one optic and one acoustic like phonon), for $\text{mod}(n-m,3) = 2$ nanotubes. In 2007 Stephen observed step like dispersive behavior of these IFM along with asymmetric shape. The peaks in the range of $460\text{-}510\text{ cm}^{-1}$ exhibit a sharp edge on the higher frequency side and a tail towards the low frequency side, the peaks in the $390\text{-}460\text{ cm}^{-1}$ range exhibit this edge on the low frequency side and tail off to higher frequencies. Such close similarity in the intermediate frequency modes provides strong evidence that such features should originate from a similar mechanism. In addition to these, broad and symmetric features were observed centered at 511 , 528 and 610 cm^{-1} along with 473 cm^{-1} peak; 473 cm^{-1} was considered to be overtone of RBM mode observed at 236 cm^{-1} .

On the other hand, there are reports which claim these as defect induced modes. Changes in the IFMs of SWCNTs were observed upon 30 keV Ar^+ ion irradiation [145]. Using Surface enhanced Raman spectroscopy, peaks at 1139 and 1183 cm^{-1} have been found to originate from pentagon-heptagon pair defects [109, 163].

(iii) Defect induced D-Band: Intensity of D-bands is taken as a measure of structural defects/disorder in CNTs or, graphitic materials. D-band originates from A_{1g} -symmetric mode activated by loss of translational symmetry due to defects. It was first attributed to an A_{1g} breathing mode at K, activated by the relaxation of the Raman fundamental selection rule $q = 0$ [164]. It was further linked to maxima in the vibrational density of states in graphite at M and K points [165, 166]. But it does not explain: (a) dispersion of D position with photon energy [167, 168], (b) observed D peak overtone at $\sim 2710\text{ cm}^{-1}$, even in the case when no D peak is present and (c) Dispersive behavior of $I(D)/I(G)$ ratio

[167, 168]. Ley et. al. empirically proposed that the D peak arises as resonant Raman coupling in which there is a strong enhancement of the Raman cross-section of a phonon of wave vector q , when it equals the wavevector K of the electronic transition excited by the incident photon ($K = q$ “quasi-selection rule”). The physical reason for quasi-selection rule was unclear and did not explain why amongst all phonons satisfying this condition only those on one particular branch are seen. Through calculations, Thomson and Reich identified double resonance process at k-point in Graphite as mechanism behind the D-band [169].

The D-band frequency is highly dispersive and increases with increasing laser excitation energy by $\sim 50 \text{ cm}^{-1} / \text{eV}$ [170]. The dispersive nature of D-band [171] as well as discrepancy between the D-band stokes and anti-stokes frequencies is explained in terms of double resonance process [172]. The double resonance effect occurs when both the scattered intermediate state and the initial (or final) state are actual electronic states [169, 173].

For the SWCNT's, the double resonant process results in two different phonon frequencies suggesting that the observed D-band spectra should be fitted by two Lorentzian bands [171]. Fine structure of D-band band has been extensively studied by Kuzmany group [174]. They have shown that D-band of SWCNT is characterized by a sharp band of comparatively strong intensity and more than one broad sub-band of lower intensity. The high intensity band originates from ‘triple resonance effect’. Dresselhaus et al showed that the intensity of the D-band is proportional to the density of defects in CNTs [175]. However, the nature of defects or disorder responsible for D-band and its excitation energy dependence is not understood clearly.

(iv) Defect Induced Changes in the G-band: The graphitic G-band in CNTs splits into two peaks structure G^- (1570 cm^{-1}) and G^+ bands (1590 cm^{-1}). Charge transfer during functionalization leads to shift in the tangential vibrational modes (G^+ band). Substitution of electron donors (like K, Rb) leads to down shift while the electron acceptors leads to up shift (Like Br_2) of the G-band [176]. G^- band frequency is sensitive to the nature of the SWCNTs, whether it is metallic (Breit-Wigner-Fano (BWF) lineshape) or, semiconducting (Lorentzian lineshape). Charge transfer to SWCNTs reflects in the intensity (increase or decrease) of the BWF feature [177]. Relative intensity of BWF line (1550 cm^{-1}) to the (1570 cm^{-1}) line has been used as a quantitative tool to monitor defect induced transitions from metallic to semi-conducting behavior [178]. Similar to the other crystalline materials, disorder induced broadening of these G^- and G^+ modes are expected. The broadening of G-band has been observed by Doorn and group in presence of IMJs [178]. Interestingly, we have found a new feature at $\sim 1620\text{ cm}^{-1}$ (D'-band) in case of MWCNTs that has been attributed to structural defects.

(v) Raman Modes between $1600\text{-}2400\text{ cm}^{-1}$: Overtone, combination or Defects induced modes?: Dispersion effects in the solid materials makes the overtone and combination modes broad and very weak. In case of SWCNTs, they are observed due to combined effect of double resonance process and the presence of van Hove singularity states. Consensus about the origin of Raman features in the range $1600\text{-}2400\text{ cm}^{-1}$ is lacking in the literature. Similar to the controversy over IFM modes, a few groups have reported their origin as the combination modes while other as defect induced modes.

Basically in this region, peaks have been observed at 1750 cm^{-1} (known as M mode) and $\sim 1950\text{ cm}^{-1}$ (iTOLA mode, i.e combination of iTOLA and LA mode). Analysis of

the 1750 cm^{-1} mode indicates that it has a two peak structure, M^- and M^+ components. Lower frequency component (M^-) mode is weakly dispersive, while M^+ do not respond to the change in the laser energy. These M modes are attributed to the overtones of infrared active (oTO) modes, generally observed at $\sim 867\text{ cm}^{-1}$ in graphite. The M^+ features is though to arise from an intravalley $q=0$ scattering process while M^- from intervalley $q=2k$ process. Opposite to the M modes iTOLA modes are highly dispersive and upshifts from 1864 cm^{-1} to 2000 cm^{-1} as the E_L varies from 1.58 to 2.71 eV [179]. This mode is assigned to combination of two intravalley phonons, one from the in-plane transverse optical branch (iTOL) and second from the longitudinal acoustic branch (LA). LA phonon is accounts for the large dispersion of iTOLA observed experimentally [179].

Contrary to the explanation regarding the origin of these modes ($1600\text{--}2400\text{ cm}^{-1}$) from combination modes, a number of theoretical and experimental findings claim their origin from structural defects (pentagon rings) or, encapsulated linear carbon chains like polyyynes. Calculation of Raman peaks of IMJs in CNTs using non-reactive bond polarizability model has shown that a number of peaks lies in this range, characteristic of pentagon defects. It was shown that frequency of the SW defects lie in the range $1820\text{--}1962\text{ cm}^{-1}$ depending upon the local curvature of the tube [108]. Similarly, it has been shown that divacancy-induced Raman peaks lie out of the SWCNT's G band and their positions depends on the tube's chirality and divacancy's symmetry (1760 cm^{-1} for asym-divacancy and 1748 cm^{-1} for sym-divacancy for zigzag SWCNTs and reverse for armchair CNTs) [142]. Peak at 1962 cm^{-1} has been shown as the finger print of SW Defects through simulations [153]. A broad peak observed at 1697 cm^{-1} has been accounted for pentagon defects [163]. Apart from these modes, divacancies give rise to new RBM modes, since C-atoms around the divancy move in a reverse direction with different displacement from

others. These features may also arise from the sp hybridized systems encapsulated in the CNTs. Theoretically Raman peaks have been predicted in this region due to linear carbon chains [180]. Pimenta et. al. have observed peaks at 2066 cm^{-1} for $\text{C}_{10}\text{H}_2@\text{SWCNTs}$ and at 2020 and 2050 cm^{-1} for $\text{C}_{12}\text{H}_2@\text{SWCNTs}$, known as P-bands (between $2000\text{-}2100\text{ cm}^{-1}$) [181]. Strong bands has been observed from carbyne molecule (linear carbon chain from pure sp hybridized molecules) encapsulate in the MWCNTs ($\sim 1850\text{-}1860$ (strong) and $1780\text{-}1830$ (weak)), Known as L-bands. Presence of a different linear carbon chain structure Cumulenes may also give rise to peaks in the $1900\text{-}2300\text{ cm}^{-1}$ spectral range, Known as C-bands. C-band shows two peak Gaussian structures at about 2100 cm^{-1} (C1 band, due to Polyynes ($-\text{C}\equiv\text{C}-)_n$) and at 1980 cm^{-1} (C2 band, due to Cumulenes ($=\text{C}=\text{C}=)_n$) [182]. Similarly a peak at $\sim 1850\text{ cm}^{-1}$ has been observed due to coalescence induced short and odd carbon chains formed after heat treatment of DWCNTs [180].

(vi) **Sensitivity of G' and 2G Modes to Structural Defects:** G' band is the second order harmonic of disorder induced D-band, usually occurring at $\sim 2\omega_D$. Since a phonon at the K-points can choose momentum arbitrarily and such phonons have singularity at $q=0$ and $q=2k$ giving rise to 2450 cm^{-1} peak (non-dispersive) and G' peak (dispersive peak) [183]. Similar to the D-band, G' band is also sensitive to the diameter and chirality of CNTs. Since the G' band is less sensitive to the structural defects, the ratio of intensity $I_{G'}/I_D$ is usually taken as the measure of defect content in the CNTs. In defective CNTs, a new peak has been observed at $\sim 2591\text{ cm}^{-1}$ along with the G'-band [184]. The second order peak of the characteristic G band has been experimentally observed at 3182 cm^{-1} , known as 2G modes. In contrast to the G band, second order G' peaks are thought to be

insensitive to the structural defects. There have been instances when the intensity ratio of 2G band to the D band has been taken as a parameter for defect estimation.

(b) Photoluminescence (PL) spectroscopy

Photoluminescence is an important technique to study the band structure and defects in solids. Depending upon the chirality, SWCNTs show fluorescence usually in the NIR region (900-1600 nm) [26, 185]. Contrary to the expected NIR luminescence from CNTs, a number of authors have experimentally observed visible fluorescence from as-grown and chemically processed CNTs, a brief summary of which is presented in Table 1–2. It is interesting to observe visible emission from materials which possess a band gap in the near-infrared region. Strong visible photoluminescence (PL) has been observed from CNTs after functionalization with amine [186] and propionylethylenimine-co-ethylenimine (PPEI-EI) polymers [187]. Visible PL has been observed from SWCNTs grown from microchannels of Zeolite [188, 189], Ruthenium doped MWCNTs [190], from metal-semiconductor transition induced in composites of CNTs with noble metal nanoparticles [191]. Bright visible fluorescence is highly desirable to use CNTs as a biological labeling material [192]. There has been a number of attempts to tune the fluorescence of CNTs in the visible region by chemical functionalization [186, 193] polymer wrapping [187, 194] etc. In this study we have explored the origin of visible photoluminescence from structural defects. Further, we have attempted to modify the CNTs by using laser irradiation and chemical functionalization and have explored the role of defects in the visible photoluminescence observed from CNTs and details are presented in Chapter-4.

Table 1-2: Summary of literature reports about Visible Photoluminescence from CNTs.

Sl. No.	Emission (nm)	Excitation (nm)	SW /MW	Origin	References
[1]	400-800	400-600	SW, MW	Polymer bound CNTs, Strong λ_{ex} dependent PL	Y. Sung, 2000 [187]
[2]	565, 610	500	SW	Aniline dissolved CNTs. Trapping of excitation energy by defects.	Y. Sun, 2001 [186]
[3]	515	449	MW	Ruthenium doped	D. Jacques, 2001 [190]
[4]	620, 750	488	SW	Zeolite crystals	Z. K. Tang, 2002 [188]
[5]	730	488	SW	CNTs in Zeolite template	Z. K. Tang, 2004 [189]
[6]	~525	450 (400-600)	SW	Functionalized CNTs, Trapping of excitation energy at defect sites	Y. Sun, 2005 [186]
[7]	980, 1050, 1150, 1235	660	SW	Ultraviolet illumination	B. Nalini, 2006 [152]
[8]	529 (SW) 532 (MW), 604	488	SW, MW	Defects	D. Singh, 2007 [195]
[9]	600, 650 and ~670 nm	514.5	SW	Interaction b/w nanotubes and NPs leads Semiconducting to metallic transition	T. Pradeep, 2007 [191]
[10]	Visible range	-	SW	Diameter dependent colours of CNTs	H. Kataura, 2009 [196]

Electron Paramagnetic Resonance (EPR) spectroscopy

EPR is a very sensitive probe for electronic structure in materials and can provide information on the chemical environment of the unpaired electrons. It monitors effective g-value for both conduction and localized (defect) electron states in materials in which unpaired electrons exists. It has been widely used for studying paramagnetic defects in various allotropes of carbon like amorphous carbon [197], graphite [198], diamond [199] and CNTs [200]. EPR has been used to study the modification of graphite upon proton

irradiation [198] and MWCNTs upon electron irradiation [201]. In one of the earliest reports on defect studies, Tanigaki and group had monitored the effect of annealing and structural defects in CNTs using EPR spectroscopy [202]. The position of the Fermi level as monitored by the 'g' factor was found to be very sensitive to the presence of defects in the rolled graphene plane [203]. EPR measurements on MWCNTs samples had provided experimental evidence of both the Aharonov-Bohm effect pertinent to the nanotube geometry as well as characteristic typical of quasi-2D graphitic structures most appropriate for large diameter nanotubes [203]. The relative percentage of scrolled to concentric feature for MWCNTs can be calculated using EPR [204]. EPR has been used to monitor defect induced adsorption of hydrogen on CNTs [205]. An exchange interaction between the conduction electrons and the localized spins originating from the impurities or from irradiation shows modification in the EPR line shape [206]. Conduction electron spin resonance (CESR) can probe the doping dependence of the electronic structure. The temperature independent Pauli paramagnetism of conduction electrons is a signature of metallicity, and susceptibility χ_p is a direct measure of the density of states at the Fermi energy $N(E_F)$ [207].

EPR signals from CNTs mainly originate from localized spins due to impurities, and for conduction electrons originating from metallic or semiconducting nanotubes with a small gap [208, 209]. In addition to CESR from metallic and graphitic particles [210], a ferromagnetic resonance (FM) may also be present from residual metallic catalyst particle [207, 211]. EPR spectra of CNTs at room temperature consist of usually three overlapping lines. A wide symmetric line located at lower resonant fields and typically having a line width of $\sim 10^2$ - 10^3 Gauss (FMR peak), another broad asymmetric line closer to the free electron g-value (but not at $g = 2.0023$) known as CESR peak and the third sharp line at

higher resonance fields called as defect peak [208, 209]. The broad symmetric line arises due to the catalyst metallic residues [212]. Broad symmetric line is located at lower resonance field because of combined action of external (H_R) and local magnetic fields (H_M) on the uncoupled electron spin [213]

$$h\nu = g\beta(H_R + H_M) \quad (1-1)$$

CESR peaks are not located at the free electron g value due to the incomplete quenching of the angular momentum. The deviation of the resonance line position is controlled by the spin orbit coupling λ , by the energy difference ΔE between the corresponding electronic energy levels belonging to the same wave vector [214].

$$g = g_{th} + \frac{\lambda}{\Delta E} \quad (1-2)$$

The asymmetry α is related to the spin diffusion time and the spin-spin relaxation time given as

$$\alpha = T_D / T_2, \quad (1-3)$$

where, T_D is the spin diffusion time, i.e, time it takes to diffuse through the skin depth and T_2 is the spin-spin relaxation time. A narrow line arises from the paramagnetic impurities and structural defects. Even a very small amount of residual catalyst metal relaxes the conduction electrons very effectively due to their long mean free path and diffusion length, enveloping the characteristic lines under broad FMR peak, while the higher dimensionality of MWCNTs results into higher probability of CESR observation [200]. The position of the Fermi level as monitored by the g factor has been found to be very sensitive to the presence of defects in the rolled graphene plane [200]. Defects are expected to modify the local Fermi surface and vary the density of states at the Fermi

level, as well as the g factor and the spin dynamics [200]. Every phenomenon that involves electrons of the Fermi surface should thus be sensitive to the geometrical properties of these nanostructures. This inspired us to probe the curvature and strain effects on the EPR spectral line profile, giving a spectroscopic method of diameter estimation of MWCNTs, presented in Chapter-5.

Conduction electron spin resonance (CESR) can also be used to probe the doping dependence of electronic structure. The temperature independent Pauli paramagnetism of conduction electrons is a signature of metallicity and χ_p is a direct measure of the density of states at the Fermi energy $N(E_F)$ [207]. Also, CESR shows line width proportional to the variation in the temperature and doping. Opposite to this, temperature independent contribution χ_c (Curie type term) to the susceptibility gives estimate of the localized defects.

Single vacancy may possess an uncoupled electronic spin and a narrow absorption line is expected near $g = 2.000$. Di-vacancies can be characterized with an effective electronic spin $S = 1$ or $S = 0$ both. ESR fingerprint of di-vacancies corresponding $S = 1$ is expected at $g = 4.0$, while $S = 0$ would be ESR silent [94].

We have used EPR spectroscopy to explore the diameter dependent spectral line shape profiles for MWCNTs of wide diameter range. Further, results of structural defects monitored through EPR absorption peak profiles for SWCNTs and MWCNTs have been presented in Chapter-5. Ion-irradiation induced defect creation and structural improvement have been monitored through EPR spectroscopy and presented in Chapter-6.

1.4 Defect Engineering Using Ion Irradiation

Properties of CNTs are highly sensitive to atomic arrangements of carbon in nanotubes. Defects in tube lattice can alter original properties with a degradation or, improvement of specific chemical or, Physical characteristics. Controlled introduction of defects or removal can be performed using ion-irradiation. Capability of irradiation to knock out atoms from CNTs makes it a potential tool for nano-engineering of nanotubular structures. Ion implantation has been used successfully for years to tune the properties of carbon based materials like Diamond, Graphite and carbon fibers [215]. Recently huge interest has been generated in controlled structural modification of CNTs for nano-engineering with the prediction of single molecular electronic and optoelectronic devices based on intermolecular junctions [80], possibility of band gap tunability (from metallic to semiconducting) [216], tunability of conductivity [93] and observations of enhanced properties with structural defects. Structural defects like vacancies have been found to improve greatly the gas sensing properties of CNTs [217].

Harnessing of irradiation as a tool for controlled modification of material properties at the nanoscale requires a proper understanding of the microscopic picture of defect production and annealing in nanomaterial targets. CNTs are expected to respond differently to different ion irradiation as compared to bulk graphite, since: (a) larger surface area results in higher sputtering yield (b) high surface to volume ratio shows enhanced annealing and (c) only a small portion of the energy carried by ions is deposited on the surface.

An energetic particle after penetration in the material releases its energy through two mechanisms (a) Electronic energy loss and (b) Nuclear energy loss. At low eV or KeV) incoming ions are quickly neutralized by capturing electrons from the target.

Nuclear energy loss arises from ballistic collisions between ions leading to transfer of ion energy to the target resulting in the ballistic motion of the target ions [218]. The electronic stopping is governed by the inelastic collisions between the moving ion and the electrons in the target. A number of physical processes contribute to the electronic stopping: ionization of the target atoms, excitation of electrons in the conduction band, collective electronic excitations such as plasmons, etc.

Recent theoretical as well as experimental results on the irradiation of CNTs with energetic particles have revealed about coalescence and welding of nanotubes under electron irradiation, ion irradiation-induced changes in electrical coupling between nanotubes, surface reconstructions, modification of mechanical properties, Metallic to semiconductor transition in SWCNTs and doping. Ion-irradiation has been used to tune the conductance of SWCNTs [93]. Recent review articles summarized about the possibility of engineering CNTs using electron and ion-beams [83, 219, 220]. While majority of the works are based on theoretical predictions, some experimental studies have also been reported already. Summary of the important experimental findings reported in literature about effect of ion-irradiation on CNTs is presented in Table 1-3, while the theoretical predictions about structural modification upon ion-irradiation are summarized in Table 1-4.

When a charged particle bombards CNT, due to the high thermal and electrical conductivity of graphene shells, the dominant mechanism for defect creation is the knock on atomic displacements due to kinetic energy transfer [219]. The irradiation induced structural transformations in CNT are due to defects mainly in the form of vacancies and interstitials. The threshold energy (E_d) required to produce a Frenkel pair in graphene system is estimated to be 20 eV [98]. Different kind of metastable defects can be created

by irradiation. In case of graphite, interstitial-vacancy pair is well-known paramagnetic defects of neutron-irradiated graphite. Trapping of electrons by vacancies can create extrinsic holes in the Π -band. Coalescence of vacancies can also occur and form extended defects. Natural bond rotation defects may also be present which are expected to modify the local density of states. Nitrogen doping of CNTs has been achieved by 3 keV N^+ ion irradiation [225].

Along with ion-irradiation induced structural changes and defect engineering, it has helped to understand origin of new Raman active modes and spectroscopic properties of defects. Modification of Raman vibrational modes of SWCNTs have been observed under electron irradiation [137]. Modification in the intermediate frequency modes (IFMs) of SWCNTs in Raman spectra has been observed as a result of Ar^+ ion irradiation [145]. Some of the literatures are focused on spectroscopic studies of structural defects created by ion-irradiation on CNTs [137, 138, 236]. Similarly EPR spectroscopy has been used to study paramagnetically active defects produced upon ion irradiation. It has excellent sensitivity and resolution in detecting radiation induced modifications such as vacancies, di-vacancies (with $S = 1$), dangling bonds, conducting electrons, and magnetic nanophase etc. ESR has been used to study the ion irradiation induced structural modifications of SWCNTs [237] and MWCNTs [201]. In spite of a number of ion-irradiation experiments, consensus about the energy required for knock on of carbon atoms from CNTs, parameters and nature of ion required for controlled introduction of a particular kind of defect and possibility of structural improvement upon low energy ion irradiation lacks in literature. There are reports which claim 120 kV as the knock-on threshold of carbon [97, 83, 238] while, others have observed formation of pillbox like compartments in MWCNTs upon 50 keV Ga^+ ion irradiation. There are some theoretical attempts to explore the stopping of

Table 1-3: Summary of reported effects (experimental) of ion-irradiation on CNTs

Sl. No.	Ions-Irradiated	Energy	Sample	Effects observed	Reference
[1]	Electron	--	SWCNTs	Diameter shrinking through surface reconstructions.	Ajayan, 1998 [97]
[2]	Ga ⁺	30 and 50 keV	MWCNTs	(a) With 50 keV ions at $\sim 10^{13}$ ions/cm ² inner layers organize into ordered pillbox like ~ 5 nm diameter compartments of varying lengths b/w 2-20 nm. (h) Higher dose 10^{15} ions/cm ² results into formation of amorphous rod.	G. Ramanath, 2003 [221]
[3]	Ar ⁺	30 keV	MWCNTs	Hillocklike protrusions on nanotube walls	L. P. Biró, 2005 [222]
[4]	Ar ⁺	120 eV	SWCNTs	(a) Change in resistance: Localization length decreases from 216 nm to 61 nm upon irradiation (b) Tuning of conductance in SWCNTs by ion irradiation demonstrated.	F. Flores, 2005 [93]
[5]	Photon and electron	20 eV-Photon and 20, 1 keV-Electron	SWCNTs	(a) Thinner SWCNTs are more easily damaged. (b) Curvature induced strain energy is important for formation of defects.	Y. Kobayashi, 2006 [223]
[6]	Ar ⁺	3 keV	SWCNTs	(a) At low dose: formation of localized defect states. (b) For large doses: sp ³ carbon appears due to amorphisation.	M. R. C. Hunt, 2007 [224]
[7]	N ⁺	3 keV	SWCNTs	Nitrogen atom can bind to C in sp ³ configuration / knock out C and doped in CNT forming sp ² bond with three C neighbours, or with two carbon atoms in a defective pyridine-like structure.	L. Papagno, 2007 [225]
[8]	Ar ⁺ and N ⁺	30 keV	SWCNTs	Ion-irradiation increases localization of charge leading to reduction in conductance.	S. Roth, 2008 [226]
[9]	N ⁺ and C ⁴⁺	30 keV N ⁺ and 23 MeV C ⁴⁺	SWCNTs	23 MeV C ⁴⁺ ion creates less defect.	S. Roth, 2009 [227]

Table 1-4: Important theoretical findings on the effect of ion-irradiation in CNTs

Sl. No.	Ions-Irradiated	Energy	Sample	Important predictions	Reference
[1]	Ar ⁺	50-3000 eV	SWCNTs	(a) Maximum damage production for 600 eV.(b) Most common defects are vacancies.	J. Keinonen (2001)[228]
[2]	Ar ⁺	Wide energy range	SWCNTs	Stability of irradiation-induced point defects (a) With low temp irradiation, single vacancies and the 5-6 defects are likely stable on macroscopically long time scales and hence they might be experimentally found.	K. Nordlund, 2002 [229]
[3]	Ar ⁺	100 eV- 2 keV	SWCNTs	Production of defects in supported CNTs :(a) Damage is higher for heavy atom substrate because sputtered atoms produce extra damage. (b) Most proficilic defects are single and multi-vacancies.	J. Keinonen, 2002 [230]
[4]	He, C, Ne, Si, Ar, Kr and Xe	50-500 eV	SWCNTs	(a) Most prolific defects are vacancies. (b) Higher damage in case of heavy ions due to higher values of the cross-section for defect production in a SWCNTs.	J. Koinonen, 2003 [231]
[5]	All inert gas ions	0 – 3 keV	MWCNTs	Irradiation gives rise to formation of vacancies on shells of MWCNTs and intershell links as a result of saturation of dangling bonds at carbon interstitials and atoms nearby the vacancies.	J. Keinonen, 2004 [232]
[6]	Ar ⁺	0-10 keV	SWCNTs	Relative abundance ratio of single and double vacancies has minimum at 0.5 KeV and saturates towards 3 at high energies.	K. Nordlund, 2007 [233]
[7]	C ⁺ and Ar ⁺	25 eV - 1 keV	SWCNTs	(a) Different stability of small radius CNTs under C ion irradiation is due to high self-healing capacity and high curved CNT surface. (b) Different stability variation with CNT diameter under C and Ar ion irradiations due to difference b/w the interaction properties of C and Ar ions. (c) Zigzag CNT is more stable than armchair.	P. Huai 2009 [234]
[8]	C, Ar, B, N, Ne and Si	25 eV - 1 keV	SWCNTs	(a) Bonding action or the chemical effect of the ions (such as C, B, N and Si) enhances their damage capabilities. (b) Bonding effect of ions increases their implantation probabilities into CNT compared to non-bonding ions.	P. Huai, 2009 [235]

energetic ions in CNTs [231, 232], and effect of tube diameter and chirality on the stability of SWCNTs under irradiation [234, 239], but hardly any experimental study exists giving comparison of effect of nature of ions and energy, nature of nanotube whether SWCNTs or MWCNTs etc under ion irradiation. Stability of ion-irradiation produced defects has become a matter of concern [229], because experiments have shown that single vacancies or, divancies created upon irradiation transforms quickly to other kind of defects [97]. Recently few serious attempts in this direction have been made in-situ using Scanning transmission electron microscopy [240] and focused electron beam irradiation [241, 242]. In this thesis, we have studied the effect of H^+ , N^+ , C^+ and Ar^+ ions at low energies (30 keV and 80 keV) and various fluence level for structural improvement and defect introduction in SWCNTs and MWCNTs, as presented in Chapter-6. Further we have obtained spectroscopic signature of defects through Raman spectroscopy and EPR spectroscopy in irradiated CNTs. We have demonstrated to fabricate novel carbon based nanostructure like carbon nanosprings with ion irradiation. These carbon nanostructures would be very useful in future for fabrication of carbon based nano-electromechanical systems.

1.5 Defect Enhanced Properties

Structural defects are not always undesirable. In some cases, structural defects in CNTs have been found to play a critical role in improving the characteristic properties required for future potential applications. Defects have shown a number of technological applications such as potential to fabricate single molecular devices through IMJs (inter molecular junctions) and a number of defect enhanced properties. In the past few years, many defect mediated and defect enhanced properties of CNTs has been observed.

Although a huge amount of theoretical work has been carried out already to understand the energetics and possible origin of various kinds of structural defects in CNTs, very little is known experimentally about behavior/characteristics and influence on device performance. There is an ongoing effort to understand the nature and possibility of defect engineering of CNTs through various processes like chemical functionalization, laser irradiation and ion-beam modification. Many attempts have been made to synthesize defect free CNTs or, nanotubes rich in a particular kind of defect. Understanding and control of defects, including dopants in low dimensional systems, especially CNTs hold great promise for CNT based engineered materials and nanoscale devices.

Stone-Wales defects have been found to reduce CNT's emission current, while vacancy-related defects give rise to enhanced current [105]. A structurally stable pentagon-octagon-pentagon topological defect produced by the divacancy gives rise to an unoccupied localized state in the band gap. [92]. Calculations have shown that band rotation defects closes the gap in large-gap nanotubes, open the gap in small-gap nanotubes, and increase the density of states in metallic nanotubes [36]. In case of MWCNTs, cross-shell bridging via sp^3 bond formation upon ozone exposure leads to three fold increase in CNT conductivity and 50 % decrease in carrier transport activation energy [133]. They have further shown the possibility of tailoring structure and electrical properties of CNTs using KeV ions [221]. Negative differential resistance has been observed due to H_2 and N_2 plasma induced defect induced sharp electronic states in the SWCNT band gap created at the defect sites [243]. Recently possibility of tuning of conductance of SWCNTs by Ar^+ -ion-irradiation induced defects (particularly divacancies) has been demonstrated in Anderson localization regime. [93] Defect enhanced photoconductivity has been observed in case of MWCNTs. [39] By selective removal of

various layers of a large diameter MWCNTs, band gap tuning has been achieved on chip for fabrication of infrared sensors [244]. Structural defects enhances the loading of metal nanoparticles like Pt, TiO₂ etc on CNTs [245]. Using ion-irradiation the possibility of tuning electrochemical properties of CNTs has been demonstrated for chemical sensors and capacitors [246]. In spite of immense potential of structural defects of in CNTs, the signature of various kinds of defects and their methods of characterization is not established. Further, We have explored in detail about the nature of interaction of well known fluorophores with CNTs containing defects through photoluminescence and adsorption studies. We discovered defect enhanced efficient photoluminescence quenching of CNTs [247]. A detailed discussion on the role of structural defects towards photoluminescence quenching has been presented in Chapter-7.

1.6 Motivation and Focus of the Present Work

Like other nanostructured materials, the properties of CNTs are greatly influenced by defects present in the as-grown or processed CNTs. Review of literature on structural and defect related properties of CNTs shows that there are many unresolved issues such as diameter dependent properties of MWCNTs, nondestructive evaluation of defects CNTs, role of structural defects on the structure and oxidative stability of CNTs, controlled introduction of defects in CNTs by ion irradiation, potential applications of defects in CNTs etc. During the growth of CNTs, the number and nature of defects is decided by various factors like growth temperature, carbon source feeding rate, carrier gas flow rate, nature of carbon source being used etc. The identification of various kinds of defects and their methods of characterization is not well established for SWCNTs and MWCNTs using traditional methods like Raman spectroscopy, electron spin resonance (ESR),

photoluminescence (PL) spectroscopy etc. Use of the sophisticated techniques like ultrahigh vacuum scanning tunneling microscopy (UHV-STM), high resolution transmission microscopy (HRTEM) for monitoring structural defects in CNTs are often time consuming and can not be used for the bulk characterization. In the literature, UHV-STM and aberration corrected low voltage HRTEM have been used recently to obtain evidence of defects and defect dynamics in nanotubes. However, nondestructive techniques like Raman spectroscopy, PL spectroscopy and ESR spectroscopy are not explored in the literature to study the presence and influence of structural defects in the structural and optical properties of CNTs.

This thesis focuses on the spectroscopic studies of diameter dependent structural properties, defects and defect engineering in SWCNTs and MWCNTs. Defect engineering of CNTs through controlled introduction of defects by low energy ion irradiation at different doses and defect removal by vacuum annealing are achieved in this study. Further, application of defects in CNTs as an efficient quencher of fluorescence from several common fluorescent dyes is demonstrated. A large number of samples of SWCNTs and MWCNTs of very wide range of diameters (5 nm-100 nm) grown by CVD method have been studied systematically. Some samples were grown in-house with a home-built CVD setup and some of the samples studied were procured commercially. The pristine and processed (e.g. vacuum annealed, laser annealed and ion irradiated) nanotubes were studied systematically to understand the spectroscopic signature of various structural defects and the influence of defects, interlayer interactions, strain/curvature in the microstructure and optical properties of the nanotubes. Microstructure of the nanotubes is investigated by powder X-ray diffraction (XRD), HRTEM, scanning electron microscopy (SEM) and atomic force microscopy (AFM), while the thermal stability and oxidation

kinetics of the nanotubes as a function of nanotube diameter are studied by thermogravimetry analysis (TGA). Role of defects, strain and possible influence of metal catalysts in the thermal stability is studied in details. Electron paramagnetic resonance (EPR) studies are performed to study paramagnetic defects in the as-grown and processed nanotubes. Raman spectroscopy is extensively used in this work to obtain spectroscopic fingerprint of different types of defects in CNTs, for the first time. Optical absorption and photoluminescence studies enabled us to identify defect related emission bands in CNTs. Covalent functionalization of the nanotubes yields absorption and emission in the visible range of wavelength, as compared to the near-infrared emission expected from defect-free nanotubes. Controlled introduction of defects and dynamic annealing of defects for improvement in the structure of the nanotubes are studied by low energy ion-irradiations at various doses with different ions. Defect mediated efficient quenching of fluorescence from several common dyes using CNTs is demonstrated. This will find important applications in biosensing and imaging.

Several significant new results have been reported in this thesis through different chapters of the thesis. Firstly, diameter dependence of interlayer separation, strain/curvature effects have been probed systematically by spectroscopic studies and results are corroborated by HRTEM analysis. Diameter dependence of the oxidation kinetics of as-grown and vacuum annealed nanotubes have been observed and explained on the basis of defects and strain in the nanotubes. Secondly, Raman active modes due to structural defect in the pristine and processed nanotubes are probed by Raman studies. Several new Raman active modes due to modification of the phonon density of states induced by defects are observed and are thought to be fingerprints of well known structural defects such as pentagon/heptagon rings, Stones-Wales defects in nanotube

walls. Origin of various IFM modes are studied in details and novel results are found and reported. Thirdly, defect related visible photoluminescence emission from as-grown and functionalized CNTs have been observed for the first time and the role of defects is elucidated through excitation and emission spectroscopy studies. Further, defect engineering of CNTs through vacuum annealing and low energy ion irradiation at various doses has been demonstrated. In particular, defect removal by thermal annealing, controlled introduction of defects by low dose ion-irradiation, irradiation induced reconstruction and structural improvement of nanotubes, and evolution of nanotube structure to novel carbon nanospring like structures with higher ion doses have been presented in this thesis. On the basis of these studies, difference in mechanism of defect formation in single walled and multiwalled nanotubes is elucidated. Finally, the application of surface defects on the efficient quenching of fluorescence by SWCNTs and MWCNTs for common fluorophores has been demonstrated. Mechanism of quenching is studied through quantitative analysis of absorption and emission spectra.

The work has been presented in *eight chapters*. The first two Chapters of the thesis provide introduction to defects in CNTs, review of literature, motivation for the present work and details of the experimental techniques developed in-house and used for the growth as well as characterization of defects in nanotubes. Chapters 3, 4, 5 discuss results of various microscopic and spectroscopic studies of diameter dependent properties and defects in the pristine and different processed nanotubes of wide range of diameters. In Chapter 6 and Chapter 7, different aspects of defect engineering in CNTs are presented. Finally, Chapter 8 summarizes salient conclusions of the work and presents an outlook on the further works.

Chapter -2

Experimental Details and Data Analysis

2.1 Introduction

In this chapter, we discuss a brief account of various experimental techniques used and the methodologies adopted to critically analyze the data presented in this thesis. It also includes details of the experimental setups designed and developed in-house for the present work. The critical role of spectroscopic line shape analysis for Raman spectra and EPR spectra in the study of defects in carbon nanotubes has been brought out. The suitability of different microscopic and spectroscopic techniques for understanding defects in CNTs has been discussed. Details of carbon nanotubes samples grown in our laboratory and commercially procured samples used in this study are presented in this chapter. Also the details of processing techniques and conditions used for controlled introduction and /or removal of structural defects in CNTs through chemical functionalization, high vacuum annealing, air annealing, laser annealing and ion-irradiation at various ion doses for different ions are presented in this chapter.

2.2 Characterization Techniques and Methods of Data Analysis

As discussed in Chapter-1, structural defect have immense potential to tune the band structure and characteristic properties of materials. Particularly, due to limited size of the nanomaterials, atomic scale defects are one of the most influential factors in determining their physical properties [248]. For a detailed understanding of the role and effects of various kinds of defects in CNTs, a number of analytical techniques ranging from conventional optical spectroscopy to advanced microscopic techniques such as high resolution transmission electron microscopy (HRTEM) have been used. It has remained a

challenge to identify the characteristic spectroscopic features of defects in CNTs through spectroscopic techniques. Imaging techniques are limited at the atomic size scale, and probing of limited volume of samples. In this chapter, we discuss on the use of various microscopic and spectroscopic techniques to identify the spectroscopic fingerprint of structural defects in CNTs. In the context of structure and defects in CNTs, principles of the different analytical techniques used in this dissertation are discussed briefly as follows.

2.2.1 Microscopic Techniques

Visual perception of topography of nanomaterials using light has been a challenging task due to diffraction limit imposed by Rayleigh criterion of resolution for visible wavelength spectrum range. There have been ongoing efforts to cross this barrier through a number of techniques like confocal microscopy, near field microscopy etc. Interestingly electron gives the path to access the morphological characterization of sub-micron structures over the visible photons. The de-Broglie wavelength associated with accelerated electrons is extremely small, and can be used to image sub-micron structures. Mathematically the de-Broglie wavelength of an electron accelerated by a potential V is expressed as,

$$\lambda = \frac{h}{\sqrt{2m_0E}} = \frac{h}{\sqrt{2m_0eV}} \quad (2-1)$$

Where, h ($= 6.626 \times 10^{-34}$ J-sec) is the planck's constant, m_0 ($=9.1 \times 10^{-31}$ Kg) rest mass of electron, e is electronic charge (1.6×10^{-19} Coulomb) and V is the accelerating voltage.

Typically for an electron accelerated with a potentials 10 KeV and 200 KeV, the associated de-Broglie wavelengths are 0.123 and 0.025 Å, respectively. These are the

typical voltage ranges used for scanning electron microscopy and transmission electron microscopy. Such small de-Broglie wavelength associated with accelerated electrons make it capable of morphological studies of sub-micron structures. Although these calculation shows that we can use electron microscopy to even image within atoms, but in practice maximum achievable resolution is 0.194 nm for point and 0.14 nm for lattice imaging (in a typical HRTEM machine). Such limitations arise due to energy distribution of emitted electrons and focusing limitation using electrostatic and magnetic lenses. Basically, there are two types of electron microscopes namely scanning electron microscope (SEM) and transmission electron microscope (TEM). They differ in terms of their working principle and energy range of electrons used. Increasing the acceleration further and further do not give more advantage in terms of resolution achieved, rather electrons having higher energy damages the specimen under view. Ongoing efforts to achieve higher and higher resolution has resulted into many new advanced version of these techniques like Field emission scanning electron microscopy (FE-SEM), Energy filtered TEM, Low voltage electron microscopy, aberration correction HRTEM and many more.

Electron microscopy is coupled with a number of techniques depending on the nature of interaction between material and energetic electrons. Energetic electron either gets scattered or gives rise to emission of secondary electrons or radiation in various frequency range. Scattered electron or emitted secondary electron carries morphological information, while the emitted radiation carried information regarding the nature and composition of material under examination. Fig. 2-1 shows various possible physical processes after interaction of an accelerated electron with specimen. Each process gives rise to a unique characterization technique like backscattered electron and secondary

electrons are used in SEM, while directly transmitted beam is used for TEM. Elastically scattered electrons are for creating “selected area diffraction (SAD)” pattern carrying

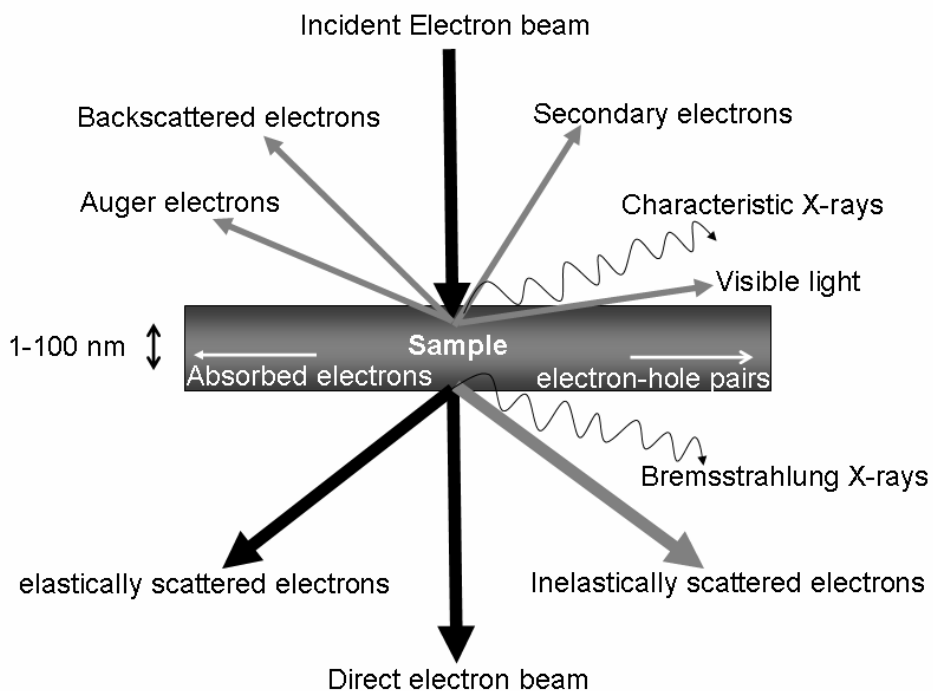


Figure 2-1: Interaction between accelerated electrons and sample leading to scattering, secondary electron emission and characteristic radiation.

information about the crystal structure and order of crystallinity of the material. Inelastically scattered electron is used in electron energy loss spectroscopy (EELS), which carries information regarding composition and electronic state. Inelastic collision gives rise to loss of energy of incident electrons, which excites many characteristic emissions like X-rays, visible photoluminescence, Auger electrons etc. Most commonly emitted X-rays are used to analyze composition and for mapping distribution of elements and it is called Energy dispersive X-ray spectroscopy (EDX). A brief account of these techniques and their use for studying CNTs are discussed below.

(a) Scanning Electron Microscopy (SEM)

SEM utilizes backscattered and secondary electrons emitted from the sample surface after interaction of accelerated electrons. Fig. 2-2 shows the photograph of the SEM used. A focused beam (very small diameter) of electron is incident on the sample surface and using electric and magnetic field it is rastered over the sample surface. Electrons after interacting with the constituting atoms of the sample, produces characteristic signals containing information about the sample's surface topography, composition and many other properties. Apart from electrons many other characteristic emission are obtained like X-rays, light (cathodoluminescence), specimen current and transmitted electrons. The signals result from interactions of the electron beam with atoms at or, near the surface of the sample. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. The magnification can be adjusted over a large range 10 X to 100 KX.



Figure 2-2: Photograph of the Scanning electron microscope used (LEO 1430 VP).

Back-scattered electrons (BSE) are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For SEM the sample should be conducting to avoid the accumulation of static charge over surface leading to decrease in signal to noise ratio. Non-conducting samples are analyzed after coating with very thin layer of gold/ silver to enhance the conductivity. Analysis of water containing samples is performed in variable pressure mode, to avoid breakage of vacuum. Depending upon the mechanism of emission of electron from the filament, thermionic or field emission, conventionally they are called as SEM or FE-SEM, respectively. FESEM offer better resolution of imaging than conventional SEM.

We have used a SEM (LEO 1430 VP) machine with spatial resolution of ~ 10 nm to image the quality of as-grown/procured and chemically functionalized CNT samples for this study.

(b) High Resolution Transmission Electron Microscopy (HRTEM)

Transmission electron microscopy (TEM) uses the transmitted electron beam for topological characterizations. It basically works on the principle of optical projectors; when an object is placed in front of a light source, its image is enlarged, a shadow is created on a screen placed at a very large distance behind. In TEM electron are usually accelerated at much higher voltage compared to the SEM to achieve higher resolution (usually, 80 -300 KeV). In TEM, usually the optics of the electron microscope is adjusted to image the intensity electrons emerging from the sample. Variation in the intensity of electron diffraction across a thin specimen known as “diffraction contrast” is used for

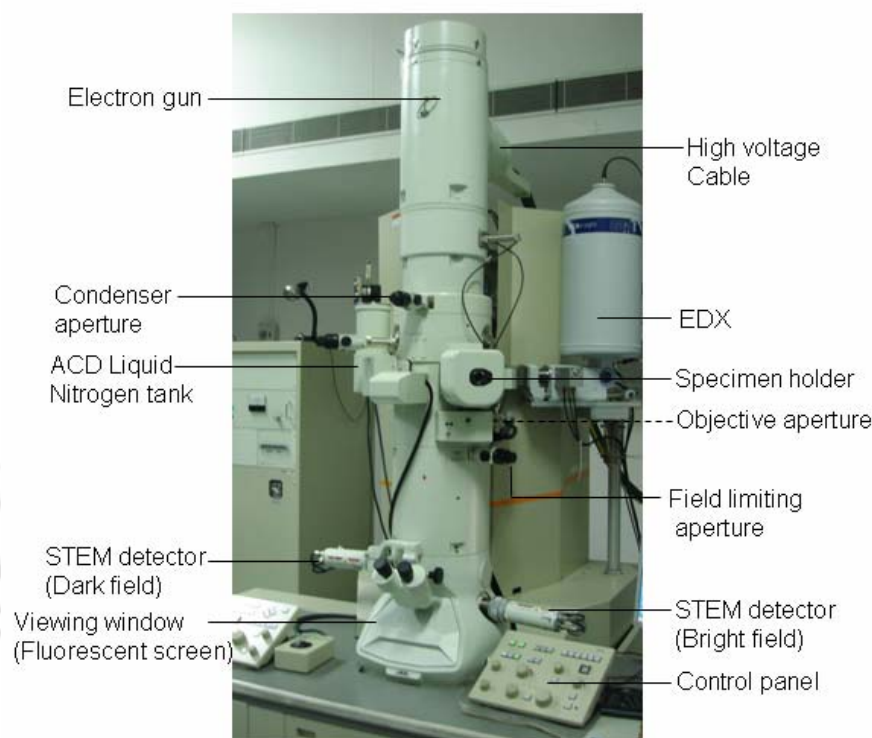


Figure 2-3: Image of High resolution transmission electron microscope (JEOL-2100 F) used for the present study. Names of important components are indicated against them using line.

making images of defects such as dislocations, interfaces and presence of secondary phase of materials. In a high resolution TEM, the phase of the diffracted electron wave is preserved and interferes constructively or, destructively with the phase of the transmitted wave. Since we can not measure the phase of the transmitted wave, instead of it we measure the amplitude of the resulting interference. The phase of the electron wave still carries the information about the specimen and generates the contrast in the image (interference amplitude image) with the assumption that thin samples slightly affects the amplitude variations under weak phase object approximation. This technique of “phase contrast imaging is used to form images of columns of atoms. High energy electrons cause’s electronic excitations of sample giving rise to characteristic X-rays and energy

loss of transmitted electrons. Using these, two types of spectrometries are performed: energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). Electron diffraction techniques have been used for the determination of chiral indices (n,m) of carbon nanotubes [249]. Wang and Hui have successfully reviewed the topic of electron microscopy and electron diffraction of nanotubes [250].

Fig. 2-3 shows an image of the HRTEM (JEOL-2100 F) used for the present study. It consists of an electron source (electron gun), Condenser lens aperture assembly (to control illumination), Sample specimen holder with goniometer (for positioning and manipulation during experiment), Objective lens (to control angle of the beam scattering caused by specimen) Objective aperture, Selected area diffraction (SAD) aperture and projector lens (for magnification) and CCD (for acquiring image). It is attached with an EDX spectrometer (elemental detection and quantification), STEM detector (for bright and dark field imaging) and EELS. We used thermionic electron emitted from Lanthanum hexaboride (LaB_6) crystals. SF_6 gas is used as dielectric to isolate the interference from column accelerating voltage and also to avoid voltage coupling to the column bar. A high vacuum level is maintained using combination of rotary pump, diffusion pump and sputter ion pump. A liquid nitrogen trap is maintained near the sample insertion point to trap desorption of molecules from the sample after electron strike, capable of disturbing the vacuum levels in the column. Fig. 2-4 shows the image of the specimen holder. It holds sample of 3 μm sizes and thickness of few microns only. It has arrangement for Z-tilting of the sample.

The sample for TEM measurement is prepared over a ~ 3 mm circular Cu-grid (disk) of thickness few microns containing few hundred hollow meshes of one micron square area. These grids (Pacific Grid, USA) are coated with very thin film of amorphous

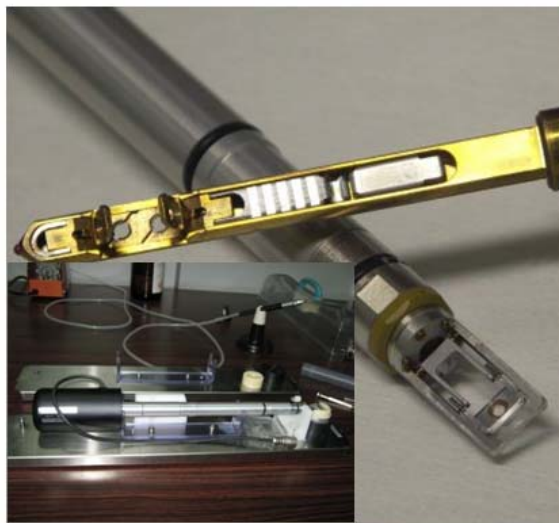


Figure 2-4: Shows the specimen grid holder. It has arrangement of tilting the specimen under view.

carbon to provide electrical contact to avoid accumulation of surface charges and simultaneous mechanical strength to hold the sample. Carbon nanotube samples were dispersed in ethanol and ultrasonicated for prolonged duration for proper dispersion. Extremely dilute solution of dispersed CNTs were drop casted on the grid to dry and image. The imaging was performed typically at 200 kV with minimum exposure of beam. In the high resolution lattice imaging mode, it offered a resolution of 0.14 nm. One can get a magnification of 1,500 KX with this machine. With the help of Fourier transform imaging and other softwares, we can get improved resolution for lattice imaging. We have used 'Digital Micrograph (GATAN, USA) software for processing and analysis of images. In addition to imaging, we have used selected area electron diffraction (SAED) in our studies to distinguish between amorphous and crystalline portions of samples. Further, EDS spectra were recorded using the same machine and used to identify as well as quantify the catalyst particles present in sample in as grown and commercially procured samples.

(c) Scanning Probe Microscopy (SPM)

Scanning probe microscopy images a surface by rastering a physical probe over it. Image is obtained by mapping the specimen line by line through mechanical movements of a

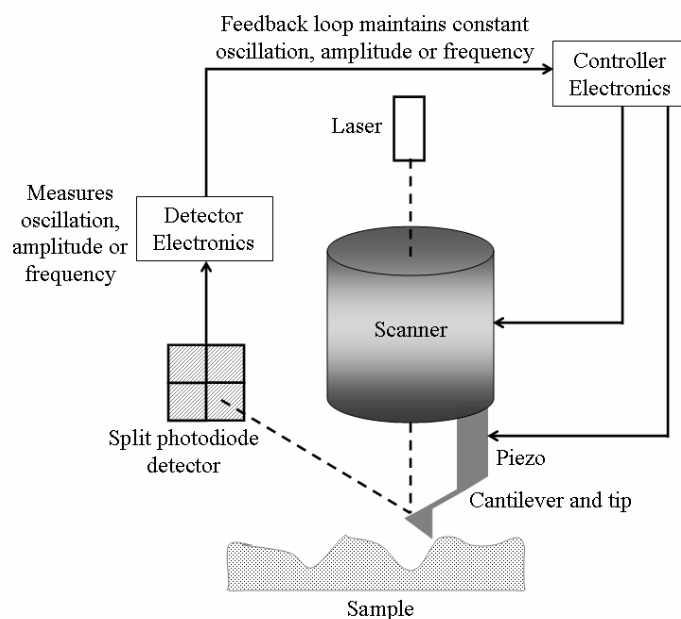


Figure 2-5: Schematic of working principle of a scanning probe microscope in non-contact mode of operation.

probe using a piezoelectric motor. It maps various interactions between the sample surface and the probe tip like van der waals force, electrostatic forces, magnetic force etc.). Depending upon the requirement and nature of sample, various modes of imaging is feasible such as contact mode, non-contact mode and tapping mode.

Schematic of a typical SPM is shown in Fig. 2-5. A basic SPM contains a laser source (preferably He-Ne, large wavelength higher scattering), a scanner head, piezoelectric assembly with feedback system and detector electronics with amplifiers. Depending upon the requirement of resolution appropriate scanner head is selected. Scanner head capable of scanning smaller scan area gives higher resolution as compared to

one which can scan larger area. Also separate scanner head noses are used for different mode of operation to make out appropriate electrical connections to gather electrical signals, if required. Probe tips are normally made of silicon, silicon nitride, platinum, iridium and gold. Depending upon the application and nature or interaction to be mapped, probe tip of a specific material and a certain spring constant is selected. We have used the SPM (Agilent 5500) in contact mode to image the size of catalyst nanoparticle used for CNT synthesis. For this purpose, we used a silicon tip with a scanner head of 10 μm . Further, SPM has been used for analysis of few layer graphene synthesized by chemical method.

(d) Confocal Laser Scanning Microscopy (CLSM)

CLSM is an optical technique to get high resolution images along with probe depth selectivity. High resolution and contrast is achieved by using point illumination source (Laser) and a spatial pinhole to eliminate out-of-focus light. By adjusting the focal depth it enables the 3D construction of images. It acquires images by point by point scanning of



Figure 2-6: Photograph of CLSM used (Model. Zeiss LSM 510 Meta)

the sample and further processing with software to contrast the data to form an image. Photograph of CLSM setup (Model. Zeiss LSM 510 Meta) used for the present work is shown in Fig. 2-6 (b). In a CLSM, the confocal aperture (pinhole) is arranged in a plane conjugated to the intermediate image plane. Thus, the detector (PMT) detects only the light which passes through the pinhole. The pin hole diameter is variable (usually infinitely small), and thus the detector looks at a point. The laser is focused to a diffraction-limited spot which illuminates only a point of the object at a time. The point illuminated and the point observed lie on conjugate planes; i.e they are focused onto each other, a confocal ray path. By varying the pinhole diameter, the degree of confocality is adjusted to requirements. Image contrast is improved by suppression of stray light by pinhole arrangement. CLSM typically has a resolution of 200 nm. We have used CLSM for the purpose of imaging CNTs with or, without fluorophores. This helps in understanding the mechanism of fluorescence quenching by CNTs.

2.2.2 Spectroscopic Techniques

(a) UV-Vis-NIR Absorption spectroscopy

Optical absorption spectroscopy has been established as a technique to determine the diameter and chirality of the nanotube [25, 31, 251]. It is also used for estimating the carbonaceous impurities in the carbon nanotube samples [252]. In case of carbon nanotubes to observe sharp transition peaks, sample preparation becomes critical due to bundling properties of SWCNTs. Also since the most prominent region of absorption due to transition between first singularity states of semiconducting tube lies in the range 900-1500 nm, solvent to be used for dispersing should not absorb in this spectral range. Water has a very strong absorption peak in this region. Thus choice remains to use either D₂O

(costly) or DMF or CCl_4 . Very dilute solution is prepared (usually 0.1 mg/ml) by dispersing SWCNTs with the help of surfactants like sodium dodecyl sulphate (SDS), Tween-80 etc and prolonged sonication using tip sonicators followed by centrifugation. Further, bundled portions of samples are separated by high speed centrifugation. Bundled samples give rise to broad spectral peaks. For our studies, we have used Perkin Elmer made Lambda 750 model of UV-Vis-NIR absorption spectrometer.

(b) Photoluminescence Spectroscopy

Photoluminescence (PL) is the process of emission of light with photo excitation and it occurs due to transition of electron from higher electronic energy level to lower energy levels. Emitted radiation carries the information regarding the optically allowed transition between energy levels. Maximum emission is observed when it is excited at its absorption maxima or, in other words at the band gap. In fact, optical absorption and emission spectroscopy are complimentary to each other in a broad sense. The spectral profile of photoluminescence peak carries information about the population of emitting species (in terms of intensity), relaxation process (peak width) etc. When a sample is excited, the emitted photons decay slowly with time. A measurement of intensity of emitted photon versus time at a fixed wavelength is known as time resolved photoluminescence spectroscopy (TRPL). Knowledge of life time of emission is essential to understand the mechanism / origin of PL in a material.

Fig 2-7 (a) shows the photographs of the steady state PL spectrometer used for the present study. It consists of a broad source of light (Xenon lamp, 450 W) with on the excitation and emission side. Generally for visible range, photomultiplier tubes or, the CCD cameras are used as emission detector, while for NIR studies InGaAs detectors are

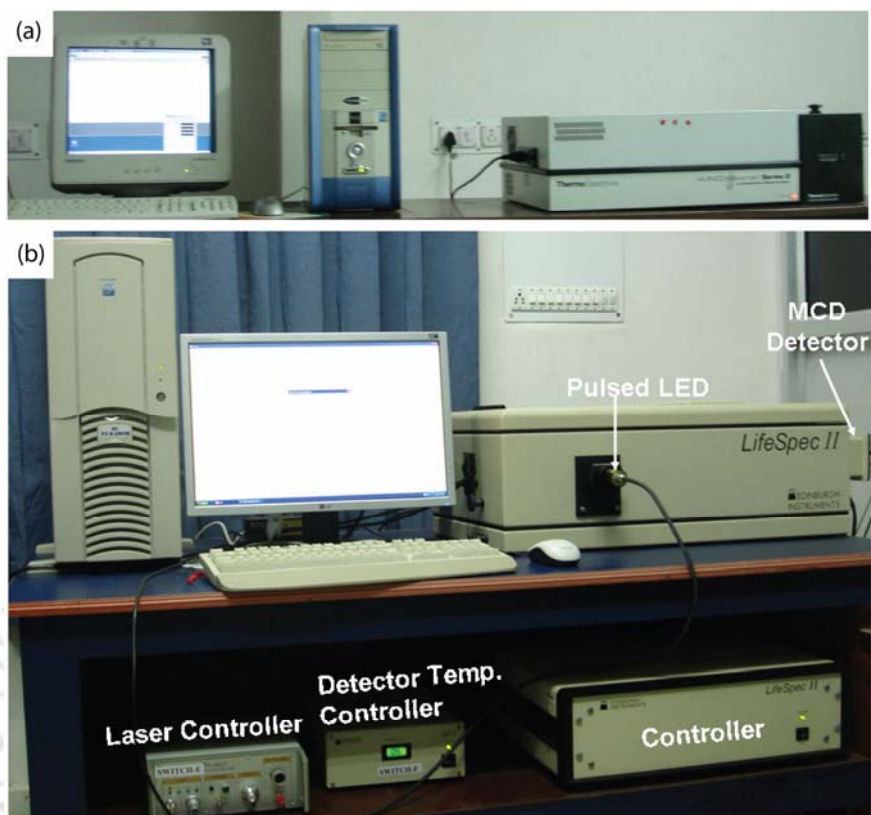


Figure 2-7: Photographs of PL spectrometers used. (a) Steady state PL (Thermoelectron, AB2 357) and (b) Time-resolved PL (FSP 920).

used. PL spectra can also be recorded using lasers because usually the absorption peak profiles of materials have sufficient broadness. We have used two different commercial PL spectrometers: one from Thermoelectron (Model. No. AB2357), other from Edinburgh instruments (Model No. FSP 920) and a home built Raman setup (using 488 nm laser excitation) for the PL studies. Fig. 2-7 (b) shows a photograph of the TRPL spectrometer used. For time resolved measurements, picosecond sources are used to monitor the dynamics of sub-nanosecond time scale. We have used picosecond pulsed diode lasers (Model No. EPL Series, Edinburgh Instruments) or, sub-nanosecond pulsed LEDs (from

PicoQuant GmbH, Model No. PDL 800D driver) as source for TRPL spectroscopy. Emission spectra are recorded using multichannel charge couple photodetectors (MCP).

In case of steady state PL spectroscopy, peak position, FWHM (Full width at half maxima) and intensity of the peak carry the information about the physical process, while in case of lifetime spectroscopy it's the time of decay. Steady state PL spectra are usually Gaussian in lineshape expressed by

$$y(x) = a_o \exp \left[-\frac{1}{2} \left(\frac{x - a_1}{a_2} \right)^2 \right] \quad (2-2)$$

where, a_o is the amplitude (intensity), a_1 represents centre (Peak position) and a_2 represents a measure of width. a_2 multiplied by 2.3548 (i.e. $2\sqrt{2\ln 2}$) gives a measure of FWHM for a Gaussian profile. The spectral profiles of measured PL spectra have been estimated by fitting with a Gaussian line shape or combination of number of them using either Peakfit or Matlab depending upon requirement.

For TRPL measurements, the instrument response time was estimated by recording the scattering of light by a well dispersed dilute solution of dry milk powder. TRPL data usually follow an exponential decay dynamics or combination of such functions depending upon the number of decay pathways of PL. It is expressed as,

$$I(t) = I_1 \exp(-t / \tau_1) + I_2 \exp(-t / \tau_2) + I_3 \exp(-t / \tau_3) + \dots + K \quad (2-3)$$

where, $I(t)$ expresses the number of counts observed experimentally, I_1, I_2, I_3 are decay channel strengths, τ_1, τ_2, τ_3 are the decay time or called decay constants and K accounts for scattered light through sample and internal optics and electronics of spectrophotometer i.e background noise. For time resolved measurements, we used Lifespec-II model from Edinburgh Instruments with a time resolution of ~50 ps.

(c) Raman spectroscopy

Raman spectroscopy probes the inelastically scattered photons by most elementary excitations associated with degrees of freedom of ions and electrons of a material. Its one of the main technique for probing phonon spectra. Raman spectroscopy allows the non-destructive identification of the symmetries of molecular structure, bonding and energies of the fundamental excitations of the solid. Interestingly, the measurement of the intensity of symmetry-forbidden Raman shifts quantifies the degree of disorder of the system. For the present work, we have designed and developed a dispersive Raman spectrometer. Details of the various components and working have been discussed later in section 2.3.1. Some of the high resolution Raman spectra have been recorded using a commercial micro-Raman spectrometer (Jovin Horiba, LabRam HR 800). Raman spectral profile contains information about structure and phonon confinement effects in CNTs. In presence of defects and disorder, the spectral profile carries additional information that can be extracted only through proper deconvolution of the spectra and analysis of the spectral profile.

Spectral line shape Analysis: Raman spectra usually shows Lorentzian spectral line profile mathematically expressed as

$$y = a_0 \frac{1}{1 + \left(\frac{x - a_1}{a_2} \right)^2} \quad (2-4)$$

Where, a_0 is the peak intensity, a_1 represents the Raman shift and $2a_2$ gives the measure of FWHM. Lorentzian spectral line profile expressed by eqn. (2.4) represents the solution of equation of damped harmonic oscillators. Sometimes, spectra better fits with Voigt

lineshape. Voigt spectral line profile is a combination of Lorentzian and Gaussian line profile mathematically expressed as

$$y = \frac{\int_{-\infty}^{+\infty} \frac{a_0 \exp(-y^2)}{a_3^2 + \left[\left(\frac{x - a_1}{a_2} \right) - y \right]^2} dy}{\int_{-\infty}^{+\infty} \frac{\exp(-y^2)}{a_3^2 + y^2} dy} \quad (2-5)$$

Where, a_0 is the peak intensity, a_1 represents the peak position, a_2 width related to the FWHM of Gaussian component and a_3 represent the ratio of Lorentzian FWHM to the Gaussian FWHM. Mathematically it can be expressed as

$$a_3 = \frac{FWHM(Lorentzian)}{FWHM(Gaussian)} \sqrt{\ln 2} \quad (2-6)$$

Voigt lineshape is not unique to Raman spectra, such lineshapes are commonly observed in powder x-ray diffraction (XRD) diffraction pattern, PL spectroscopy and many other types of spectra. Gaussian component may arise due to Doppler broadening (distribution of velocities of molecules), particle size distribution (major contributor to Raman profile) and instrumental broadening (important in case of XRD line profile analysis).

Interestingly, in case of metallic carbon nanotubes, a broad asymmetric lineshape is observed for G- mode, know as the Breit-Wigner-Fano (BWF) lineshape at $\sim 1550 \text{ cm}^{-1}$, as shown in the inset (right side) of Fig. 2-8. Experimentally observed Raman spectra were deconvoluted using a combination of Lorentzian and Fano line shape. G-band is deconvoluted into usual 3 components, one asymmetric and two symmetric Lorentzian line shapes (G^- (s) and G^+) features. BWF resonance lineshape is mathematically expressed as

$$I(\omega) = I_o \frac{\left[1 + \frac{1}{q\Gamma}(\omega - \omega_{BWF})\right]^2}{1 + \frac{1}{\Gamma^2}(\omega - \omega_{BWF})^2} \quad (2-7)$$

Where, ω_{BWF} is the frequency of the peak, I_o intensity, Γ width and $1/q$ is the measure asymmetry of the peak. BWF spectral shape occurs when a discrete energy excitation level interacts with a continuum of energy excitations, causing a resonance and anti-resonance effect ($1/q$), and thus giving rise to a non-symmetrical spectral lineshape for the discrete state [253]. BWF function expressed by eqn. (2-7) represents a pair of coupled, forced and damped oscillators. In case of $1/q = 0$, i.e. when the coupling strength is negligible, eqn. (2-7) boils to Loretzian eqn. (2-4). In case of metallic carbon nanotubes, BWF line shape arises due to coupling between Plasmon and phonon and coupling strength is expressed in terms of coupling strength parameter ($1/q$) [254, 255]. Depending on the strength of the interaction, both the peak position and the width of the spectral line changes, with the asymmetry depending on whether the continuum of states is centered above or below the discrete state in energy. Charge transfer to SWCNTs can lead to an intensity increase or decrease of the BWF feature.

Raman spectroscopy is thoroughly used for the present work to study diameter dependent properties of CNTs and to establish spectroscopic fingerprint of various defects in CNTs. Through a systematic study, we have isolated the defect induced modes from that of the combination modes. More details about the linewidth and recent finding of the different peaks of Raman spectra of SWCNTs and MWCNTs is given in line with discussion of our experimental results and findings summarized in Chapter-3, 4, and 6.

(d) Electron Paramagnetic Resonance (EPR)

Electron has a magnetic moment and the energy levels are quantized in an external magnetic field and the transitions are induced between these levels by an oscillating magnetic field of suitable frequency. The g-value for the observed resonance peaks can be calculated from eqn.

$$g = \frac{h\nu}{\mu_B B} = 71.44836 \left(\frac{\nu(\text{GHz})}{B(\text{mT})} \right) \quad (2-8)$$

Where, ν is the microwave frequency in GHz and B is the resonant magnetic field in mT, μ_B is the dipole moment of a electron (Bohr magneton) equal to $9.274 \times 10^{-24} \text{ JT}^{-1}$ and h is Planck's constant equal to $6.626 \times 10^{-34} \text{ J-s}$. In CNTs, a number of g-values can be observed depending on the structure of nanotubes, presence of impurities or paramagnetic defects, catalyst particle etc. Our purpose is primarily to obtain spectroscopic signature of defects in CNTs through ESR spectroscopy.

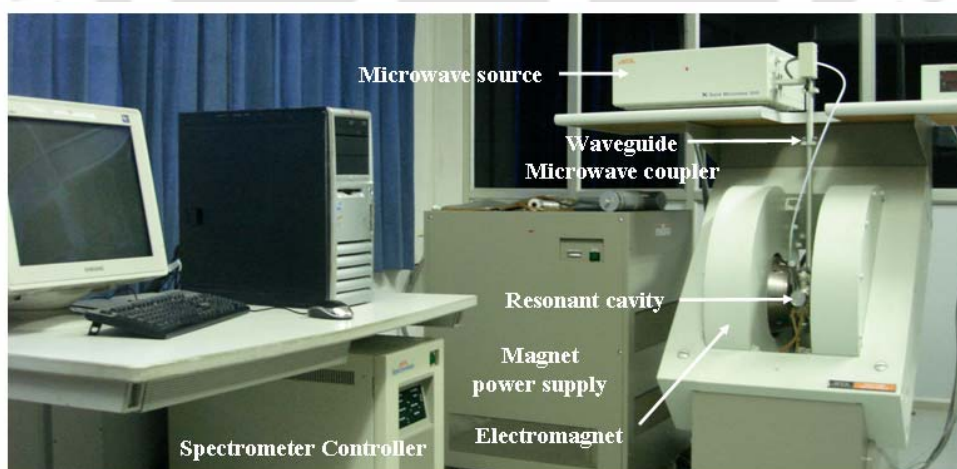


Figure 2-8: Image of the X-band EPR spectrometer used for the present study.

Fig. 2-8 shows the photograph of the EPR spectrometer (Model No. JEOL JES-FA 200, X-band) used for present study. For our experiments, we used X-band spectrometer

operating at frequency $G \sim 9.5$ GHz (wavelength 3 cm). During measurements, modulation width was kept at 0.35 mT and modulation amplitude was 500. Constant weight of the samples was taken for comparative study. Spectrometer was calibrated using standard Mn^{2+} marker. For temperature dependent study, we had used a different resonant cavity cooled with flow of liquid nitrogen vapor, and having temperature control accuracy ± 1 °C.

Analysis of the EPR spectrum: For a sharp peak, the g-value (peak centre) can be accurately determined from the centre of the maximum of dP/dT and minimum. But in case of broad peaks as observed in case of SWCNTs/ MWCNTs, spectral deconvolution is essential. Interestingly, spectral deconvolution gives measure of the width of the ESR peaks, from which the relaxation time can be estimated. During deconvolution, we found that Gaussian line shapes give better fit to the experimental data than the commonly used Lorentzian line shapes. Gaussian line shapes may arise due to superposition of many Lorentzian components arising due to diameter distribution in the sample. Non-interacting electronic spins are responsible for Gaussian like resonance shapes whereas motional effects distort the resonance line towards a Lorentzian one [214]. For deconvolution the differentiated spectra observed should be directly fitted, because the integrated spectra lose the resolution of sharp peaks.

For Gaussian lineshape, we used the differentiated form of the equation (2-2) given by

$$y_1 = \frac{dy}{dx} = -\left(\frac{a_0}{a_2}\right)\left(\frac{x-a_1}{a_2}\right)\exp\left[-0.5\left(\frac{x-a_1}{a_2}\right)^2\right] \quad (2-9)$$

Where, a_0 the amount of power absorbed or, intensity of the peak. a_1 represents the resonant field and a_2 represents the peak width. While fitting any spectra we first attempted to deconvolute it using Lorentzian component, then the Gaussian line profile was attempted to obtain a better fit. The Lorentzian lineshape used can be mathematically expressed as:

$$y_2 = \frac{dy}{dx} = -\frac{2a_0(x-a_1)}{[a_2 + (x-a_1)^2]^2} \quad (2-10)$$

ESR signals from carbon nanotubes mainly originate from localized spins due to impurities, and for conduction electrons originating from metallic or semiconducting nanotubes with a small gap [208, 209]. In addition to conduction electron spin resonance (CESR) from metallic and graphitic particles [210] a ferromagnetic resonance (FM) may also be present from residual metallic catalyst particle [207, 211]. The line shape has been found to vary from symmetric (Lorentzian / Gaussian) to asymmetric (Dysonian). Even a very small amount of residual catalyst metal can relax the conduction electrons very effectively due to their long mean free path and diffusion length. The higher dimensionality of the electronic system in MWCNTs provides a less efficient relaxation pathway in the presence of metal particles and makes the CESR more likely to be observed [200].

The Dysonian lineshape (asymmetric line) arises due to the skin depth effects. If the length of the sample along the propagation direction of microwaves is larger than the skin depth, then the microwave field is damped within the sample. Dysonian line shape is a combination of absorption and the dispersion components of a symmetric Lorentzian. An additional spectral parameter α , the ratio of the amplitude of the left peak to the right peak

of the derivative EPR signal, or equivalently, α the asymmetry parameter, which is the fraction of the dispersion added on to the absorption, necessary to describe such an asymmetric signal [256]. Based on the theoretical calculations of Dyson, the analytical EPR lineshape of a thick conducting sample with surface area A and conductivity σ was derived by Feher and Kip [257] as follows:

$$P_{EPR}^{(abs)}(\omega) \propto -\delta A \omega R^2 T_2 \left[\frac{R^4 (x^2 - 1) + 1 - R^2 x \left(\frac{2\xi}{R\sqrt{1+x^2}} + R^2 (x+1) - 3 \right)}{\left((R^2 x - 1)^2 + R^4 \right)^2} + \frac{2R^2 - 2xR^4}{\left((R^2 x - 1)^2 + R^4 \right)^2} \left(\frac{2\eta}{R\sqrt{1+x^2}} + R^2 (x+1) - 3 \right) \right] \quad (2-11)$$

Where, δ is the skin depth, R denotes the ratio between the transit time T_D of the charge carrier through the skin depth and the spin relaxation time (T_2) given by

$$R = \sqrt{\frac{T_D}{T_2}} \quad (2-12)$$

Other functions used in equation (2-11) are expressed as follows

$$x = (\omega - \omega_0) T_2, \quad (2-13)$$

$$\xi = \sin(x) \sqrt{\sqrt{1+x^2} - 1}, \quad (2-14)$$

and

$$\eta = \sqrt{\sqrt{1+x^2} + 1}. \quad (2-15)$$

Where, ω represents the angular frequency of the applied electromagnetic radiation and ω_0 is the resonance frequency due to the Zeeman effect in the external magnetic field B_0 with

$$\omega_0 = \frac{g\mu B}{\hbar} B_0 \quad (2-16)$$

For fitting the analytical form of Dysonian line shape, simplified form of eqn. (2-11) can be expressed as [256]

$$P = a_0 \left[\frac{a_2 + \alpha(x - a_1)}{4(x - a_1)^2 + a_2^2} + \frac{a_2 - \alpha(x + a_1)}{4(x + a_1)^2 + a_2^2} \right] \quad (2-17)$$

to deconvolute the differentiated spectra observed experimentally we have used the following equation obtained after differentiation of eqn (2-17) with respect to x ,

$$y_3(x) = \frac{dP}{dx} = a_0 \left[\left(\frac{\alpha}{4(x - a_1)^2 + a_2^2} \right) - \left(\frac{\alpha}{4(x + a_1)^2 + a_2^2} \right) - \left(\frac{8(x + a_1)(a_2 - \alpha(x + a_1))}{(4(x + a_1)^2 + a_2^2)^2} \right) - \left(\frac{8(x - a_1)(a_2 + \alpha(x - a_1))}{(4(x - a_1)^2 + a_2^2)^2} \right) \right] \quad (2-18)$$

In eqn. (2-18), term a_0 represents the amplitude, α is the asymmetry parameter, a_1 represents the resonant magnetic field (B_0) and the peak width (ΔB) is represented by a_2 . The asymmetry in the line shape may also have contribution from incomplete rotational averaging of the asymmetric g-tensor [258]. The modification of g-factor in graphitic materials is significant since it is sensitive to the band structure details at the Fermi level. In fact, in case of graphite line width is governed by a subtle motional

narrowing of the g-value distribution over the Fermi surface, and thus depends on the spin diffusion. In graphite both g shift, i.e., g factor minus free electron value and the line width are strongly anisotropic. When the magnetic field is parallel to the graphene planes g-factor has a minimum value 2.0026 slightly higher than free electron value due to the small spin-orbit coupling with carbon atoms [200]. This is a special property of graphite due to the position of the Fermi level near the π bands crossing at K points of the hexagonal Brillouin zone [259]. When a magnetic field is applied perpendicular to the plane, electrons condense on the $N = 0$ Landau level, which induces this unusual anisotropic behavior [260]. When the field is parallel to the planes, no closed orbits are accessible and the effect disappears. In case of carbon nanotubes this picture is modified due to cylindrical wrapping especially when the tube radius is small compared to the cyclotron radius (r_c) then closed orbits can not form. Usually average g value 2.0012 of nanotubes is different from g value of graphite 2.0018. It is expected that g shift would decrease with the tube diameter since it becomes more and more difficult to form Landau levels [201]. A strong g-shift is measured at $g = 2.05$ when the field is perpendicular to the planes [261]. Due to motional averaging, one measures a g value of 2.018 at room temperature in polycrystalline graphite [200].

(e) X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron spectroscopy utilizes photo-ionization by X-ray photons and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample. For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the photoelectron

spectrum at kinetic energies determined by the photon energy and the respective binding energies.

The line shapes of the XPS peaks give information about the chemical bonding environments in the sample. An estimate of the sp^3 hybridization in each of these samples can be found from the ratio of the corresponding sp^3 peak area to the total C1s peak area. For our measurements, we had used XPS (VG Instrument, IOP Bhubaneswar) with a Mg K_α source at an emission angle of 30° . Experimentally recorded spectra were deconvoluted using XPS peak 4.1 software with Shirley background. We have used XPS spectroscopy to study the structural changes in the carbon nanotubes after irradiation, as presented in Chapter-6.

2.2.3 Powder X-ray diffractometry (XRD):

Powder XRD is a nondestructive tool to obtain information on the interlayer spacing, the structural strain and the impurities in CNTs. Diameter and chirality distribution are also observed as well as various numbers of layers for MWCNTs. This leads to a statistical characterization of CNTs.

When a beam of X-rays falls on an arrangement of atoms, it diffracts into various directions depending upon the nature of atoms (scattering factor), its atomic arrangement (structure factor), Lorentz factor (geometry of spectrometer), multiplicity factor and many other factors. These diffracted beams interfere to give a diffractogram. The condition of constructive interference of these diffracted beams is known as “Bragg’s law” mathematically expressed as

$$2d \sin\theta = n\lambda \quad (2-19)$$



Figure 2-9: Photograph of the powder X-ray diffractometer used (Model: Bruker D8-Advanced tools).

Where d is the interplanar spacing between the diffracting adjacent planes, θ is the angle of the X-ray beam with the lattice plane, n represents the order of diffraction (usually taken $n=1$, because second order peaks are mostly difficult to detect experimentally) and λ is the wavelength of the X-ray used ($1.5405 \text{ \AA}$), for $\text{Cu K}_{\alpha 1}$ -radiation used in our experiment). X-ray diffractogram is typically a plot of intensity of interference pattern of diffracted beams versus the angle of incidence θ or, 2θ . There are two commonly used geometries of powder XRD namely (a) Bragg-Bentano geometry and (b) Göbel mirror geometry. Bragg-Bentano geometry is used for powder samples. In this geometry the incident X-rays do not fall parallel to the sample. Since in powder form crystallites are oriented in various possible orientations, giving reflections from all possible planes.

We have used a powder XRD (Bruker D8-Advanced tools) for studying the diameter dependent features mainly in MWCNTs. Experimentally observed XRD spectra were

deconvoluted using Voigt line shape (given by eqn. 2-5) for line shape analysis. For irradiated samples, along with other spectroscopy techniques we have used it to monitor structural modification and change in lattice strain; results are presented in Chapter-6.

2.2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analyzer measures the change in weight of sample with temperature and difference in temperature between a sample and reference which are exposed to the same heating schedule via symmetric placement with respect to the furnace. The reference material is any substance, with about the same thermal mass as the sample, which undergoes no transformations in the temperature range of interest. The difference between the sample and reference is measured by a “differential thermocouple” in which one junction is in contact with the underside of the sample crucible, and other side is in contact with the underside of the reference crucible. Differential thermocouple signal amplifier is a critical component which amplifies minute voltages along with eliminating random noise. When a sample undergoes a transformation, it will either absorb (endothermic) or release (exothermic) heat. For example, the melting of a solid material will absorb heat, where that thermal energy is used to promote the phase transformation. Instrument detects sample cooler than the reference and will indicate the transformations as an “endotherm” on a plot of differential temperature (ΔT) versus time. It also determines change in the weight with temperature. TGA instruments have high degree of precision measurements of weight ($\sim$ micro gram), temperature (0.01 °C), and sensitivity to the temperature change. Usually derivative of the weight loss curve is used to tell at which point weight loss is most apparent. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control

the instrument. Fig 2.10 shows the image of the TGA instrument used for the present study. It consists of a furnace, microbalance, and temperature controller, sensor for temperature monitoring and electronics for control and data acquisition.



Figure 2-10: Image of the TGA /DTA instrument used (Metler–Teledo TGA 1100).

TGA is a standard analytical technique for the determination of the amount of metal catalyst and relative amount of different forms of carbon [262]. Different forms of carbon show different oxidation rate and temperature for maximum oxidation temperature for a particular heating rate and gas flow rate. For recording TGA and DTA spectra, 40 sccm of air flow and 5 °C/min heating rate has been suggested as optimum for CNT characterization [263]. Amount of metallic impurity is estimated by calculating the weight percentage of metallic residue left after complete oxidation minus the weight increase due to oxidation of metals at high temperature (usually taken as 20 %) [263, 264]. Defects and derivatization moiety in nanotube walls can lower the thermal stability. TGA studies by Bom et al have provided evidence for defects playing a significant role in the thermal stability of MWCNTs [63]. We have carried out TGA studies using a commercial TGA apparatus (Metler–Teledo TGA 1100) under 40 sccm flow of air and heating rate was kept constant at 5 °C/min. Using TGA study we found a strong diameter dependence

of oxidation temperature for a large diameter range of MWCNTs presented in chapter-3. Further TGA results have been used for studying the improved stability of vacuum annealed samples.

2.2.5 Other techniques

We have used a few other analytical techniques to provide supporting information for the studies of defects in CNTs. In particular, Fourier transform infrared spectroscopy (FTIR) spectroscopy has been used for characterization of attached functional groups before and after chemical reactions to modify the surface of the nanotubes. A commercial FTIR (Perkin Elmer) spectrometer is used for this purpose. Measurements have been made at room temperature. Further, we have used a vibrating sample magnetometer (VSM) (Make: Lake Shore 7410) for the study of magnetic property of the CNTs. In particular, magnetization measurements were used for better estimation of metallic catalyst contents and compared with the results of TGA.

2.3 Design and development of various setups

Carbon nanotubes have been ever advancing field of study and it requires expertise over a group of techniques ranging from optical absorption spectroscopy to electron microscopy. Similarly, there have been ongoing efforts to synthesize ultralong defect free carbon nanotubes. Many attempts were made to control the diameter and chirality of nanotubes during growth. There has been a race to grow smaller and smaller diameter CNT because they are preferably semi-conducting. In literature a number of recipes with couple of techniques have been used for synthesis depending upon availability and requirement. During study we designed and developed (a) Raman spectrometer for

characterization (b) Gas phase thermal chemical vapor deposition setup and (c) High temperature high vacuum annealing setup. The details of these custom made equipments are presented below.

2.3.1 Laser Raman setup

We have designed and developed a dispersive Laser Raman setup for the study of CNTs. Fig. 2-11 shows the ray diagram of the optics assembled in the lab to record Raman spectrum. Various components used for the setup are mentioned in the diagram. Optical components assembled show backscattering (180°) geometry of Raman spectroscopy. We have used air cooled 488 nm (blue) Ar^+ ion laser with a variable emitting power capability (Model No. 177-G1205, Spectra Physics) as the excitation source. Emitted power range at the laser head could be varied between 8 -100 mW and diameter of the focused laser spot was ~ 0.2 mm.

M1, show the dielectric mirror to placed at 45° to bend the light. After bending through the dielectric mirror M1 laser spot is passed through a metal pin hole. Basically pinhole S1 cuts a large portion of the emitted laser plasma. Any gas lasers, apart from the characteristic emission lines, emits many other lines due to ionized plasma oscillation frequency. These lines are usually very sharp and intense and may fall in the desirable frequency region. But care has to be taken so that it does not cut a portion of emitted laser spot.

Next to the pin hole a plasma filter is placed, which is basically a rejection filter. Except the excitation line $488 \text{ nm} \pm 50 \text{ cm}^{-1}$, it rejects other frequencies. After passing through the plasma filter it falls on a small angle prism so that it is reflected at 90° . The

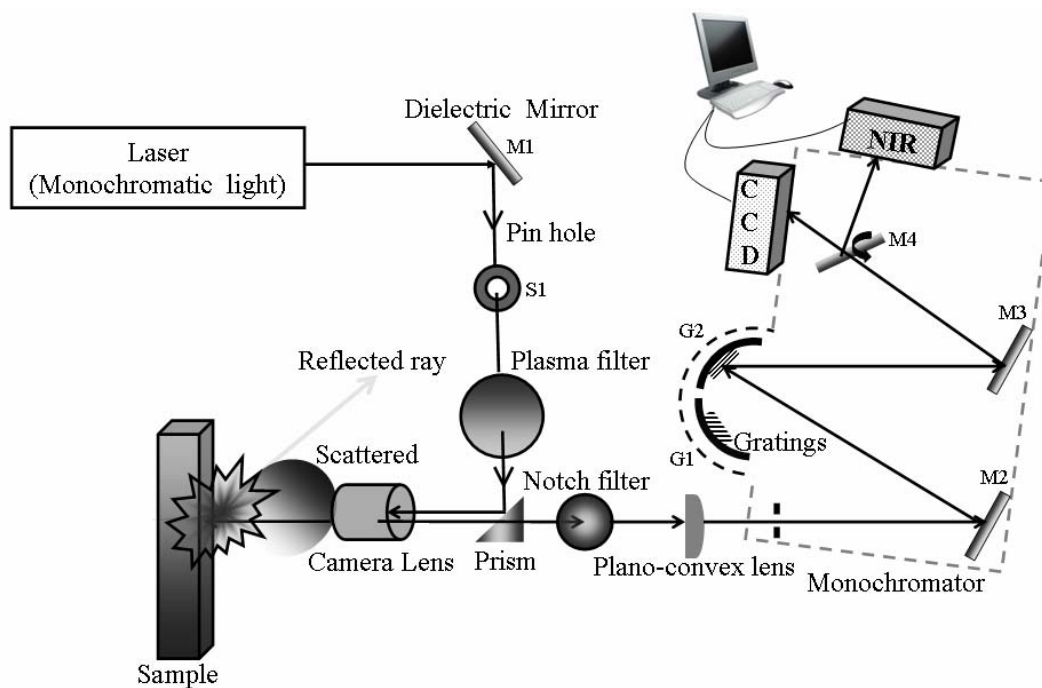


Figure 2-11: Ray diagram of Laser Raman spectrometer setup developed in house.

reflected light from the prism is focused on the sample through a camera lens (MINOLTA, Model No. MC ROKKOR-PF, $f = 58$ mm). Sample is kept at some angle with the incident beam so that the reflected ray (elastically scattered) light do not enter in the monochromator. Scattered light is collected back through the camera lens. After passing through the prism it is focused by a antireflection coated plano-convex lens into the monochromator. In between the prism and monochromator we used a Notch filter to remove / suppress the Rayleigh component of scattered light (488 nm). While recording spectra, the angle of the notch filter (angle between notch filter and incident laser light on it) is so adjusted that we do not observe the Rayleigh tail is extended to a minimum frequency.

Use of the Notch filter allowed us to record both stokes and antistokes spectra, which otherwise would not have been possible with commonly used edge filter. But notch

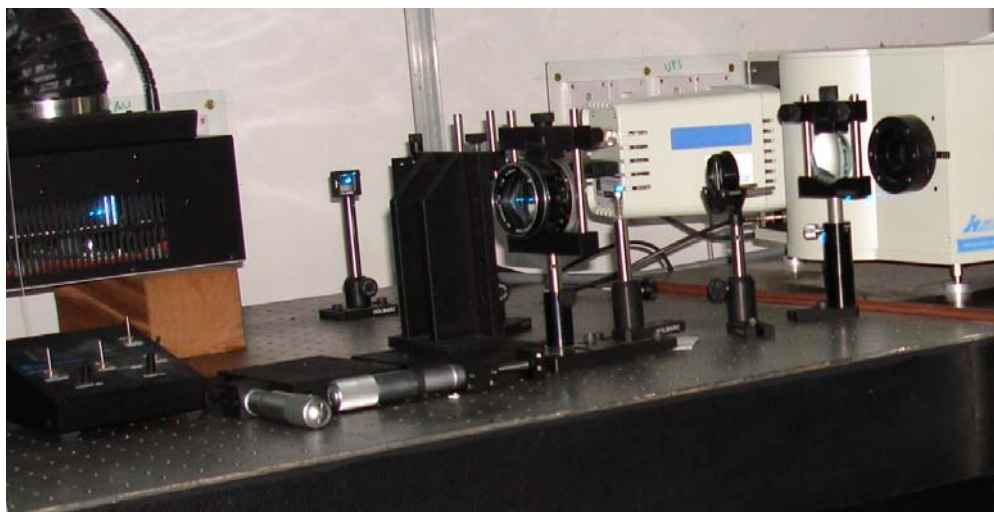


Figure 2-12: Photograph of the dispersive Raman spectrometer setup in the Lab.

filters have a limited lifetime period and care has to be taken to avoid any exposure to the reflected beam of light, which otherwise may damage it. Monochromator is kept / adjusted to illuminate the complete pixel range of CCD detector (Model No. CCD-1024×256 OPEN-STE, Jobin Yvon). Data is acquired by interfacing the monochromatic and CCD through a computer. The same setup has been used for recording PL spectra with 488 nm laser excitation. Optionally a NIR detector can be used to record PL by deflecting the beam with a motor controlled mirror in between the mirror M3 and CCD. Fig. 2-12 shows the photograph of the assembled setup. This setup is used for the study of SWCNTs and MWCNTs with wide range of diameters.

2.3.2 Chemical Vapor Deposition System

Chemical vapor deposition (CVD) is the most commonly used method of carbon nanotube synthesis. Schematic diagram of the thermal CVD setup developed in-house is shown in Fig. 2-13. Fig. 2-14 shows photograph of the CVD setup fabricated during this study for CNT growth. Basically it consists of carbon source gas, furnace, Quartz chamber and

vacuum pump. Quartz tube of diameter 34 mm was used as chamber to crack the carbon source gas, acetylene (C_2H_2). At the mouth of the quartz tube vacuum flanges were attached properly with aradalite adhesive on both sides. One side of the tube was coupled

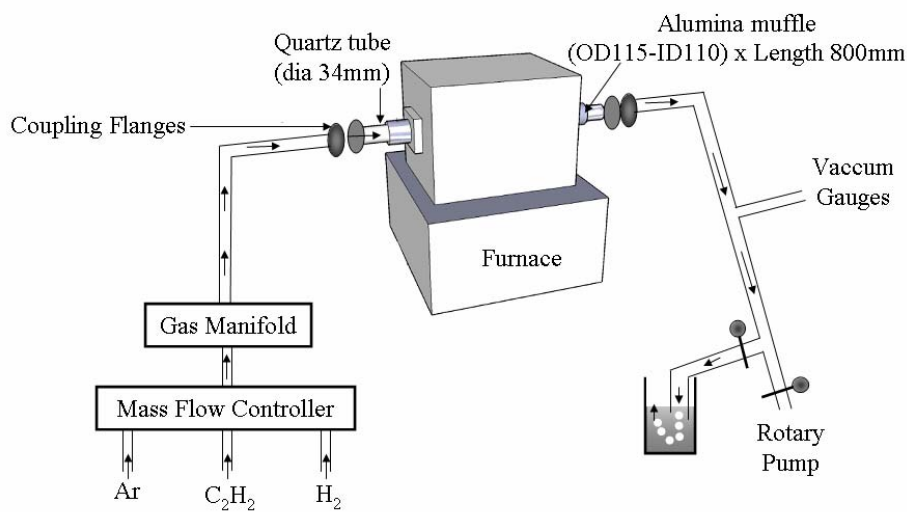


Figure 2-13: Schematic of the Thermal CVD setup developed in-house for carbon nanotube growth.

with gas manifold through the brass machined arrangement compatible to be coupled with vacuum flanges attached with the mouth of quartz tube. Other side of the tube is coupled through a metal hose pipe to the exhaust line having rotary pump or, a gas exhaust through water bath as optional. Vacuum level in the quartz tube was monitored using a pirani gauge attached at the mouth of the quartz tube on exhaust line side. We achieved a vacuum of 70×10^{-3} mbar with the running rotary pump under no flow of gases. With the flow of 200 sccm of Argon, 40 sccm of acetylene and 15 sccm of H_2 , chamber pressure falls to 91×10^{-2} mbar. The pin valve at the mouth of rotary pump is adjusted to achieve

the desired pressure in the chamber. Deposition at the atmospheric pressure was attempted by passing the exhaust gas through water and blocking the rotary valve during growth.

Mass flow controller (MFC) was obtained from MKS (Type 247, Four channel readout). Before the use, MFC reading was corrected for the respective gas correction factors. Gas correction factor (GCF) is used to indicate the ratio of flow rates of different gases which will produce the same output voltage from a mass flow controller. The output

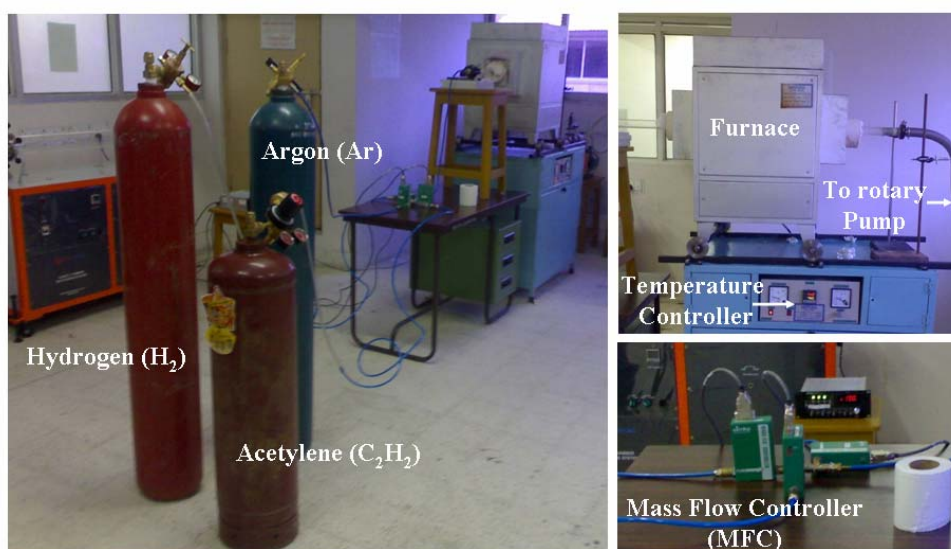


Figure 2-14: Photograph of different portions of the gas phase Thermal CVD system developed for carbon nanotube growth using acetylene as carbon source.

voltage from a MFC depends upon specific heat, density and molecular structure of gases. Since the flow controllers are usually calibrated with nitrogen, nitrogen is used as baseline gas ($GCF = 1$ at $273\text{ }^{\circ}\text{K}$).

GCF for pure gases is calculated using following formula

$$GCF_x = \frac{0.3106 S}{d_x CP_x} \quad (2-20)$$

Where, GCF_x is gas correction factor for gas x . Factor 0.3106 is the product of standard density of nitrogen and specific heat of nitrogen (N_2). S is the molecular structure correction factor where it equals to 1.030 for monatomic gas, 1.000 for diatomic gas, 0.941 for triatomic gas and 0.880 for polyatomic gas. d_x represents standard density of gas x (mg/litre at $^\circ C$ and 760 mm of Hg). CP_x indicates specific heat of gas x in cal/gm $^\circ C$. For very precise control, temperature correction factor has to be incorporated for calculation gas correction factor.

During CNT synthesis, appropriate substrate with patterned metallic catalyst was kept at the centre of the furnace. Before starting the synthesis process, system was evacuated and purged with argon to avoid presence of oxygen. Oxygen free environment is essential to avoid flame and explosion with acetylene and hydrogen. Furnace was heated under flow of carrier gas Ar mixed with the reducing agent H_2 . Flow of H_2 etches surface of metal nanoparticles and avoids agglomeration of nanoparticles by coalescence while heating the furnace. After reaching the desired growth temperature, carbon source gas acetylene was mixed with flowing Ar and H_2 . The flow rate of acetylene or gas ratio was adjusted slowly to avoid any thermal shock to the quartz tube arising from the flow of compressed cold gas. Synthesis was attempted with different gas flow rates, a number of catalyst type and chamber pressure as summarized in Table 2-1.

2.3.3 High Vacuum Furnace

To study the effect of annealing on the structural properties of carbon nanotubes, we have developed a high temperature and high vacuum furnace. Fig. 2-15 shows the photograph of high vacuum furnace developed to explore the possibility of structural

improvement of CNTs through thermal treatment. A one-side open quartz tube was used as the chamber for this setup. Similar to the CVD setup, arrangements were made to

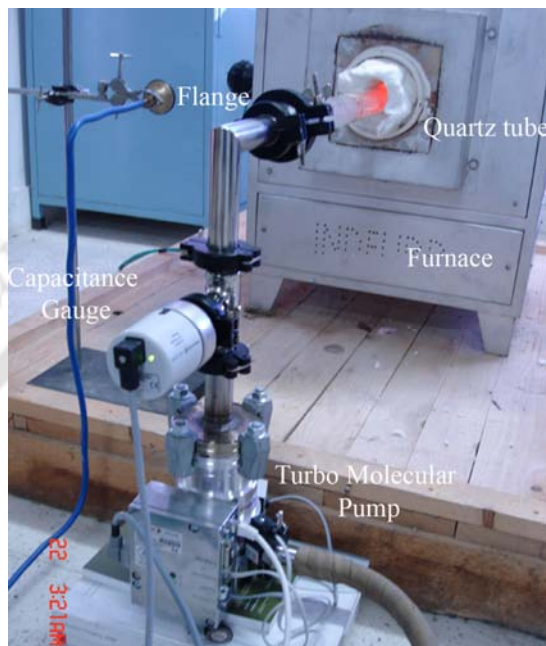


Figure 2-15: High vacuum annealing furnace setup developed in the lab.

connect it through vacuum compatible flanges. It was pumped through a combination of turbo-molecular pump (Preiffer, Model No. TC600) and rotary pump. After pumping, the samples were heated to anneal at desired temperature. We achieved a vacuum level of 1×10^{-6} torr and maximum temperature $1000\text{ }^{\circ}\text{C}$ in this furnace.

2.4 Details of Samples Preparation

2.4.1 Synthesis of Carbon Nanotubes

We synthesized low diameter CNTs using the thermal CVD setup discussed above. Synthesis of CNTs involved catalyst preparation, control of various parameters like gas flow rates, temperature of growth and finally characterization. As an initial attempt, we had synthesized carbon nanotubes using thermal decomposition of alcohol in an autoclave.

with slightly modified reaction condition, we achieved very high quality monolayer of graphene sheets in this process.

(a) Low Temperature Chemical Synthesis of Carbon nanotubes and Graphene

We attempted to prepare CNTs by high pressure thermal decomposition of ethanol by modified Wolf-Kishner Reduction process [265, 266]. The schematic of the high pressure autoclave used is shown in Fig. 2-16. It consists of a cylindrical iron vessel, thermocouple and pressure gauges for monitoring temperature and pressure within the vessel with control electronics, a heater coil and arrangement to tighten the cover to maintain pressure within the vessel. CNTs synthesis was achieved through thermal decomposition of ethyl alcohol in presence of strong alkaline solution of sodium hydroxide in a medium pressure autoclave with stainless steel chamber (Amar Equipments, India). In a typical reaction, 80 ml of ethyl alcohol was mixed with the solution of 4.3 gm of NaBH_4 and 15ml of 10M NaOH solution. Reaction was carried out with and without addition of Sodium dodecyl sulphate (SDS). Amount of SDS added was 2 wt % of ethyl alcohol i.e. 1.26 gm was added to the solution. Reaction was carried out for 20 hrs at 180 °C. The pressure in the reaction vessel was noted around 46 Kg/cm^2 . The reaction product obtained was filtered with water and alcohol repeatedly to reach a pH value 7. This product was dried for 10 hrs in hot oven at 60 °C. The measured weight of the product was ~125 mg. As produced nanotubes contained impurities like amorphous carbon, graphite, fullerene and some fraction of iron. Iron impurity in the sample was introduced from the stainless steel reaction chamber (vessel) during synthesis. The as-synthesized product was purified through refluxing with 3M HNO_3 . During the reaction, KMnO_4 solution was added slowly

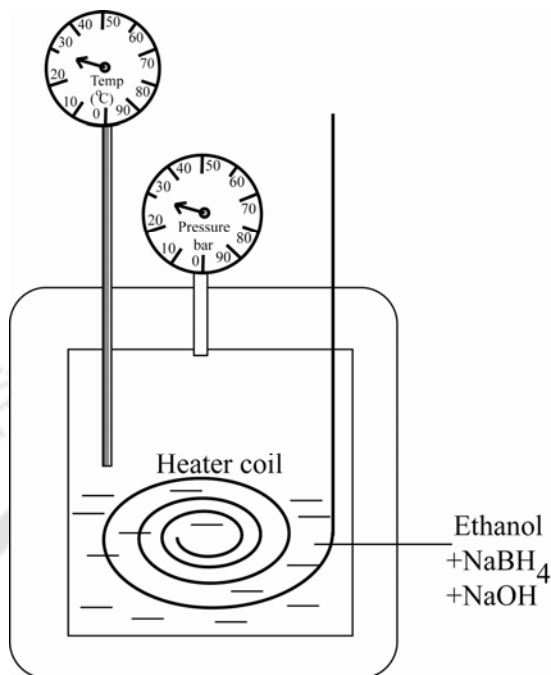


Figure 2-16: Schematic of the high pressure reactor used for carbon nanotube and graphene synthesis.

through dropping funnel. This reaction was carried over oil bath at constant temperature of 150 °C for 5 hrs. The product obtained was continuously washed with water and dried.

Fig. 2-17 shows the low resolution TEM of CNTs grown in the autoclave. It shows that even after purification CNTs contains various types of impurities (like amorphous carbon) and structural defects. It has been reported that alcohol reacts directly with NaBH_4 to produce H_2 , alkyl borates, and alkoxy borohydrides [267]. Therefore, this reaction method was attempted for the possible chemical synthesis of carbon nanotubes. The growth of CNTs in our case may be similar to the pressure induced carbon condensation growth mechanism [268]. A high density fluid phase, from which growth occurs, changes its compositions rapidly as carbon condenses, traversing a range of compositions during which different phenomena take place. This is likely to be responsible for the formation of CNTs in our experiments.

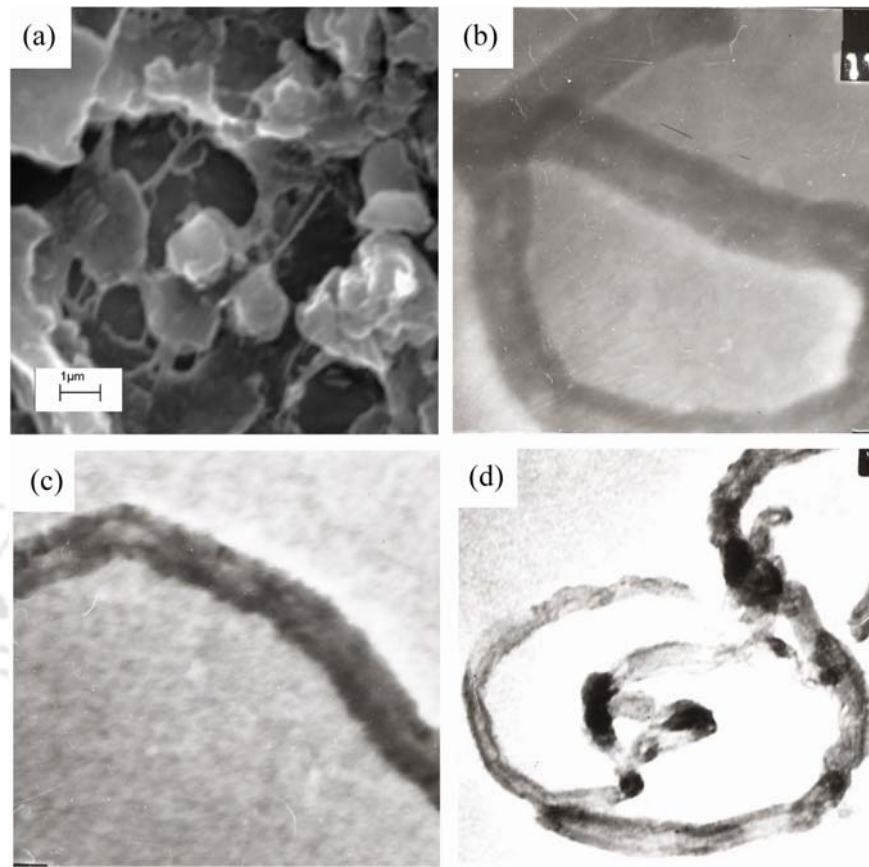


Figure 2-17: Shows (a) SEM image of CNTs synthesized using high pressure thermal decomposition of alcohol (b)-(d) shows HRTEM image of various types of structure observed in as synthesized CNTs. (b) shows CNT with bents (c) shows amorphous carbon deposits on the surface of CNT and (d) shows as produced damaged CNTs.

Interestingly, when the growth temperature was increased to 230°C and correspondingly the pressure in the chamber was increased to 69 Kg/cm^2 , high quality graphene were produced, as shown in the Fig. 2-18. SEM and TEM image of as produced graphene is shown in Fig. 2-18(a) and 2-18(b) respectively. Dark regions in the Fig. 2-18(b) represent the folded edge of the graphene sheets. AFM was used to determine the thickness. Thickness measurement shows presence of monolayer ($n=1$) to trilayer ($n=3$) graphene in the sample. Fig. 2-18(c) shows AFM image of a monolayer of graphene, as confirmed from its height 0.343 nm . This is an important achievement. Our synthesis

method has several advantages over the other physical methods of production of graphene [162]. Firstly, the ethyl alcohol acts as a carbon source as well as the solvent,

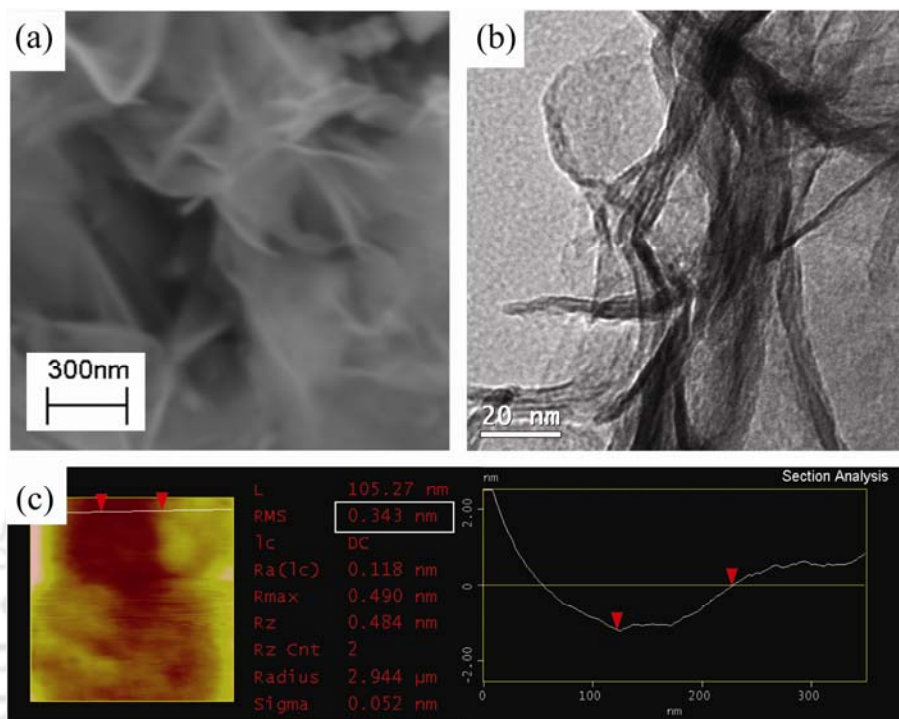


Figure 2-18: Shows (a) SEM image of graphene synthesized using high pressure thermal decomposition of alcohol (b) TEM image of as synthesized graphene showing large and separated sheets. (c) Shows AFM image and sectional analysis of as synthesized monolayer graphene. Number of layer varies from $n = 1$ to $n = 3$.

which decreases the cost of production and allows the reaction to be performed under mild conditions. Like other chemical methods of synthesis, it is less expensive, simple and has the potential for the industry scalable production capacity. Recently, gram-scale production of graphene has been reported by reduction of ethanol using sodium metal, followed by pyrolysis of the ethoxide product, and washing with water to remove sodium salts [269]. Use and handling of sodium metal in their report makes the process complicated and requires expert laboratory handling. We have used sodium borohydride as reducing agent in place of sodium metal and reaction conditions are similar to the report

of bulk synthesis methodology. We do not require any post pyrolysis of produced product in the reactor. Our method avoids harsh reaction conditions involved in the earlier reports for synthesis of bulk quantity of graphene. In contrast to the reported method, our method essentially uses surfactant during the reaction to achieve improved yield and long sheets of graphene. Our study show that gram scale synthesis of graphene sheets by a relatively safer and easier chemical method using an autoclave is quite feasible in this method.

(b) Synthesis of CNTs using Thermal CVD

CVD involves the process of decomposition of carbon containing gases like acetylene (C_2H_2) or methane (CH_4) at high temperature. The decomposed carbon is carried to the chamber by the carrier gas, usually Ar. The decomposed carbon forms an intermediate phase with the transition metal catalyst like with iron it forms γ -Fe-C phase (up to 9 atomic % of C). Since it can take limited amount of carbon, with further increase of concentration, carbon precipitates and gives rise to carbon nanotube growth. The size and nature of the catalyst is one of the important governing factors of diameter and quality of the nanotubes produced.

There have been a number of approaches for catalyst preparation like (i) post annealing of metallic thin films prepared through various physical vapor deposition methods. (ii) Chemical impregnation of various porous materials like zeolite (ZSM-5) and MgO. Apart from this various types of metallic catalyst including transition metals and noble metals both, bimetallic systems like Fe/Co or Fe/ Ni has been attempted in the literature. Nature of the catalyst has been found to affect the diameter, chirality, purity and the type of the nanotubes synthesized. For our work we had prepared catalyst through two methods:

- (i) *Zeolite supported metal nanoparticles*: Zeolite supported metal catalyst was prepared according to the method reported by Shinohara's group [270]. Iron acetate $(\text{CH}_3\text{CO}_2)_2\text{Fe}$ and cobalt acetate $(\text{CH}_3\text{CO}_2)_2\text{Co}\cdot 4\text{H}_2\text{O}$ were dissolved in ethanol (typically 20ml) and mixed with zeolite powder [ZSM-5-SAR-100, Ranbaxy] (typically 1 gm). The amounts of Fe and Co were 2.5 weight % each. The solution was then sonicated for 10 min and dried for 24 hr at 80 °C. The resultant white-yellow powder on the quartz boat was placed in a quartz tube inside of an electric furnace. While heating up to the desired reaction temperature, more than 200 sccm Ar flow was kept. After reaching the desired growth temperature, mixture of carbon source gas and carrier gas was passed for ~30 min. Carbon nanotubes grown using Zeolite supported metal catalysts were of very low diameter.
- (ii) *Annealing of the RF sputtered metal thin film*: A SiO_2 layer was grown over Si wafer by heating at 1000 °C for 6 hrs in air flow. Thin film of Fe (Iron) was sputtered on SiO_2

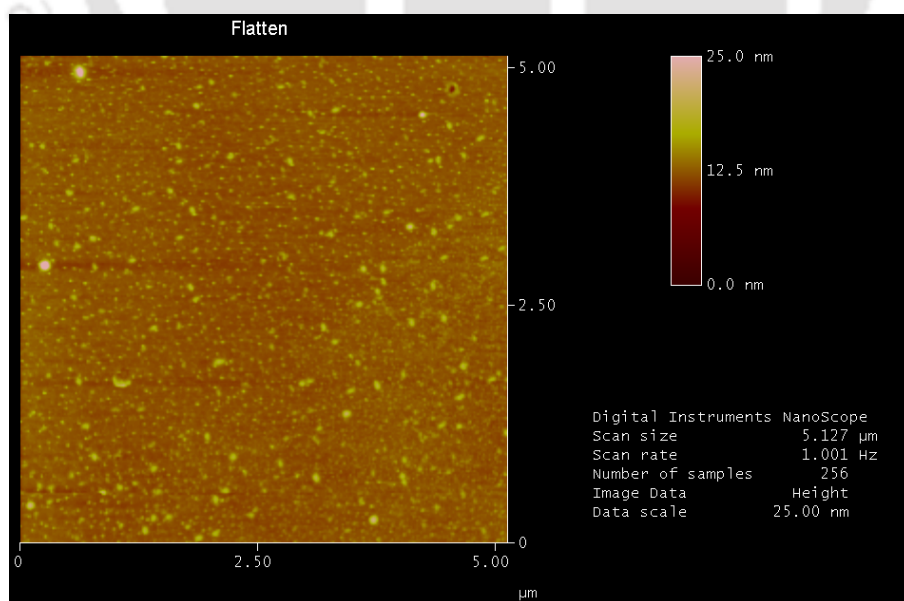


Figure 2-19: Shows the AFM image of catalyst Fe nanoparticles (size ~ 25 nm) grown on SiO_2 wafer by RF sputtering and post annealing under flow of H_2 .

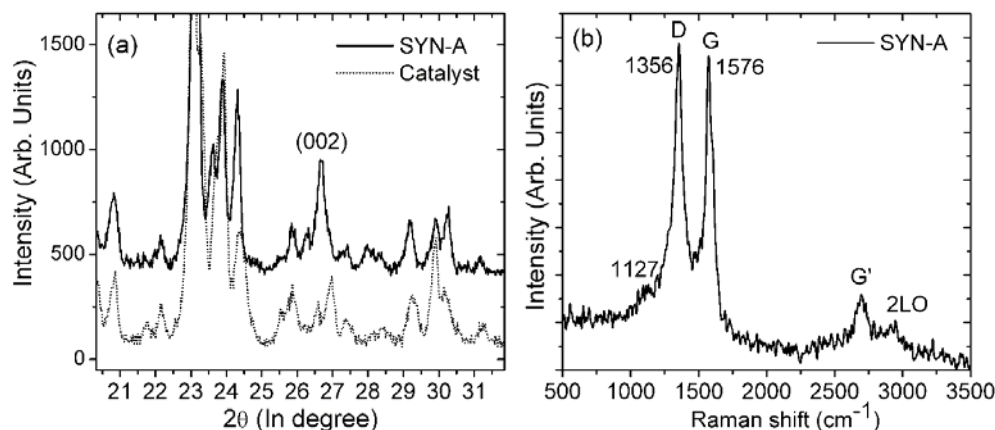


Figure 2-20: (a) XRD spectra shows presence of graphitic (002) peak in as synthesized sample, different from the catalyst peaks. (b) Raman spectra of as synthesized carbon nanotube sample (SYN-A).

using argon at the 0.03 mbar pressure using 40 W power. Iron was sputtered for 10 minutes and the sample was annealed at 900 °C for 1 hour. AFM image shows particle size ~ 25 nm, as shown in Fig. 2-19.

During CNT synthesis we had used a combination of gas flow ratios, temperature range, pressure within the chamber and growth time. Details of the growth conditions are summarized in Table-2-1. Fig. 2-20(a) shows the XRD spectra of Zeolite impregnated catalyst and as grown mixture of CNTs and catalyst. Presence of (002) reflection shows formation of graphitic structures. It was further verified from the presence of intense G peak along with D and second order G' peak in the Raman spectra as shown in Fig. 2-20(b). Electron microscopies of as grown samples are shown in Fig. 2-21. Fig. 2-21(a) and (b) shows the TEM images of CNTs grown using sputtered catalyst, whereas (c) and (d) shows CNTs grown using Zeolite impregnated catalyst. Interestingly CNTs grown using sputtered catalyst showed cleaner surface as compared to Zeolite supported growth. But CNTs grown using Zeolite impregnated catalysts had relatively much lower diameter and

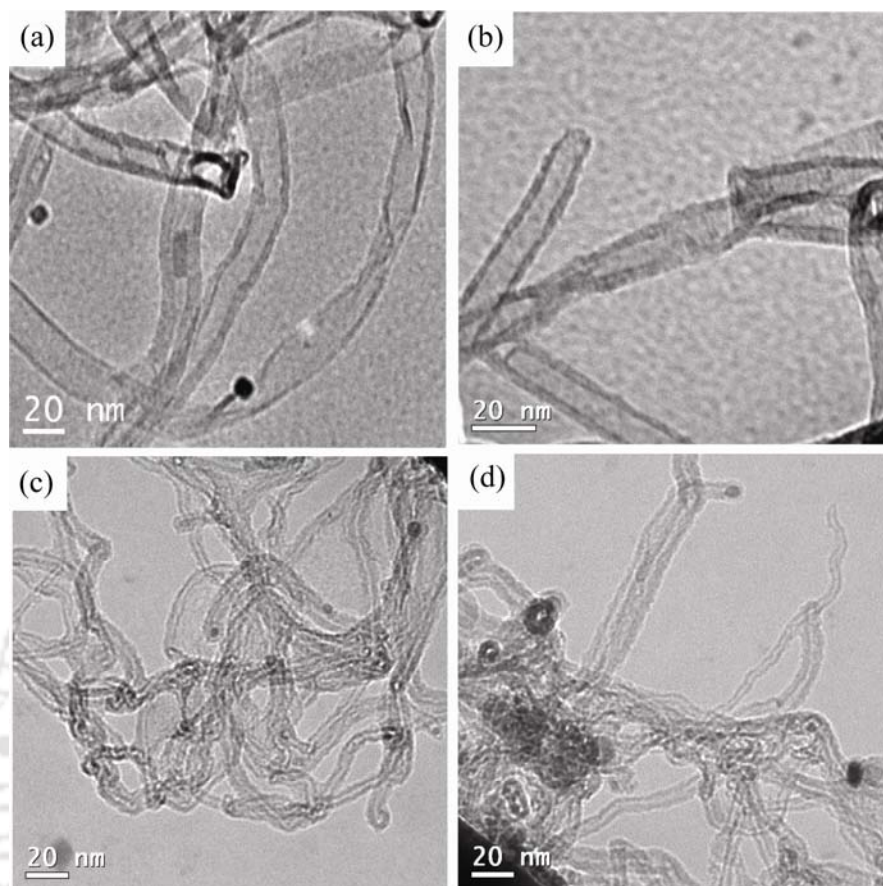


Figure 2-21: (a) and (b) HRTEM images of carbon nanotubes grown using sputtered catalyst. (c) and (d) shows comparatively lower diameter CNTs growth using Zeolite supported metal catalyst particles.

Table 2-1: Details of the growth parameters of CNTs grown using CVD.

Sample Name	Catalyst type	Temp. (°C)	Time (min)	Gas flow rate (sccm/min)			Chamber Pressure (mbar)
				Ar	H ₂	C ₂ H ₂	
SYN-A	Zeolite templated metal Catalyst (Fe-Co nanoparticle)	800 °C	30	400	15	40	8.92
SYN-B	Fe- sputtered on SiO ₂ film.	800 °C	30	200	15	40	910 x 10 ⁻³
SYN-C	Fe- sputtered on SiO ₂ film.	900 °C	60	200	15	40	630 x 10 ⁻³
SYN-D	Fe- sputtered on SiO ₂ film.	900 °C	60	400	0	40	1.3

higher density as compared to the sputtered catalyst grown CNTs. Sample SYN-A showed highest density and lowest diameter of CNTs among all the attempts of CNTs growth.

2.4.2 Procured Samples

Besides synthesized CNTs, we have used commercially procured SWCNTs and MWCNTs of various diameters from Shenzhen Nanotech, China. These were grown by catalytic chemical vapor deposition (CCVD) using metal catalysts and were subsequently acid purified. MWCNTs are 5-15 μm long and of six diameter ranges: <10 nm, 10-20 nm, 10-30 nm, 20-40 nm, 40-60 nm and 60-100 nm that have been studied to understand the diameter dependent properties. The samples are named as per the average diameter found from HRTEM imaging (details given in chapter-3), which was quite consistent with the diameter range specified by the supplier. For example, sample CNT-7 indicates an average diameter of ~ 7 nm for the lowest diameter (<10 nm) MWCNTs. Details of the procured samples are presented in Table 2-2. We had estimated the amount of metal residue present

Table 2-2: Details of the commercially procured samples.

Sl.No.	Sample Name	Diameter range	Avg. dia. (TEM)	Length (μm)	Single / Multi walled	Metal residue (TGA)
1	SWCNT-A	< 2 nm	0.5 nm	5-15	Single-walled	9.3 %
2	SWCNT-B	< 2 nm	0.5 nm	5-15	Single-walled	-
3	MWCNT-A	10-20 nm	15.0 nm	5-15	Multi-walled	1.1 %
4	CNT-7	< 10 nm	7.0 nm	5-15	Multi-walled	4.56 %
5	CNT-15	10-20 nm	15.2 nm	5-15	Multi-walled	NILL
6	CNT-20	10-30 nm	21.5 nm	5-15	Multi-walled	NILL
7	CNT-30	20-40 nm	31.0 nm	5-15	Multi-walled	0.12 %
8	CNT-50	40-60 nm	50.0 nm	5-15	Multi-walled	3.0118 %
9	CNT-80	60-100 nm	92.0 nm	5-15	Multi-walled	1.201 %

in the sample through TGA studies, as reflected in the Table. 2-2. In subsequent chapters / discussion, we would use these nomenclatures to refer these samples.

2.4.3 Vacuum Annealing

We have annealed various CNTs under high vacuum with the aim to improve the structural properties through defect removal by thermal treatment at various temperatures. For this purpose, we have used a home-built high temperature high vacuum furnace as discussed in section 3.3.3. For annealing, the quartz tube was first evacuated to 1×10^{-6} torr and then the furnace was ramped to desired temperature (in the range 300-1000 °C) at the heating rate of 5 °C/min. Samples were annealed for 2 hours with running pump and were cooled naturally in vacuum. These samples were studied in detail using microscopic and spectroscopic techniques to explore the optimum annealing condition for defect removal and role of defects on the oxidative stability of CNTs as presented in the Chapter-3. Details of the annealing condition with sample code are summarized in Table. 2-3.

Table 2-3: Details of the vacuum annealed CNTs

Sample	Annealing Temp (°C)	Duration	Sample Code
SWCNTs-A	300	2 hrs	SW-300A
	500		SW-500A
	700		SW-700A
	1000		SW-1000A
MWCNTs-A	300		MW-300A
	500		MW-500A
	700		MW-700A
	1000		MW-1000A
CNT-30	1000		CNT-30-1000A

2.4.4 Chemical Functionalization

We have chemically functionalized the CNTs to study the influence of structural defects and origin of visible photoluminescence from CNTs. Chemical functionalization leads to breaking of chemically inert sp^2 bonds, attachment of functional group at the broken bonds or, defect sites and saturation of dangling bonds. We have primarily functionalized CNTs with two functional groups: carboxylic acid and aniline (amine). Details of the chemical reaction condition are given below.

(a) COOH Functionalization

For carboxylic acid functionalization, we followed the method reported by Smalley and co-workers [271]. We mixed 20 mg of SWCNTs (Sample, SWCNT-A) with 80 ml of 3:1 solution of conc. H_2SO_4 and conc. HNO_3 solution. This solution was ultrasonicated at 40 °C for around 3 hours. Solution obtained was stable dark black in color. Subsequently, we exposed it to 1M HCl solution to produce abundant amount of carboxyl end-groups [272]. After sonication, as obtained solution was diluted with 400 ml of Millipore water. Obtained solution was filtered through membrane filter and washed with 10 mM NaOH solution to remove the residual acid after clearing with water. Solid remaining over the filter paper was vacuum dried at 60 °C for 4 hours. A large amount of nanotube was visually seen in (black solution) obtained on filtration. Solubility of the obtained product over filter paper was checked in a number of solvents. It was nicely soluble in water and ethanol and solution was stable for a year in Methanol, DMF, DMSO, whereas it was not soluble in $CHCl_3$, THF, ethyl acetate, acetonitrile, toluene, Tetrahydrofuran, acetic acid, Hexane, 1,2 dichlorobenzene. Presence of COOH functional group was confirmed from FT-IR studies.

(b) Aniline Functionalization

Aniline was first distilled to purify from impurities (b.p 184.4 °C). The color of commercially procured aniline was red due to presence of polyaniline and sulphur. After distillation, obtained aniline was white in color. We had functionalized both SWCNTs (SWCNT-A) and MWCNTs (MWCNT-A). For this purpose, 40 mg SWCNT-A and 5 ml of aniline was refluxed at ~180 °C for 3 hrs in dark as reported earlier [186]. Dissolution of SWCNTs in aniline can be observed by the color change of the solution after reflux for

Table 2-4: Details of Chemically Functionalized CNTs

CNT used	Functional Group	Reaction temperature	Brief detail of reaction	Sample Code
SWCNT-A	-COOH	40 °C for around ~ 3 hours	Sonication with 3:1 soln of conc. H ₂ SO ₄ and HNO ₃ acid.	SWCNTs-COOH
SWCNT-A	-NH ₂	~180 °C for 3 hours in dark.	40 mg SWCNTs and 5 ml of aniline refluxed.	SWCNT-A-NH ₂
MWCNT-A	-NH ₂			MWCNT-A-NH ₂

a shorter time. Thus with continuous heating, the original colorless aniline solution became brownish and then turned dark red. After cooling to room temperature, a CNT solution was obtained by filtration through a filter paper. The solubility of SWCNT in aniline is up to 8 mg/ mL [186]. This aniline-SWCNT solution can be readily diluted with other organic solvents such as acetone, toluene and methanol. We have collected functionalized SWCNT (F-SWCNT) by filtration using 0.2 PVDF membrane filter paper. Filtered solution and filtrate remaining over the filter paper (termed as ‘bucky paper’) both were used for characterization. Filtered solution contained CNTs dissolved in aniline.

2.4.5 Laser processing of CNTs

During the Raman experiments CNTs showed variation in the IFM modes and intensity of visible photoluminescence depending upon the exposure time and power of laser excitation. This is certainly due to structural modification in CNTs due to exposure of intense focused photon energy. Laser exposure to carbon nanotubes has been used as a

Table 2-5: Details of laser processing conditions.

Sample	Wavelength	Power
SWCNT-A	488 nm	80 mw
SWCNT-A	514 nm	250 mw
MWCNT-B	488 nm	80 mw

tool for structural improvement [273] and selective destruction [274]. We has used laser processing of CNTs to introduce controlled amount of structural defects in CNTs and had studied the defects related spectroscopic signature in Raman and PL studies, as reported in Chapter-4. Details of laser exposure conditions used for our studies like laser wavelength, power and samples are given in Table 2-5.

2.4.6 Ion-irradiation of CNTs

Ion-irradiation is a well known tool for controlled structural modification and defect engineering in wide range of materials including metals, semiconductor, polymer and carbon based materials. Different kinds of defects are expected to appear and disappear during/ after irradiation depending upon nature and charge of irradiated ion, its energy and the type of nanotubes being studied. We have attempted for controlled

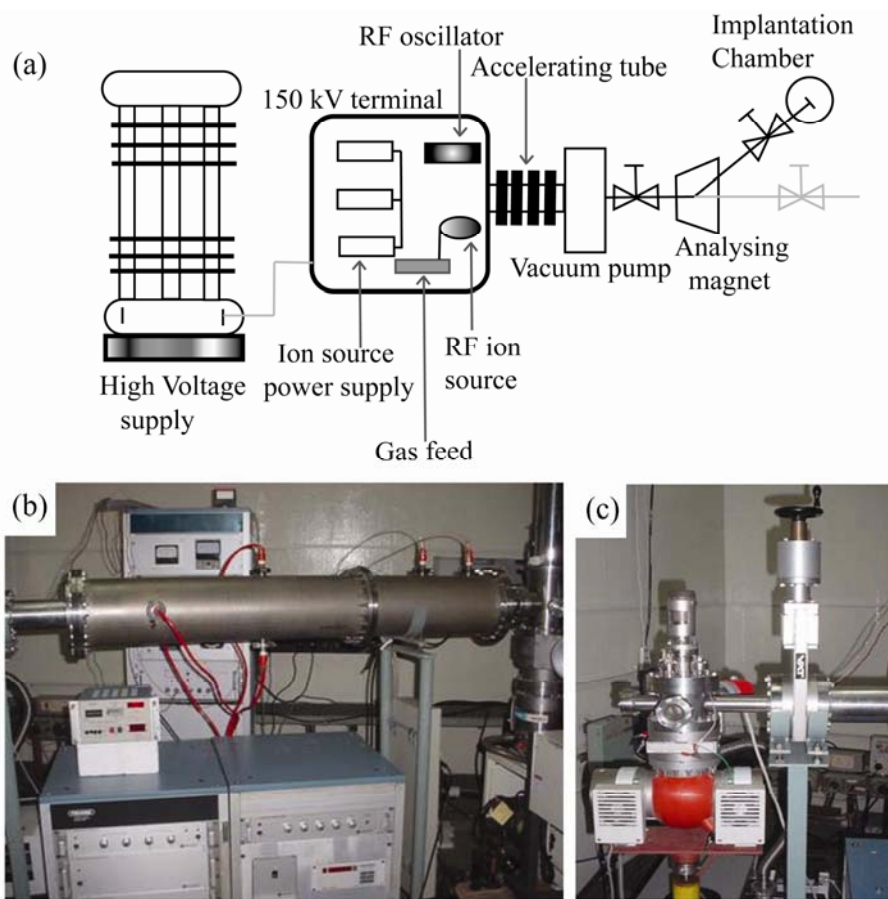


Figure 2-22: (a) Schematic of the gaseous ion implanter (150 KeV) used for ion-irradiation. (IGCAR Kalpakkam, India) (b) Photograph of Quadrupole & beam sweep of the Gaseous ion implanter used. (c) Photograph of implantation chamber.

introduction of defects and structural modification of CNTs through ion-irradiation at different doses. As-irradiated tubes were studied using various spectroscopic and microscopic tools to confirm the defects related spectroscopic features in Raman spectroscopy and EPR spectroscopy, as detailed are in chapter-6. For this purpose we have used a gaseous (150 KeV) ion implanter at Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam. The schematic of the setup used is shown in Fig. 2-22(a). It consisted of basically a gas ion source, an accelerating column, mass analyzer magnet,

Table 2-6: Details of the ion irradiation on CNTs. Electronic and nuclear energy losses are calculated from SRIM code.

Ion	Energy	Doses	Irradiated Nanotubes	Sample Code	$\left(\frac{dE}{dx}\right)_E$	$\left(\frac{dE}{dx}\right)_N$
	(KeV)	(ions/cm ²)			MeV mg ⁻¹ mm ⁻¹	
H ⁺	30	1x10 ¹²	SWCNT-A	SW-30-H12	141.3	0.6119
		1x10 ¹³		SW-30-H13		
		1x10 ¹⁴		SW-30-H14		
Ar ⁺	30	1x10 ¹²	SWCNT-A	SW-30-AR12	354.8	784.2
		1x10 ¹³		SW-30-AR13		
		1x10 ¹⁴		SW-30-AR14		
		1x10 ¹²	MWCNT-A	MW-30-AR12		
		1x10 ¹³		MW-30-AR13		
		1x10 ¹⁴		MW-30-AR14		
N ⁺	30	1x10 ¹²	SWCNT-A	SW-30-N12	326.7	145.8
		1x10 ¹³		SW-30-N13		
		1x10 ¹⁴		SW-30-N14		
		1x10 ¹²	MWCNT-A	MW-30-N12		
		1x10 ¹³		MW-30-N13		
		1x10 ¹⁴		MW-30-N14		
C ⁺	30	1x10 ¹²	SWCNT-A	SW-30-C12	298.8	104.9
		1x10 ¹³		SW-30-C13		
		1x10 ¹⁴		SW-30-C14		
		1x10 ¹²	MWCNT-A	MW-30-C12		
		1x10 ¹³		MW-30-C13		
		1x10 ¹⁴		MW-30-C14		
C ⁺	80	1x10 ¹²	SWCNT-A	SW-80-C12	451.5	60.39
		1x10 ¹³		SW-80-C13		
		1x10 ¹⁴		SW-80-C14		
		1x10 ¹²	MWCNT-A	MW-80-C12		
		1x10 ¹³		MW-80-C13		
		1x10 ¹⁴		MW-80-C14		

vacuum pumps and an irradiation chamber. Photograph of components of the ion implanter used for irradiation is shown in Fig. 2-22(b) and (c). This accelerator with RF ion source is configured from Sames J-15 neutron generator. We had used gaseous ion source. Fluence of irradiation was measured using current integrator. Irradiation spot radius was 0.6 cm. For a irradiation dose of 1×10^{14} ions/cm², the total charge required equals to $1 \times 10^{14} \times 1.6 \times 10^{-13} \times 3.14 \times (0.6)^2 \mu C = 18.0864 \mu C$. Since one count of current integrator was equivalent to $15.3 nC$. Thus for a dose of 10^{14} ions /cm² total number of counts irradiated was $18086.4 nC / 15.3 nC = 1182$ counts. Similarly, for a dose of 10^{12} ions/cm² and 10^{13} ions/cm² total number of counts was estimated to 11.82 and 118.2 counts.

For irradiation, CNT samples were prepared using multiple drop casting of the well-dispersed solution of CNTs in ethanol on Si-wafer of size 20 mm x 20 mm and thickness approximately 300 μm . Sample were implanted at an energy of 30 keV with H⁺, Ar⁺, C⁺ and N⁺ at three fluence levels 10^{12} , 10^{13} ions/cm² and 10^{14} ions/cm². Samples were implanted at normal incidence. The ion-beam was scanned and then passed through a collimator of diameter 12.5 mm. During implantation, a vacuum of 1.0×10^{-6} mbar was maintained in the target chamber. The ion type and its energy was selected keeping in view the role of electronic energy loss and nuclear energy loss in graphite as calculated from SRIM-2010 [275], although note that CNTs are expected to behave differently from graphite depending upon diameter and number of walls. In comparison to graphite, it contains a lot of void space in between the cylindrical tubule and shows huge self healing properties [84]. Our experimental parameters were chosen taking these as guidelines. Details of the irradiation conditions such as ion type, energy and samples for the irradiation are given in Table 2-6.

Chapter -3

Structural Studies of Diameter Dependent Properties and Defects

3.1 Introduction

In this chapter, we have focused on structural studies of diameter dependent properties and defects in CNTs of wide range of diameters (2–100 nm). Diameter dependent properties including interlayer separation have been explored through HRTEM, XRD, Raman spectroscopy and TGA studies. Origin of diameter dependence is discussed in the light of the experimental results. Structural defects were identified using HRTEM. As observed structural defects using electron microscopy has been correlated with the features observed in spectroscopic studies, and are presented in subsequent Chapters. We have probed the diameter dependence of interwall separation and strain in MWCNTs through X-ray diffraction and Raman scattering studies.

Next, we have explored the diameter dependence of oxidative stability of MWCNTs and the role of defects in its stability. We have also studied the effect of vacuum annealing at various temperatures on the oxidation profile of SWCNTs and MWCNTs to investigate the role of defect in the oxidative stability of nanotubes. Effects of high vacuum annealing on the structural properties are discussed in this chapter. Further, from vibrating sample magnetometry (VSM) studies we have shown that the magnetization measurement as a more sensitive tool for estimation of residual metallic catalyst in CNT samples than the TGA analysis. Our magnetization measurement study also helps us to understand the role of metallic catalyst on the oxidative stability of MWCNTs. Diameter dependent XRD profile and features in Raman spectra presented in this chapter can be used as a tool for characterization of MWCNTs.

3.2 Diameter Dependent Properties of MWCNTs

3.2.1 Scanning Electron Microscopy

We have used SEM images to estimate the quality of the samples studied as suggested by R. C. Haddon and co-workers [30]. Depending on the quality of the SWCNT soot they were classified under six grades. Fig. 3-1 shows the SEM image of various diameter MWCNTs samples studied at ~ 5 KX and 20 KX. Comparison of Fig. 3-1 (a) and

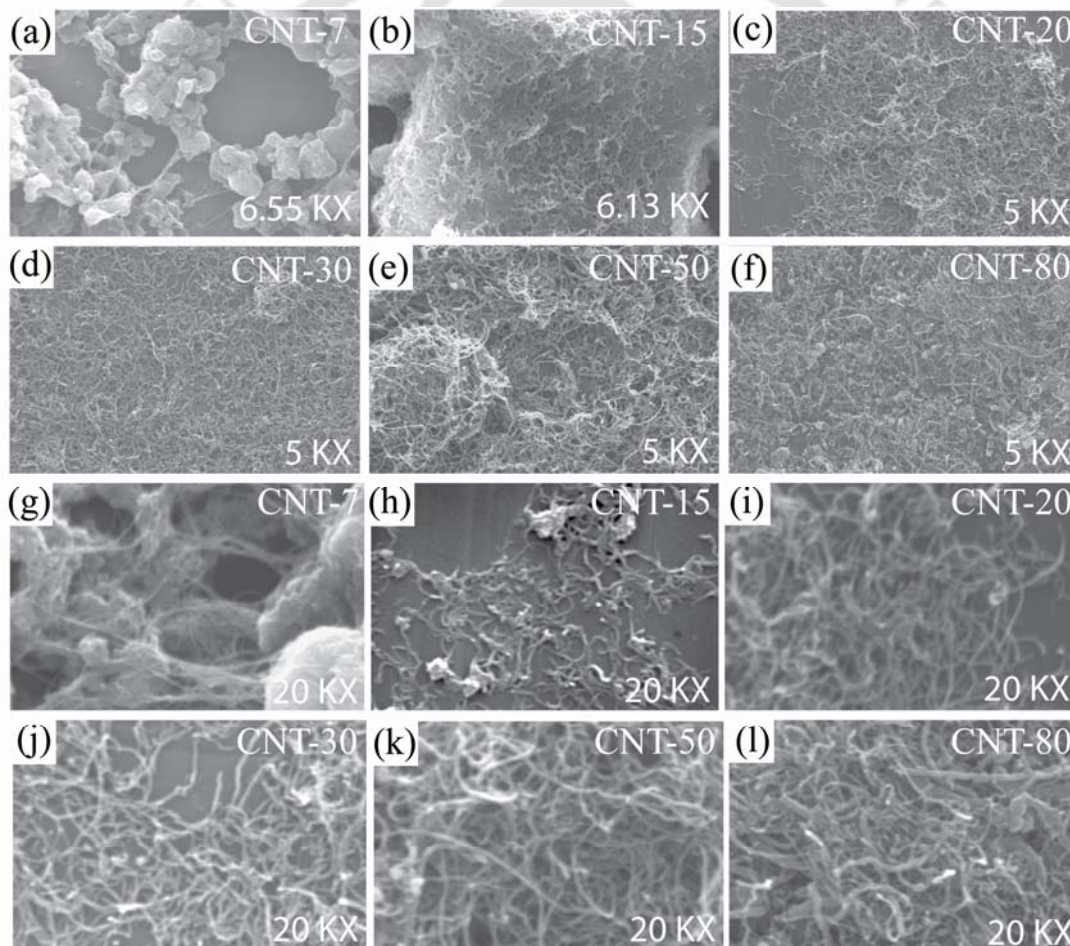


Figure 3-1: SEM images of various diameter MWCNTs at ~5 KX (Fig. (a)- Fig. 9(f) and 20 KX (Fig. (g)- Fig. (i)) magnification. (a) and (g) CNT-7, (b) and (h) CNT-15, (c) and (i) CNT-20, (d) and (j) CNT-30, (e) and (k) CNT-50 and (f) and (l) CNT-80.

3-1 (g) shows that, from low resolution images its very difficult to speak about quality and density of CNTs in case of low diameter tubes. From these images the samples studied appears to be of highest quality grade, grade-6. Sample CNT-80 appears to contain some amount of graphitic carbon (flat bundle like structures as seen in Fig. 3-1(i). If we compare the images taken at ~5 KX and at 20 KX, the same sample appears to be of different grade. For example, for lowest diameter MWCNTs sample CNT-7, in Fig. 3-1(a) and Fig. 3-1 (g) they appear to be quite different grade (images taken at the same location, with different magnifications). Thus qualitative and quantitative analysis of carbon nanotubes from SEM images suffers from a number of limitations as it does not give diameter distribution and only provides information about nanograms volume of the sample. Further, amount of metal content can not be estimated from visual inspection and the thin coating of amorphous carbon on the SWCNTs remains invisible to the SEM. Moreover, the grading by visual inspection also depends on the method of sample preparation. Study of various kinds of structural defects is almost impossible with SEM imaging. SEM studies of our samples shows that quality of the samples are very good as per the followed grading scheme and they contained small amount of metal impurities.

3.2.2 Diameter Dependent Interplanar Spacing: HRTEM Studies

HRTEM imaging is utilized to measure the actual diameter distribution and interlayer spacing in the MWCNTs. Fig. 3-2 shows HRTEM images of various diameter MWCNTs studied including the high resolution lattice images of different diameter MWCNTs. Fig. 3-2(a-f) shows the typical morphology and diameter distribution of MWCNTs as observed under microscope. Average diameter of a sample was estimated by taking average of 20 nanotubes for each sample seen under HRTEM. HRTEM studies

show that smallest diameter (<10 nm) sample has an average diameter of ~ 7 nm and higher diameter tubes have an average diameter close to the mean value of the diameter specified by the supplier. CNT-15 specified to have diameter in the range 10-20 nm is found to have an average diameter of 15.2 nm as measured from HRTEM and shown in Fig. 3-2(c). In CNT-15, TEM images recorded at various locations show presence of significant amount of carbon nano-onions and fullerenes. CNT-20 (10-30 nm) sample showed a mean diameter of 21.5 nm and CNT-30 (20-40 nm) showed 31.0 nm under

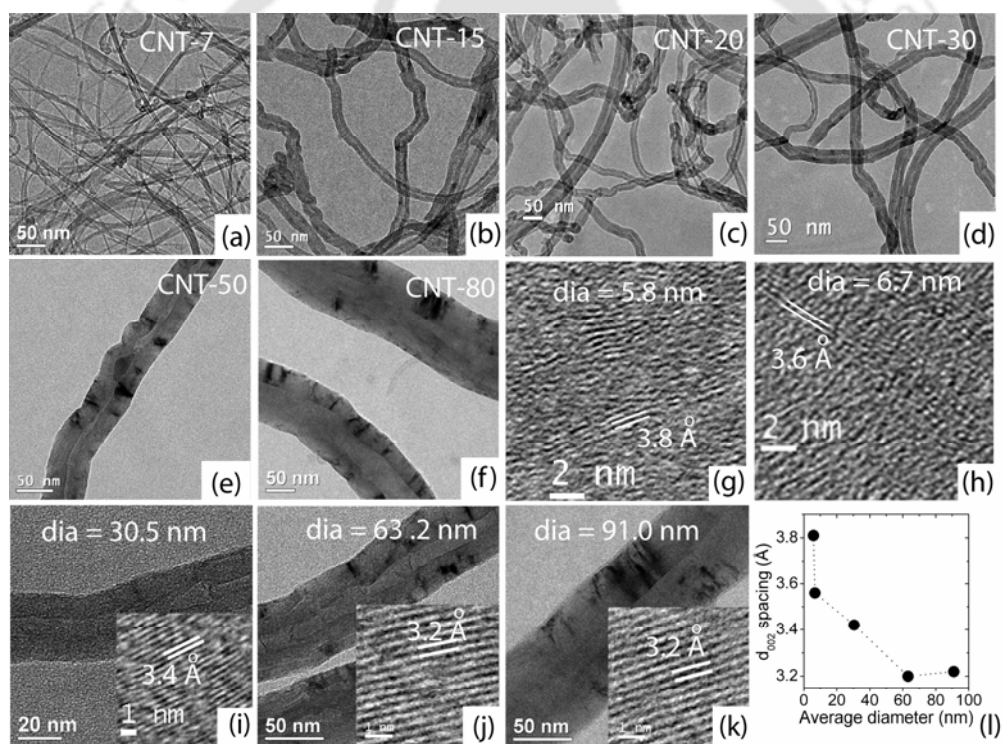


Figure 3-2: HRTEM images of various diameter MWCNTs (a) CNT-7, (b) CNT-15, (c) CNT-20, (d) CNT-30, (e) CNT-50 and (f) CNT-80. Systematic decrease in d_{002} lattice spacing as the diameter (D) increases: (g) $d_{002} = 3.8$ Å for $D = 5.8$ nm, (h) $d_{002} = 3.6$ Å for $D = 6.7$ nm (i) $d_{002} = 3.4$ Å for $D = 30.5$ nm, (j) $d_{002} = 3.2$ Å for $D = 63.2$ nm, (k) $d_{002} = 3.2$ Å for $D = 91$ nm. Inset in each image shows the HRTEM image of the corresponding tube. (l) Variation of d_{002} lattice spacing with diameter of MWCNTs as observed in HRTEM images. [276]

TEM. We noticed that CNT- 50 consists of MWCNTs of averaged diameter 50 nm along

with small fraction of MWCNTs of diameter ~ 20 nm as impurity. TEM studies of CNT-80 (60-100 nm) showed an average diameter of 92.0 nm. The large diameter nanotubes (CNT-50, CNT-80) show some dark regions in the HRTEM images. Though it appears like amorphous regions at low resolution, high magnification imaging reveals that these regions are graphitic layers with higher inter-planar spacing than the other regions with better image contrast. For example, the sample with diameter range of 20-40 nm has an average diameter of 30.5 nm. To calculate the interplanar spacing we had taken average of interplanar spacing over a number of lattice fringes. HRTEM images shown in Fig. 3-2 (g)-(k) shows that the interplanar spacing d_{002} varies with the diameter of MWCNTs. We have observed a systematic and significant reduction in d_{002} spacing from 3.8 Å to ~ 3.2 Å as the diameter increases from 5.8 nm (CNT-7) to 63.2 nm (CNT-50), shown in Fig. 1(l). It is also evident that as the diameter of the MWCNTs increases, the number of coaxial cylindrical layers increases. Earlier studies using HRTEM showed that interplanar spacing decreases exponentially and approaches 3.4 Å lattice spacing of turbostratic graphite as the diameter of the MWCNTs increases to 10 nm [59]. Interplanar spacing between the coaxial layers is highest in case of lowest diameter MWCNT and slowly decreases with increasing outer diameter. Our HRTEM studies show a decrease in interplanar d_{002} spacing for MWCNTs having diameter even much larger than 10 nm. We also looked for a possible variation in the interlayer separation from inner walls to the outer walls of the MWCNTs. A careful analysis of the HRTEM images reveals that the inner wall separation is only about 3% higher than the outer wall separation for diameter up to 60 nm. However, for very large diameter (80-100 nm) nanotubes the wall separation first decreases as the one move from the innermost wall to the outer walls and then it again increases near the outermost walls that may be due to the structural defects at the outer walls of the

MWCNTs as seen from HRTEM images (shown in Fig. 3-11).

We have found that the decrease in intershell spacing with higher diameter nanotubes results primarily from interlayer interactions and defect mediated structural stabilization of nanotube layer [276]. Note that lower diameter tubes possess high curvature and associated high strain that results in the higher d -spacing. Some of the fluctuations in the spacing observed is accounted for the jumps in the spacing at points where the helix angle changes as well as the inter layer staking fault defects like edge and screw dislocations occurs. Due to these defects, the interlayer spacing in higher diameter MWCNTs is even smaller than that of turbostratic graphite.

The variation in d_{002} spacing with increasing diameter is consistent with our XRD results discussed in section 3.2.3. However, the d_{002} spacing calculated from the XRD analysis is marginally higher than that calculated from HRTEM analysis. XRD results show that d_{002} for large diameter tubes reduces to 3.45 Å, while the HRTEM images show a value of 3.2 Å. One probable reason for such difference is the possible fluctuations in the spacing associated with the jumps in spacing at points where the helix angle changes [277]. Note that the outer walls of the MWCNTs are less strained than the inner walls. Such a difference in strain may not allow graphitic layers to be equally spaced as that of graphite. The observed d -spacing of 3.2 Å is much smaller than that of even turbostratic graphite. Such a low d -spacing may occur, if the energy gained by the local graphitic stacking is less than the energy introduced by the defects associated with the stacking. This is consistent with the experimental observation by Liu and Cowley [278]. We believe that the increase in intershell spacing with decreased nanotube diameter results primarily from the high curvature and associated strain in the lower diameter nanotubes. It is likely that high strain in the low diameter tubes causes structural defects in the nanotube walls

that may be charged [184] and it causes columbic repulsion between the tube walls with charges of same sign. This would result in a higher d-spacing for the low diameter tubes. On the other hand, in a large diameter MWCNT the interaction among the walls increases with the increase of number of walls and as a result the inter-wall separation may decrease, as observed experimentally.

3.2.3 Diameter Dependent Strain: XRD Studies

XRD pattern of different diameter MWCNTs and the spectral profile is shown in Fig. 3-3. These high resolution (0.02° step size, and 1 second integration time) powder XRD spectra were recorded in para-focusing geometry of the Bragg-Brentano optics using lock coupled scan mode with Cu-K α line (Bruker, D8 Advanced). These spectra were corrected using software for the K α_2 contribution before analysis. The (002) peak shown in Fig. 3-3(a) gradually up shifts from 25.7° to 26.2° as the MWCNTs diameter increases from 7 nm to 80 nm. Fig. 3-3 (b) shows XRD peaks assigned to (100) and (101) peaks due to in-plane reflections. Note that due to low intensity of (100) and (101) peaks, the XRD data for the region $40-50^\circ$ were recorded with high integration time. In addition to these regular features of carbon nanotubes, we also observed a low angle peak at $\sim 12.7^\circ$ (not shown), found in all the samples which gradually shifts to higher value (12.9°) with increasing diameter. A closer look at (002) peak shows an asymmetry in line shape. The peak profile can be fitted with two Voigt spectral functions (Eqn. 2-5), as shown in Fig. 3-3(c) and the diameter dependent features are extracted for different samples, summarized in Table. 3-1. The asymmetry is assigned to the presence of different crystalline species.

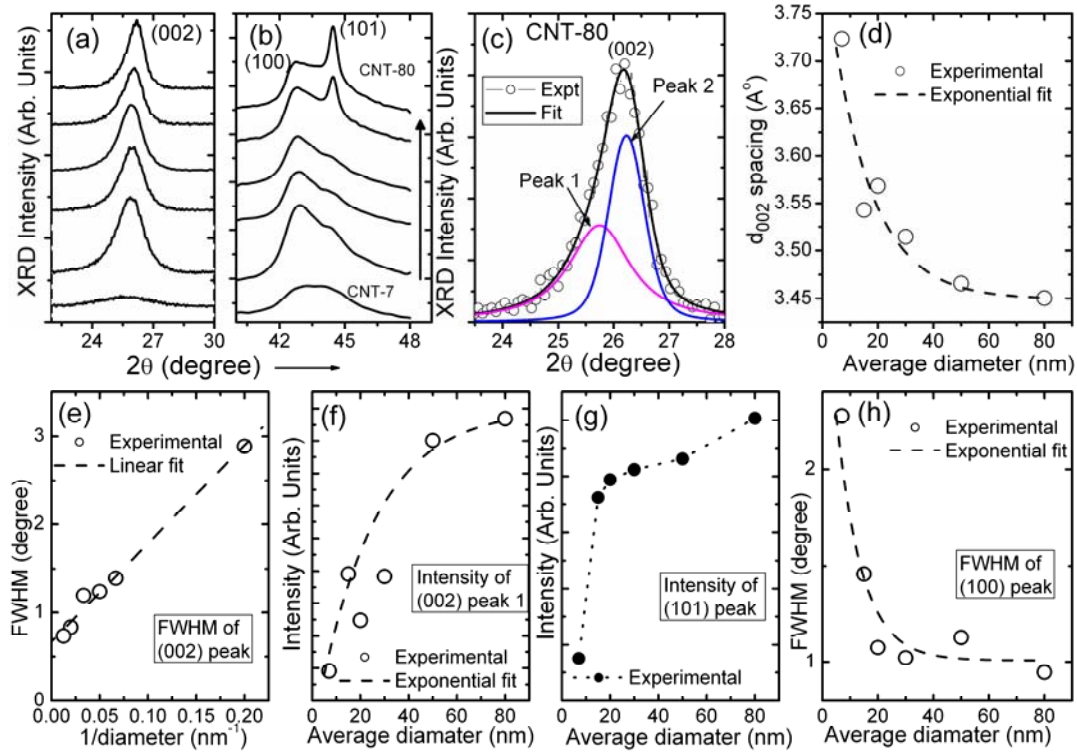


Figure 3.3: XRD pattern of different diameter MWCNTs: (a) graphitic (002) peak at $\sim 25.7^\circ$, (b) graphitic (100) & (101) peaks at 42.9° and 44.4° obtained with high integration time, (c) deconvolution of (002) peak using Voigt line shapes, experimental data shown as symbols and fitted peaks as solid lines. (d) variation of d_{002} spacing, calculated from the position of peak 2, as a function of average diameter, (e) variation of FWHM of (002) peak showing inverse diameter dependence; (f) Diameter dependent intensity variation of (002) peak, (g) Diameter dependent intensity variation of (101) peak and (h) Peak width variation of (100) peak with nanotube diameter.

Fitted parameters for peak 2 (being the stronger component) show that the Bragg angle (2θ) gradually increases and the FWHM decreases as the diameter of the MWCNTs increases. The corresponding variation in d_{002} spacing is calculated from Bragg formula and shown in Fig. 3-3(d), exhibiting a nearly exponential reduction with increasing diameter. The empirical equation for the best fit to the data is given by

$$\hat{d}_{002} = 0.345 + 0.37 \exp(-D/14.4) \quad \text{for } D \geq 0 \quad (3-1)$$

Where, D is the outer diameter of the tube and all the constants are in nm. Equation (3-1) is obtained by a least-square fit of the function $\hat{d}_{002} = A + Be^{-C/D}$ to our experimental data (where A , B and C are adjustable parameters) as depicted by the dashed curve in Fig. 3-3(d). The intershell spacing decreases exponentially and becomes 3.45 Å for the large diameter tubes.

Table-3-1: Voigt deconvolution of X-ray diffraction profiles of MWCNTs.

Sample Name /		Long (5-15µm) Multiwalled carbon Nanotubes					
Diameter Range (nm)		Peak1	Peak2	Peak 3	Peak4	Peak5	Peak6
CNT-7 (< 10)	Centre	12.76	23.95	25.72	42.90	44.41	
	FWHM	5.73	1.60	2.89	2.28	2.44	---
	Ampli.	324	18.14	55.3	461	475	
CNT-15 (10-20)	Centre	13.14	25.19	25.93	42.83	44.19	45.82
	FWHM	5.99	2.202	1.40	1.46	1.77	3.15
	Ampli	359	78.22	388	1359	762	384
CNT-20 (10-30)	Centre	13.13	25.01	25.98	42.75	43.82	
	FWHM	5.89	1.377	1.24	1.0761	3.23	---
	Ampli	386	49.53	357	586	794	
CNT-30 (20-40)	Centre	12.91	25.40	25.95	42.76	43.74	
	FWHM	6.38	2.073	1.19	1.02	3.34	---
	Ampli	414	77	331	533	812	
CNT-50 (40-60)	Centre	12.95	25.76	26.11	42.78	44.10	44.47
	FWHM	5.70	1.62	0.835	1.13	2.81	0.34
	Ampli	358	160	198	724	831	692
CNT-80 (60-100)	Centre	13.04	25.88	26.22	42.71	43.91	44.47
	FWHM	5.89	1.48	0.74	0.95	2.97	0.35
	Ampli	389	174	244	500	904	1120
Assignment		Non-hexa.	(002)	(100)	(101)		

Note that we have observed a gradual decrease of d_{002} value for MWCNTs of average diameter up to 80 nm. This is in contrast to the earlier reports from HRTEM [59] and Raman studies [66] where the change in d_{002} value was observed for diameter up to 10 nm and 20 nm, respectively. For Raman measurement, it was argued that due to limitation in the penetration depth of the laser beam, higher diameter nanotubes did not show variation in d_{002} spacing. Since the X-rays do not suffer from such limitations, probing of large

diameter nanotubes with large number of walls has been possible in the present study and indeed shows variation in d_{002} spacing with diameter, as expected. The XRD results are in close agreement with the HRTEM analysis. The variation in the Bragg angle (2θ) with diameter is consistent with the theoretical calculation for curved graphite sheets [48]. Theoretical calculations have shown that as the curvature of crystallites with graphene layers increases the Bragg angle increases monotonically from 26.27° to 26.55° and FWHM decreases from 1.35° to 1.02° [48]. Shift in the Bragg angle (2θ) is observed experimentally from 26.5° for graphite to $<26^\circ$ for SWCNTs. Lower diameter MWCNTs have higher curvature in the graphene layers, which are probed by X-rays. Our results from XRD analysis shown in Fig. 3-3(d) are consistent with the theoretical calculations and HRTEM studies shown in Fig. 3-2(g-l).

Fig. 3-3(e) shows the variation of FWHM of peak 2 as a function of tube diameter. It is found to follow an inverse relation with the diameter of the nanotubes, which is actually proportional to the number of layers in the nanotubes walls [49]. The line width of the lower angle component of (002) peak is relatively broad as compared to the graphitic ones. This asymmetry may arise from the different relative orientations of successive layers of MWCNTs forming walls of various chiralities [47]. Using the (002) peak position, the interlayer spacing is often found to be larger than that of highly ordered pyrolytic graphite.

Structural information of materials is contained in the line shape of the observed scattering pattern, rather than simply in the position and intensity of peaks [279]. For carbon nanotubes, there are two likely sources of line shape broadening [49]. First is particle size broadening i.e. diameter distribution and second is the strain broadening resulting from a distribution of d -spacings. In case of domain size broadening the FWHM

is given by [49]

$$\gamma_f = 2(\pi \ln 2)^{1/2} / Nd_c \quad (3-2)$$

Where, N is the number of layers and γ_f is independent of the order of the reflection.

Whereas the width for strain broadening is given by

$$\gamma_d = \frac{\pi l}{d_c} (\Delta d_c) \quad (3-3)$$

Where, l is index of reflection and Δd_c is FWHM of the distribution of interlayer spacing.

Thus, line width caused by size distribution and strain (induced by wall curvature) both are inversely proportional to the diameter of the nanotubes. In the present study, line shape analysis for peak 2 in different samples show that FWHM is not directly correlated with the size distribution. Hence, the strain is primarily responsible for the higher FWHM in lower diameter tubes. Contributions of two factors can be isolated if the higher order spectra is recorded. As the (004) peak was found to be very weak in our samples, isolation of the two contributions for line shape broadening was not feasible. Thus, the observed diameter dependence of FWHM of (002) peak is primarily attributed to strain broadening related to curvature of nanotubes.

Information about interlayer stacking correlations can be obtained from (hkl) diffraction peaks having nonzero h or k values. In a recent study, DWCNTs has been taken as a standard model with an aim to extend the theory to MWCNTs. For bundled DWCNTs, it was found that as the number of walls (N) increases FWHM monotonically decreases following $1/N$ behavior whereas peak position increases up to $N \sim 10$ and saturates [46]. The decrease of the interlayer spacing with the increase of diameter of the shells [262] and the inner diameter distribution [280] also modifies the shape of the (002) peaks. The intensity and width of the (002) peaks are related to the number of layers,

variations of interlayer spacing, lattice distortions [49, 281] and nanotube orientation relative to the X-ray incident beam [52]. Due to the complex interplay of a number of factors deciding intensity, no systematic diameter dependent diffraction intensity profile was found for the peak 2 (Voigt component at higher angle) of (002) reflections from our MWCNTs. However, peak 1 of (002) peak shows nearly exponential increase in intensity with increasing diameter of MWCNTs, as shown by the dashed curve in Fig. 3-2(f). This is attributed to the large number of layers present in large diameter MWCNTs.

XRD line profile analysis was performed for the (100) and (101) peak in the similar way. From fitting, we find that intensity of the (101) peak increases monotonically with increasing diameter of the MWCNTs, as shown in Fig. 3-3(g). Experimental data points of intensity vs. diameter of (101) peak fit well with a single exponential growth profile. Similarly, the line width of (100) peak systematically decreases with increasing diameter, as shown in Fig. 3-3(h). In contrast to the inverse diameter dependence of FWHM for (002) peak, the experimental data points (circles) for (100) peak follow an exponential fall with increasing diameter, as shown with the dashed line fit. Thus, the line widths of (002) peak and (100) peak have different origins. We observed an additional XRD peak at $\sim 12.7^\circ$ for all samples with different diameters and it shows a small up shift in 2θ with increasing diameter, similar to the (002) peak behavior. It is likely to be related to non-hexagonal carbon ring structures present in the samples. These could be present either as defects in the nanotubes walls or other forms of carbon usually present in CVD grown samples. However, to our knowledge, this has not been reported earlier.

Computational studies on SWCNTs have shown that the mean tube diameter, finite size of bundles and diameter dispersion of nanotubes affect the position and the width of the (100) peak to a significant degree [282, 283]. It has been reported that above

parameters lead to the systematic overestimation of the tube diameter with respect to TEM analysis. Our results for MWCNTs are consistent with this finding. Our studies reveal that d_{002} spacing calculated from XRD profile is slightly higher than that found from HRTEM analysis. Nevertheless, our XRD studies have provided clear evidence of diameter dependent interlayer d_{002} spacing and curvature related strain in the tube wall. Nanotubes with smaller diameters often have fewer shells. Higher intershell spacings of the small diameter nanotubes are primarily due to the high curvature and associated strain. In case of large diameter tubes, contribution from inner walls with relatively high curvature is relatively less in XRD pattern and thus FWHMs do not change significantly at very large diameters.

3.2.4 Diameter Dependence of Raman Spectral Line Profile in MWCNTs

Raman spectra of MWCNTs samples were recorded in the backscattering mode using 488 nm Ar laser and CCD detector coupled to a high resolution monochromator (Jovin Yvon, Triax 550), geometry as shown in Fig. 2-11 (Chapter-2). Due to large number of walls in the MWCNTs, we do not observe any measurable intensity for the RBM modes from these samples. Measurements with 632.8 nm laser using LabRam HR800 system showed some RBM features only in CNT-7. R. Saito has also observed RBM modes in case of MWCNTs, and it was accounted to originate from thin innermost tubes [284]. On the other hand, S. Lefrant and group had observed RBM modes in MWCNTs having inner diameter less than 2 nm and had accounted them to originate from RBM modes of individually coupled walls through van der Waals interaction [53]. They had predicted about the possibility of Raman spectroscopy as a characterization tool for

MWCNTs similar to the SWCNTs.

A typical Raman spectrum of sample CNT-7 (lowest diameter) in the range of 1200–1800 cm^{-1} is shown in Fig. 3-4(a). The inset shows the spectrum for CNT-80 (highest diameter). Raman spectra for all the samples show two major peaks located at ~ 1350 and ~ 1570 cm^{-1} , which are attributed to well known D and G bands, respectively. Asymmetry in the shape of G band suggests that multiple peak components are present in

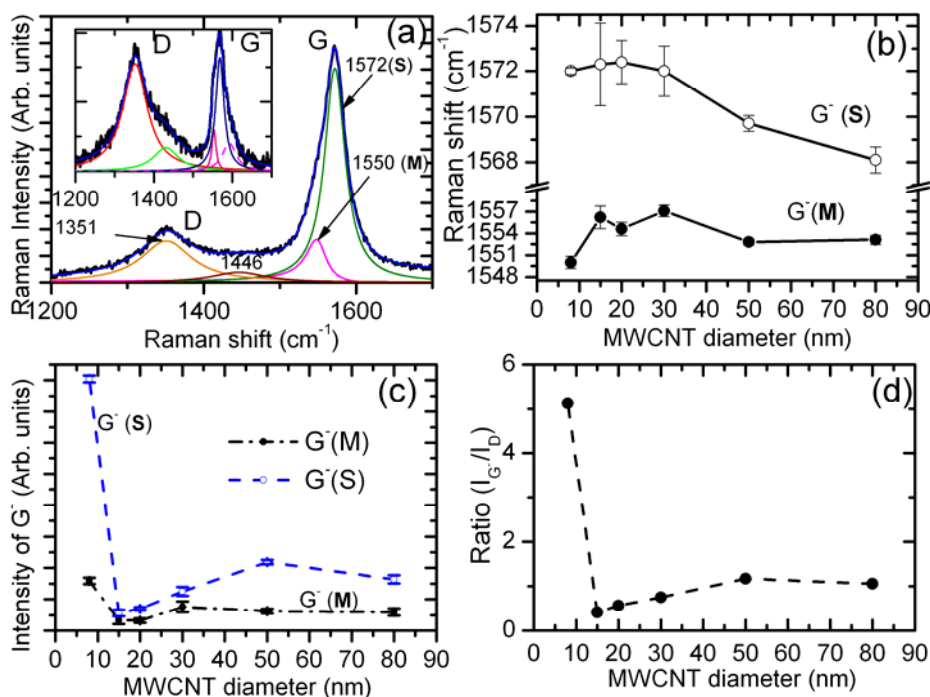


Figure 3-4: (a) Typical Raman spectra of smallest diameter (CNT-7) MWCNTs showing defect induced D-band at ~ 1351 cm^{-1} and optical phonon mode G-band at ~ 1572 cm^{-1} . Lorentzian and Breit-Wigner-Fano fitting (lines) shows two components in the G-band: a strong semiconducting $G^-(S)$ band at 1572.0 cm^{-1} and a metallic $G^-(M)$ band at 1550.0 cm^{-1} . The summary of the fitted peaks is given in Table-3-2. The inset shows the corresponding spectra for highest diameter CNT-80 sample. (b) Change in Raman frequency for $G^-(S)$ and $G^-(M)$ as a function of diameter. (c) Intensity variation of $G^-(S)$ and $G^-(M)$ bands as a function of diameter. (d) Intensity ratio of I_{G^-}/I_D as a function of diameter. Indicated error bars in each graph are obtained from the fitting.

the spectrum. These spectra were deconvoluted using Lorentzian line shapes and typical fitting for CNT-7 and CNT-80 are shown with dashed lines. A summary of the fitting parameters for different first order Raman peaks and their possible identities for different samples are given in Table 3-2. Here, we focus on the G-band and D-band that are distinct in all the samples and show clear diameter dependence. The lowest diameter sample CNT-7 shows an asymmetric G^- component consisting of $G^- (M)$ band arising from metallic CNTs at 1550.0 cm^{-1} and a relatively strong semiconducting component $G^- (S)$ band at 1572 cm^{-1} . For CNT-7, $G^- (M)$ component is found to have a Breit-Wigner-Fano resonance line shape (represented by Eqn. 2-7) having a coupling strength parameter $1/q = -0.136$, as obtained by fitting. This is due to the interaction of phonons with continuum of states [285]. Higher diameter MWCNTS shows $1/q \sim 0$ showing Lorentzian oscillators to be sufficient to fit the spectra. It is found that the low diameter CNT-7 has a strong G-band signal as compared to the D-band intensity. However, CNT-15 and higher diameter samples show a much lower intensity of G band that it is comparable to the intensity of D band, which is typical of MWCNT samples. The diameter dependence of the Raman shifts of $G^- (S)$ and $G^- (M)$ bands are shown in Fig. 3-4(b), while the intensity data for these two bands are shown in Fig. 3-4 (c). The Raman shift for $G^- (S)$ band shows a systematic down shift with increasing diameter of the MWCNTs and the $G^- (M)$ band frequency first up shifts and then does not change significantly for higher diameter tubes, as shown in Fig. 3-4(b). On the other hand, the intensity of $G^- (S)$ band first goes down drastically as the average diameter increases from 7 nm to 15 nm and then it shows a small and gradual increase as the diameter increases further, as shown in Fig. 3-4(c).

Raman frequency of disorder induced D-band slightly up shifts with increasing diameter from 1351 cm^{-1} to 1354 cm^{-1} . The FWHM of the D-band is relatively large for

the low diameter samples (CNT7, CNT-15 and CNT-20) and then it decreases slightly for the higher diameter MWCNTs. Various forms of carbon can be distinguished by the position and the line width of the D band. Amorphous carbon has a very broad line width ($>100 \text{ cm}^{-1}$), SWCNTs have D-band position at $1285\text{-}1300 \text{ cm}^{-1}$ and a line width of $10\text{-}30 \text{ cm}^{-1}$, Crystalline graphite-like forms have a typical position of $1305\text{-}1330 \text{ cm}^{-1}$ and a width of about $30\text{-}60 \text{ cm}^{-1}$ [286]. MWCNTs have been reported to behave similar to the crystalline graphite like forms [287]. In our samples, lower diameter MWCNTs shows FWHM intermediate between amorphous carbon and crystalline graphite like forms of the

Table 3-2: Summary of the fitted Lorentzian peaks for D and G modes of MWCNTs with different diameter ranges.

Sample name	Fitted parameters for deconvoluted peaks (in cm^{-1})							I_G/I_D
	Peak1	Peak 2	Peak3	Peak4	Peak5	Peak6	Peak7	
CNT-7	Centre	1351.0	1446.0	1550.0	1572.0			
	FWHM	----	80.0	108.1	32.0	32.0	----	5.14
	Ampli		3131	765	3173	16090		
CNT-15	Centre	1351.9	1432.0	1556.0	1572.3	1598.0		
	FWHM	----	89.0	68.0	15.0	25.0	29.0	0.41
	Ampli		2719	662	674	1127	496	
CNT-20	Centre	1354.2	1434	1554.6	1572.4	1579	1600	
	FWHM	----	90.0	68.0	10.0	42.0	24.0	0.69
	Ampli		2461	624	653	1709	1396	409
CNT-30	Centre	1252.0	1351.0	1427.0	1557.0	1572.0	1599.0	
	FWHM	193.0	60.0	98.0	15.8	27.0	----	0.75
	Ampli	554	3360	969	1526	2509	548	
CNT-50	Centre	1262.0	1352.0	1430.0	1552.8	1569.7	1596.0	
	FWHM	172.0	62.0	84.0	11.0	28.0	36.0	1.17
	Ampli	408	3730	882	1260	4374	761	
CNT-80	Centre		1352.0	1431.0	1553.0	1568.0	1592.0	
	FWHM	----	75.0	78.0	13.0	26.0	42.0	1.06
	Ampli		3098	679	1186	3280	814	
Assignments	--	D band	LO	$G^-(M)$	$G^-(S)$	G^+ band	Defect?	

order of $\sim 80\text{-}90\text{ cm}^{-1}$, whereas the higher diameter tubes show FWHM of D-band close to the crystalline graphite like forms of the order of $\sim 60\text{ cm}^{-1}$. We also studied the D-band line shape for SWCNTs with diameter range 1-2 nm and found that the FWHM was 13 cm^{-1} . Although the relative intensity profiles of D and G-band of SWCNTs and low diameter MWCNTs looks alike, the FWHM of D-band clearly distinguishes the two. Fig. 3-4(d) shows the ratio of intensity of $G^-(S)$ to D band. We found that D-band intensity first decreases with diameter up to 20 nm, because higher diameter rolled graphitic structure will require less bending and correspondingly less disorder. For diameter above 20 nm, it again increases because higher diameter MWCNTs have less ordered graphitic ordering as compared to low diameter MWCNTs and SWCNTs. Further, from HRTEM imaging we noticed structural defects on the outer walls of the large-diameter nanotubes. It may be noted that with the change of diameter, the change in intensity of D band is quite small compared to the change in $G^-(S)$ band intensity.

Note that with the change in diameter, the Raman shifts of $G^-(S)$ and $G^-(M)$ bands are complementary to each other. As the diameter of the nanotubes increases, the inter-shell separation decreases as evidenced by XRD and HRTEM analysis, while the tensile strain associated with the curvature of the tube decreases. One expects the G^- band frequency to decrease with decreasing tube diameter, since lower diameter tube should be under higher tensile strain that would cause a down shift of the Raman frequency and also the phonon confinement effect that is expected to lower the Raman frequency in lower diameter tubes. This change is, however, in contrast to the changes observed for $G^-(S)$ band shown in Fig. 3-4(b). Hence, the change in the $G^-(S)$ frequency cannot be explained by the curvature effect. However, the observed changes in $G^-(M)$ band frequency follows

the behavior expected from the curvature or size effect. Downshift of $G^-(s)$ band indicates higher elongation strain in graphitic lattice for lower diameter MWCNTs. This is consistent with the lower Raman shift of $G^-(S)$ observed for lesser compressed SWCNTs studied by applying hydrostatic pressure [288]. In case of graphene, G^- band Raman shift has been observed to downshift with increasing number of graphene layers [289]. Hence, lesser elongation strain and higher number of graphitic layers for higher diameter MWCNTs contribute to the downshift of the G^- band.

It has been suggested that G band frequency is affected by the interlayer bonds, which are correlated to the interlayer spacing. However, no shift in D-band frequency was observed in graphene with increasing number of layers. The authors reported a strong decrease of D band intensity with increased number of graphene layers. For MWCNTs, we observed a slight decrease in intensity of D-band with the increase in diameter up to 20 nm. In low diameter MWCNTs, large strain in the tube walls may lead to breakdown of translational symmetry in the lattice and a corresponding increase in D-band intensity up to a certain diameter. In large diameter MWCNTs, as the number of layers increases the outer walls are less strained leading to the some reduction in the D-band intensity. However, in very large diameter MWCNTs structural defects are present in the outer walls that cause a slight increase in intensity of D-band. To explain the downshift of $G^-(S)$ band frequency with diameter in MWCNTs, it is clear that as the number of walls increases the interlayer spacing decreases as evidenced from HRTEM as well as XRD analysis. Thus, the observed decrease in G-band frequency with increasing diameter is a result of increased interaction among the closely spaced walls of nanotubes. Computational study on the interwall interaction has been reported for DWNTs and interaction energies were found to be in the range of 13-25 meV/atom [290]. However, no relevant data is available

for the MWCNTs. For large diameter MWCNTs, due to closely spaced walls the interaction energy is likely to be significant and Raman analysis allows probing of such interaction only qualitatively.

Further, the effect of diameter on the higher order Raman modes are studied and results are shown in Fig. 3-5. Raman frequency of 2nd order G' band of low diameter (7 nm) nanotubes is 18 cm⁻¹ down shifted as compared to other higher diameter MWCNTs,

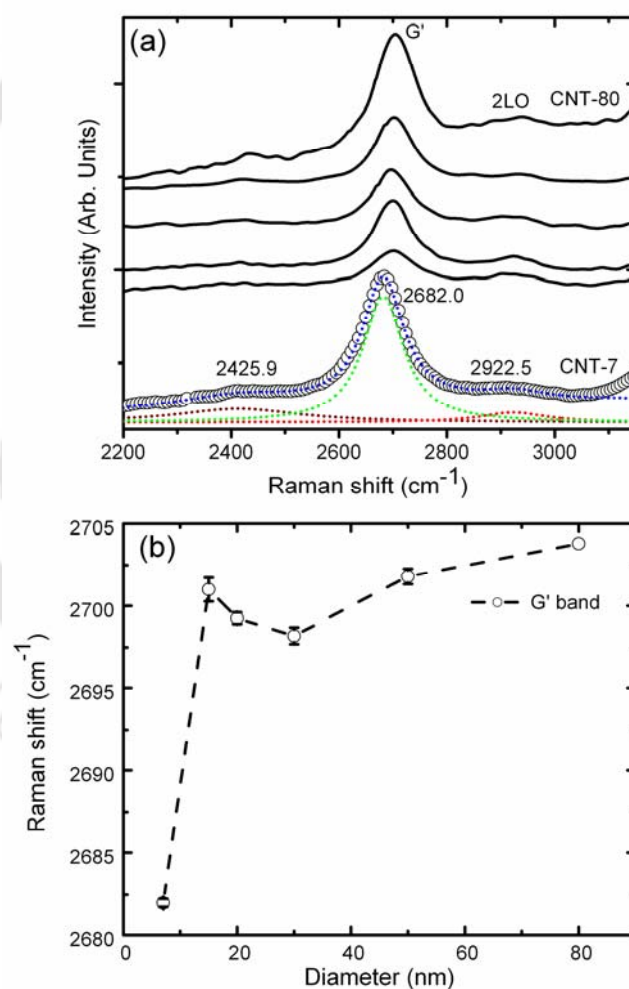


Figure 3-5: (a) Second order G'-band Raman spectra of MWCNTs with varying diameter. CNT-7 is shown with deconvoluted peaks. Summary of peak profile is presented in Table. 3-3. **(b)** Shows change in the G'-band frequency with diameter.

as shown in Fig. 3-5(a). A proper estimation of the peak position was achieved by fitting a single Lorentzian line shape (solid line) to the experimental data (symbols) in each case. The G' mode frequency shows a large up shift as the average diameter increases from 7 nm to 15 nm and then shows slow decrease with diameter for higher diameter nanotubes, as shown in Fig. 3-5(b). Note that error bar in the data is quite small compared to the magnitude of shifts observed with change in diameter. The lowest diameter MWCNTs show Raman spectral profile close to that of SWCNTs. Intensity of G' mode first decreases as the diameter increases up to 30 nm and then slowly increases with increasing diameter. Thus the observed spectral features in the Raman data are characteristics of diameter dependence of the MWCNTs. However, observed Raman shifts with diameter are definite signature of inter-wall interaction.

Table 3-3: Summary of the fitted Lorentzian peaks for second-order modes of MWCNTs with different diameter ranges.

Sample Name	Peak1	Peak 2	Peak3	$I_{G'}/I_D$
CNT-7	2425.9	2682.0	2922.5	0.1514
CNT-15	2408.4	2701.0	2920	0.0514
CNT-20	2390.6	2699.2	2924.1	0.1095
CNT-30	2397.7	2698.2	2916.3	0.0657
CNT-50	2426.8	2701.8	2909.4	0.0719
CNT-80	2431.8	2703.8	2917.2	0.1435
Assignments	Defects	G' band	LO	--

interaction in MWCNTs. Results of our XRD analysis are well corroborated by the HRTEM analysis and fully consistent with the Raman analysis. In contrast to the previous report [291], we find that Raman analysis on MWCNTs are not so much limited by penetration depth as we observed a clear diameter dependence up to a diameter of ~60 nm. On the other hand, the XRD probing does not have any such limitation. Through this study, we have demonstrated the power of XRD and Raman analysis in understanding the

contribution of inter-wall interactions and tube curvatures in MWCNTs as a function of diameter up to 100 nm. It may be noted that CNT-20 sample having the largest size distribution (10-30 nm) shows some deviations in XRD and Raman profiles as compared to the other samples. Our preliminary studies on thermogravimetric analysis of CNT-20 reveal that various phases of carbon are present as impurities in CNT-20 and due to presence of other forms of carbon; any deviation from systematic behavior is expected from such samples.

Our Raman results are consistent with a recent report where it was observed that the G-band frequency decreases with increasing tube diameter for diameters $<20\text{nm}$ and then saturates [291]. However, we have performed deconvolution of the G band and analyzed the line shape and diameter dependencies of metallic and semiconducting components separately. Hence, the observed behaviors are, though qualitatively same, but quantitatively different. It was shown that Raman spectral features are not discernable for diameters above 20 nm. However, the present study reveals that features in G^- band are sensitive up to an average diameter of 80 nm. Since the penetration depth of the 488 nm laser is of the order of radius of the large diameter MWCNTs used in this work, diameter dependence is easily probed by both the Raman as well as in XRD measurements. Our conclusion is clearly supported by HRTEM analysis.

G^- band frequency of MWCNTs is affected by the interlayer spacing, as calculated by changes observed in XRD profiles. The d_{002} spacing decreases with increasing diameter of the MWCNTs even for the largest diameter nanotubes. The shift in the Bragg angle 2θ and the FWHM of the peak show clear diameter dependence. These spectral features can be used to estimate average diameter for samples with unknown diameter and relative contribution of inter-wall interactions and tube curvature can be understood in large

diameter MWCNTs. This is the first report demonstrating that simple XRD measurements can provide valuable information about average diameter and interwall separation in MWCNTs. This technique may not be so useful in case of SWCNTs since the number of atoms participating in the scattering event is too small as compared to that in MWCNTs and hence poor signal to noise ratio is obtained.

Large intensity of G^- band in CNT-7 is analogous to the SWCNT behavior, where the G band signal is very high compared to the D-band signal. Thus the low diameter MWCNTs behave like large diameter SWCNTs, while higher diameter MWCNTs behave in a different way due to strong interaction among tube walls. As the number of graphitic layers increases, interaction between different layers becomes significant. This seizes the in-plane motion of cylindrical graphene layers in a MWCNT leading to sudden drop of I_{G^-}/I_D ratio as for CNT-15. As the diameter of MWCNTs increases further lattice strain gets reduced, leading to decrease of number of sp^3 carbon required for a stable tubular structure [77]. Due to the reduced strain, the intensity of the D-band slightly reduces and correspondingly the I_{G^-}/I_D ratio slowly increases for MWCNTs of diameter >15 nm. Thus, the phonon spectra of the lowest diameter MWCNTs are similar to that of SWCNTs due to participation of a few walls in the lattice vibration.

3.2.5 Diameter Dependence of Oxidative Stability: Thermo-gravimetric Studies

Fig. 3-6 shows TGA and DTA spectra of a SWCNT sample recorded under 40 sccm of air flow and 5 °C/min heating rate, suggested to be optimum for CNT characterization [263]. It shows oxidation temperature to be 448 °C (represented by

$dW/dT_{\max}$), presence of amorphous carbon (a small hump in DTA spectra at 350 °C) and presence of another form of carbon (represented by another small high temperature peak at 515 °C). Amount of metallic impurity is estimated by calculating the weight percentage of metallic residue left after complete oxidation minus the weight increase due to oxidation of metals at high temperature (usually taken as 20 %) [263, 264]. Defects and derivatization moiety in nanotube walls can lower the thermal stability.

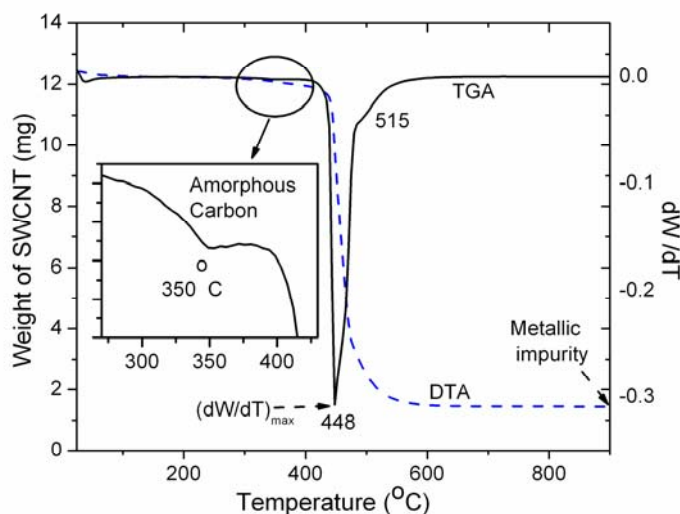


Figure 3-6: TGA and DTA spectra of a SWCNT sample.

TGA spectra of different diameter MWCNTs are shown in Fig. 3-7(a). These spectra were recorded with heating rate 5 °C/min and under 40 sccm flow of air. It is clear from the spectra that the lower diameter MWCNTs is completely oxidized at much lower temperature than the higher diameter MWCNTs. Differentiated TGA spectra shows certain asymmetry in the peak shape indicating that multiple components are present in the TGA spectra. As we expect different forms of carbon to be present in the MWCNTs, experimentally observed TGA curves shown in Fig. 3-7(a) were deconvoluted and fitted using reverse Sigmoidal function

$$y(x) = a_o \left[1 - \frac{1}{1 + \exp\left[-\left(\frac{x - a_1}{a_2}\right)\right]} \right] \quad (3-4)$$

Where, a_o is the amplitude that physically represents the weight % of different phases of carbon present in the sample, a_1 is centre of the peak that indicates oxidation temperature (T_{ox}) and a_2 is full width at half maxima (FWHM) of the peak. TGA curves obtained for all samples required three reverse Sigmoidal components for proper fitting and the fitted parameters are summarized in Table 3-4. Fig. 3-7(b) shows the deconvolution of the TGA curve for CNT-7.

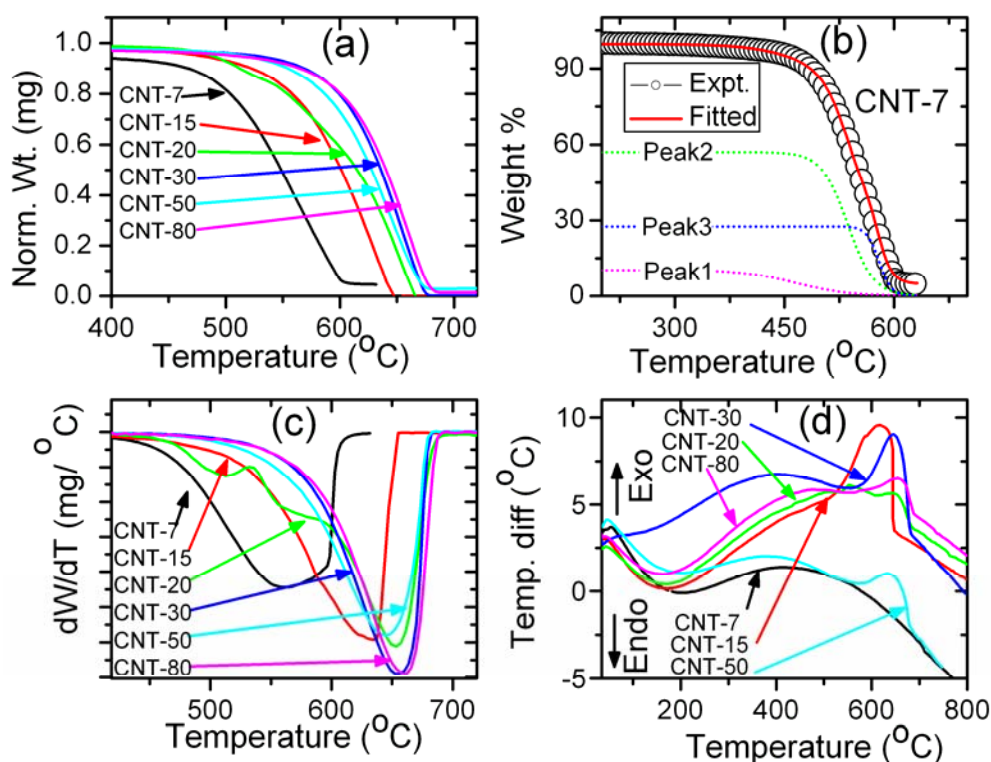


Figure 3-7: (a) TGA spectra of different diameter MWCNTs showing higher T_{ox} for higher diameter MWCNTs; (b) Deconvolution of TGA spectra of CNT-7 using reverse Sigmoidal functions; (c) DTA spectra shows an increase in $(dW/dT)_{max}$ with increasing diameter and presence of other phases of carbon; (d) SDTA plot of different diameter MWCNTs showing absence of exothermic peak for CNT-7 in the temperature range 550°-700°C.

Table 3-4: Oxidation temperature (T_{ox}) and relative weight % of different species present in the MWCNTs as obtained from deconvolution of TGA curves fitted with reverse Sigmoidal profiles. Metal residue is obtained directly from TGA spectra. Saturation magnetization (M_s) measured from VSM is proportional to the magnetic impurity content (details of VSM results is presented in Chapter-5).

Sample name	Diameter. (nm)	Oxidation temperature, T_{ox} (°C)						Metal residue	M_s (emu/gm)
		Peak1	Wt %	Peak2	Wt %	Peak3	Wt %		
CNT-7	<10	461	8.87	536	56.79	579	26.39	4.56 %	1.75
CNT-15	10-20	520	16.76	590	51.57	626	30.99	NILL	0.22
CNT-20	10-30	562	45.90	624	32.60	654	30.80	NILL	0.06
CNT-30	20-40	558	12.94	623	48.55	656	36.79	0.12 %	0.21
CNT-50	40-60	578	25.45	622	44.61	653	26.27	3.01 %	0.41
CNT-80	60-100	559	13.15	626	47.20	659	37.73	1.20 %	0.72

It is clear from Table-3-4 that all three components of the TGA spectra show systematic increase in T_{ox} with increasing diameter up to a diameter of 30 nm. For higher diameter nanotubes, the T_{ox} does not increase any further. In the literatures, usually Gaussian and Lorentzian line shapes have been attempted to fit differential thermogravimetric analysis (DTA) spectra for estimating T_{ox} and the number of carbon phases present in samples. However, the quality of fitting to the experimental data is usually very poor [292]. We find that the reverse Sigmoidal fit to TGA spectra yields a much improved fitting and matches the T_{ox} estimated from DTA spectra fitted with Gaussian line shape. In case of lower diameter MWCNTs, due to larger strain between carbon bonds, it is oxidized at comparatively much lower temperature. It is evident from our results that MWCNTs are thermally more stable than SWCNTs, due to the bigger tubular diameters which are correspondingly less strained and protected inner carbon shells as compared to the low diameter SWCNTs. Fig. 3-7(c) shows different T_{ox} for

different diameter MWCNTs. It is evident that average T_{ox} of MWCNTs increases systematically with increasing diameter. Fig. 3-7(d) shows the calorimetric signals from phase transformations monitored by standard differential thermal analyzer (SDTA) for MWCNTs of various diameters. The exotherm shown in Fig. 3-7(d) indicates more than one transformation during the heat treatment of large diameter MWCNTs. The feature of SDTA curve is similar to the earlier reported result of Illeková et al. [71], who reported peaks at 399 °C and 468 °C corresponding to amorphous carbon and SWCNTs, respectively. This is because more than one rate controlling process is dominant at temperatures around the maximum of the main oxidation peak. We have observed a broad peak at ~ 420 °C for CNT-7, CNT-30 and CNT-50, and at ~ 470 °C for other samples along with a relatively sharp peak at ~ 630 °C for all samples (except CNT-7). The two-peak SDTA profiles observed at ~ 420-470 °C and at ~ 630 °C are believed to result from the difference in lattice strain associated with different curvatures of inner and outer walls of MWCNTs. CNT-7 does not show the high temperature 2nd peak in SDTA profile, since the ultra low diameter MWCNTs contains too few layers that are strained almost equally and no relaxed graphitic layers exists in the outer walls.

Fig. 3-8(a) shows the diameter dependence of oxidation profile of various components obtained after deconvolution of experimental TGA profile. The experimental data points are shown with symbols and the dashed line is an exponential fit to each component, as shown in Fig. 3-8(a). It is interesting to note that the average T_{ox} as obtained from $(dW/dT)_{max}$ follows an exponential recovery function with increasing diameter, as shown in Fig. 3-8(b). This shows that T_{ox} saturates at 663 °C for MWCNTs having diameter 30 nm and above. Different troughs in the DTA curve indicate three

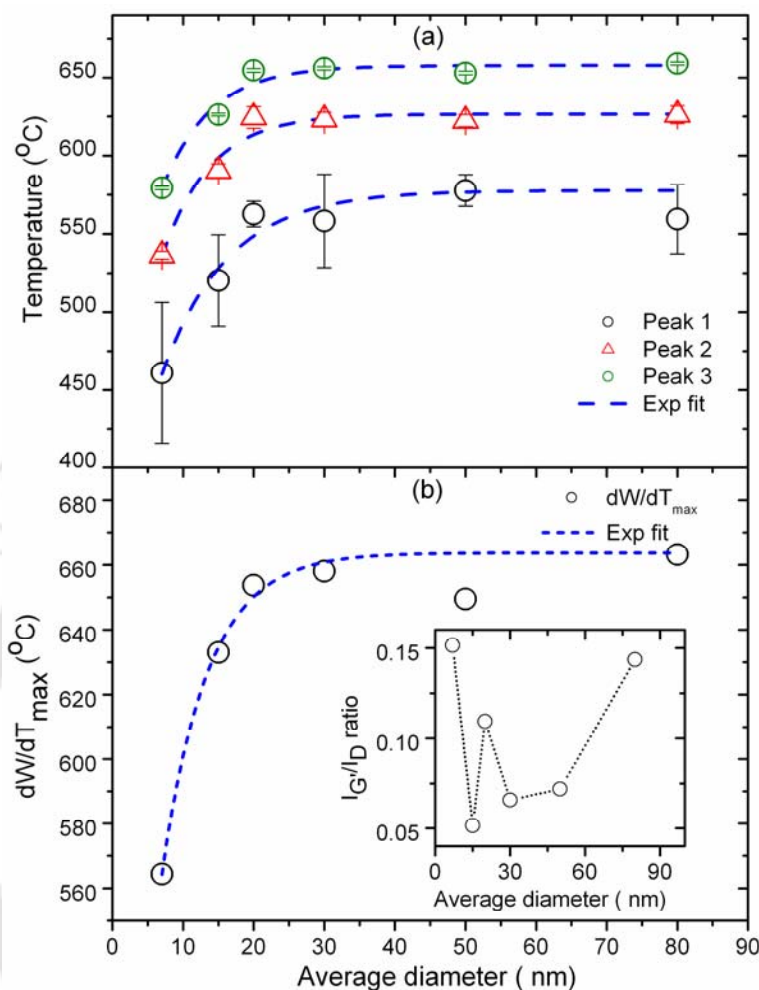


Figure 3-8: (a) variation in T_{OX} as a function of diameter for three different components in MWCNTs, as obtained from fitting; (b) Maxima of weight loss with temperature obtained from DTA curve for various diameters (closed circles) and exponential fit (dashed line).

different rates of weight loss corresponding to three different oxidation reactions. In order to understand the specific contribution of defects in the oxidative profile of MWCNTs, we performed Raman studies on MWCNTs of different diameters. The inverse of the ratio of intensity of G'-band to D-band is considered to be a good measure of defect density in CNTs. Diameter dependence of the defect density in these MWCNTs is shown as inset of Fig. 3-8(b). It is evident from the scattered data points that the intensity ratio I_G/I_D does

not follow any systematic behavior with diameter, contrary to the expectation that higher thermal stability for higher diameter MWCNTs may be partly related to lesser defect density in higher diameter MWCNTs. It may be noted that at higher diameter, I_G/I_D ratio increases with diameter, while the TGA results do not reveal any significant improvement in T_{ox} for diameter range 30-80 nm. Nevertheless, TGA data in Fig 3-8(b) show a lower T_{ox} for CNT-50 nm as compared to that of CNT-80, which is consistent with presence of lower defect density in CNT-50 as revealed from higher I_G/I_D ratio. Thus, for very large diameter MWCNTs where the strain/curvature is relatively low, the defect concentration dictates the T_{ox} . On the other hand, for smaller diameter MWCNTs as well as SWCNTs, the lattice strain primarily determines the T_{ox} overruling the effect of defects. Note that lowest diameter MWCNTs shows a high I_G/I_D ratio indicating low defect density, but have a low T_{ox} as shown in Fig. 3-8(b). TGA studies of SWCNT-A shows 448 °C oxidation temperature (Spectra presented later) [276]. Thus, lowest diameter MWCNTs behave similar to the SWCNTs, due to high curvature and lattice distortion associated with low diameter [276]. However, careful analysis of the TGA results and Raman data for higher diameter MWCNTs showed some correlation of T_{ox} and defect density, as discussed before from Fig 3-8(b). Thus, we believe that strain predominantly controls the oxidation profile of low diameter nanotubes, while the oxidation profile of large diameter nanotubes with low curvature is controlled by defects in the tube wall. In accordance with the literature, we assign the Peak1 of Fig 3-8(a) to SWCNTs containing structural defects; Peak 2 to mixture of near-perfect SWCNTs and defective MWCNTs and Peak3 to near-perfect MWCNTs. These results clearly demonstrate the diameter dependent oxidative stability of MWCNTs that is controlled by strain as well as defects in the nanotube.

3.2.6 Role of Metal Catalysts in Oxidative Stability: VSM Studies

We have explored the possible role of metallic impurities in oxidative stability through magnetization measurements performed at room temperature using VSM. Since TGA has limitation in the mass resolution for detection of residual impurities, VSM studies are performed to get a more accurate but relative measure of the amount of metal catalysts present in various samples. Conventional method of estimating the presence of metallic impurities suffers from a number of experimental limitations like weight increase of metals after oxidation, sensitivity of the TGA balance and errors in its calibration, difference in extent of oxidation of CNT encapsulated metal nanoparticles and particles at the tip.

M-H loops for different diameter MWCNTs are shown in Fig. 3-9(a). Ignoring the possible contribution of defects in the magnetization behavior of MWCNTs, saturation magnetization per gram (M_s) of a sample is expected to be proportional to the amount of catalyst present in the sample. Hence, the relative concentration of catalyst particles in the form of magnetic impurities is assessed from M_s value. The results are compared with the residual metallic catalyst estimated from TGA studies (Table 3-4). Highest value of M_s is observed in CNT-7 with lowest diameter MWCNTs, and then follows CNT-80, CNT-50, CNT-30 and CNT-15 having almost similar M_s , and the lowest M_s is observed for CNT-20. In the M-H curve, a saturation of magnetization is observed at a field of 3000 Gauss and with further increase in the magnetic field the magnetization linearly decreases indicating the diamagnetic behavior originating from the perfect tubular graphitic structure. Amount of catalyst as estimated from TGA studies are listed in Table 3-4 shows that the highest metal residue of 4.56 weight % for CNT-7, which correspondingly shows the highest value of M_s in Fig. 3-9(a). CNT-50 and CNT-80 have 3.01 and 1.20 weight %

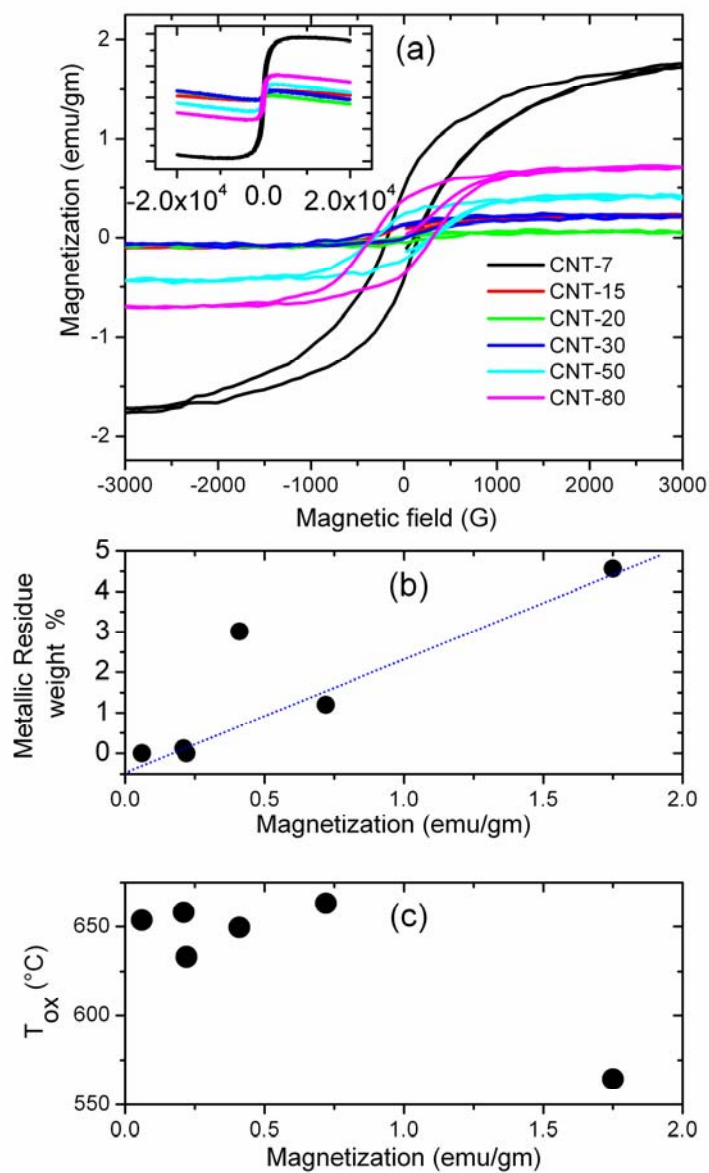


Figure 3-9: (a) M-H loop of various diameters MWCNTs. (b) Correlation between weight percent of metallic residue estimated from TGA studies and the value of saturation magnetization measured by VSM. Saturation magnetization per gm is proportional to the weight of the metallic residue estimated from TGA studies. (c) Metallic impurity content versus T_{ox} to find any possible correlation between the two.

of metal residues. Although the TGA results indicated higher metal residue in CNT-50 as compared to that in CNT-80, the M_s value observed for CNT-80 is higher. CNT-30 shows

relatively low M_s (0.21 emu/gm) value corresponding to small amount of catalyst (0.12 weight %) as estimated from TGA measurements. CNT-15 and CNT-20 shows very low M_s value which is consistent with the TGA results that showed no measurable residual catalyst. We find that magnitude of M_s is identical for CNT-15 and CNT-30. These results show that the measure of M_s is a very sensitive tool for estimating the amount of metal residues present in a sample. The advantage of using this technique would be that it does not include any complication like weight variation due to formation of metal oxides, carbon encapsulated metal particles or, free nanoparticles, heating and air flow rate dependences etc.

Fig. 3-9(b) shows the correlation between metallic impurities estimated from TGA and saturation magnetization observed from VSM studies of different diameter MWCNTs. Except in CNT-50, all other samples show a one to one correspondence between metallic impurities content and observed M_s . Fig. 3-9(c) shows the variation of T_{Ox} with the amount of catalyst present in the sample, represented by M_s . Other than CNT-7, where metallic catalyst weight is comparatively high (4.56 %) and nanotube diameter is extremely low (few walled structure), other samples do not show any significant change in T_{Ox} with change in saturation magnetization, i.e., with amount of metallic impurities. Thus, there is no direct correlation between oxidative stability (T_{Ox}) and magnetic impurity content. Therefore, it can be concluded that metallic impurity content does not influence the oxidative stability of MWCNTs. It is the curvature of the nanotube related to a specific diameter and the amount of defects present in the nanotube walls that determine the oxidative stability of MWCNTs. The oxidative stability can be considerably improved

by vacuum annealing of MWCNTs. It is found that a major improvement in oxidative stability can be achieved in SWCNTs as compared to the MWCNTs.

3.3 HRTEM Studies of Structural Defects

A HRTEM study confirms presence of various kinds of structural defects in our samples. Fig. 3-10 shows typical HRTEM images of some of the samples studied in this work. Fig. 3-10(a) show a nearly perfect SWCNT of diameter 0.5 nm without any visible defect, while Fig. 3-10(b) show a typical defective SWCNT with a topological defect such as kinks at the tube wall (shown with arrow mark). These kinks are possibly well known Stones-Wales type defects. The different bent angles require various member rings. Sharp bents is only possible with tetragonal rings or vacancy, whereas low curvature bent nanotubes will consist of pentagon-heptagon pairs with varying separation distance, or pentagon-octagon-pentagon pairs. Figure 3-10(c) depicts presence of defects/damage at the outer wall of a MWCNT, typically caused by acid purification process, while Fig. 3-10(d) shows a vacancy or hole type defect at the inner wall of the MWCNT. Fig. 3-10(e) shows bents at different angle in the MWCNT, requiring pentagon-heptagon rings and pentagon-octagon-pentagon ring type of defects at the nanotubes wall. The sharp bent in the tube wall indicate presence of tetragon rings of atoms. Fig. 3-10(f) and (g) show various forms of structural defects inside the MWCNTs, while Fig. 3-10 (h) shows that nano-onions are also present in these samples. We find that in SWCNT sample the percentage of single walled tubes are low as compared to the multiwalled tubes. Thus, besides the disordered carbon atoms, the structural defects are present in the nanotubes walls as revealed by HRTEM analysis.

While using HRTEM for estimating the variation of interplanar spacing between MWCNTs of various diameters, we found presence of a various kind of defects, different

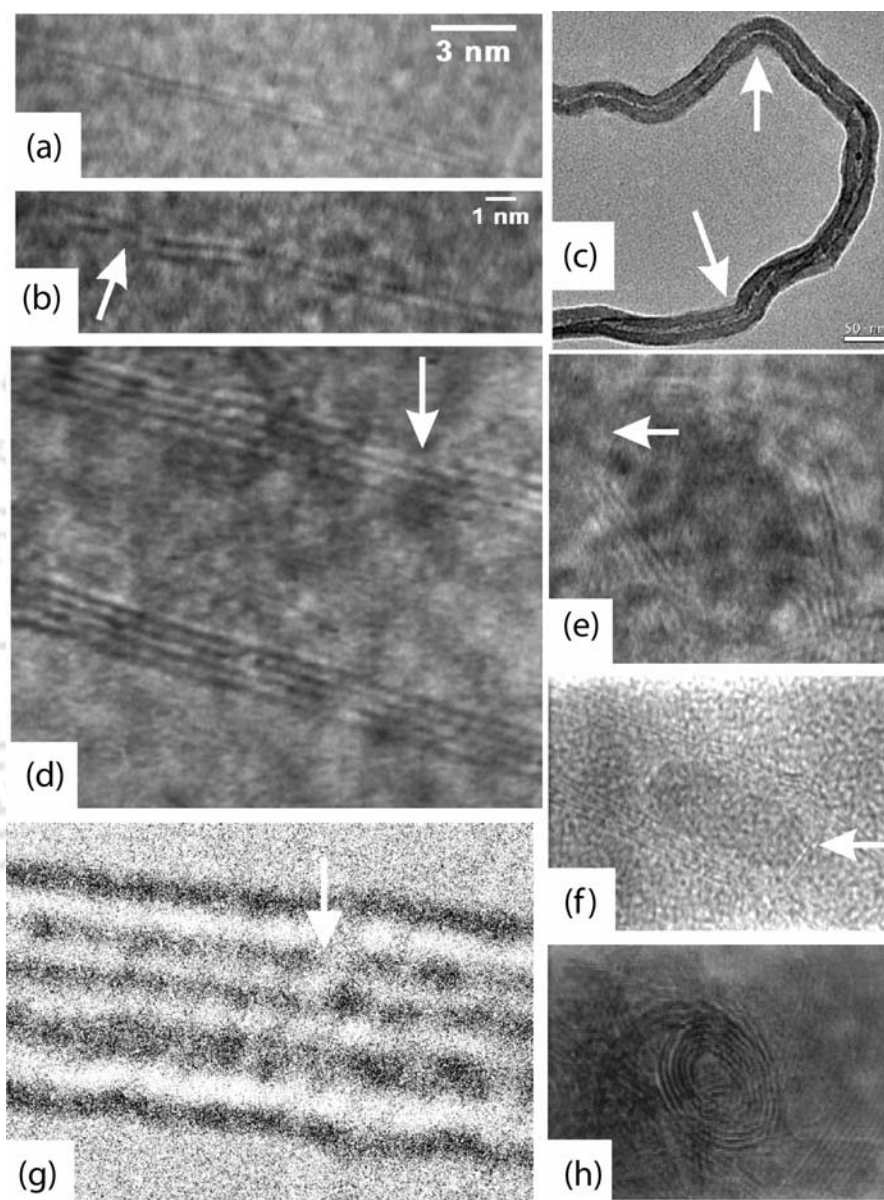


Figure 3-10: HRTEM images of (a) a nearly perfect SWCNT without defect, (b) SWCNT with a kink (defect) structure on the wall, (c) MWCNT with sharp bent and curvature that essentially requires presence of defects, (d) MWCNT with defects on the outer wall, (e) MWCNT with inner wall defect and bent, (f) metal filled nanotubes with defects at the inner wall, (g) MWCNT with a vacancy defect in the inner wall, (h) carbon nano-onions.

from that of the SWCNTs. HRTEM images of typical structural defects observed in the MWCNTs are shown in Fig. 3-11. Fig. 3-11(a) shows regions where interwall staking

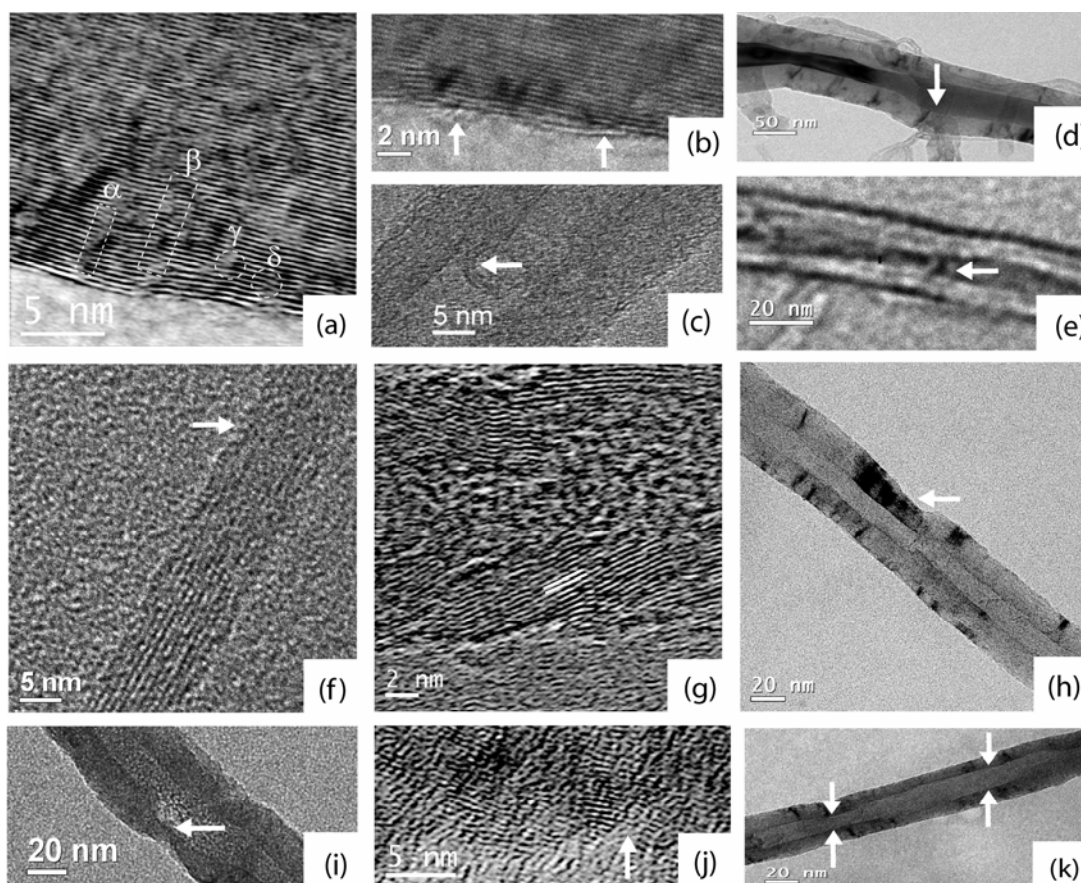


Figure 3-11: HRTEM images of defects observed in the MWCNTs that plays a significant role in the thermal stability of nanotubes: (a) interwall staking fault leads to sudden change in the interplanar d-spacing shown in regions α , β and γ , whereas region δ shows the break between layers, (b) amorphous carbon depositions on the outer walls of MWCNTs and surface terminated layers, i.e, broken outer walls, (c) encapsulated fullerene (peapods), (d) metallic catalyst filled MWCNT indicating diameter changes during growth with the changing shape of the molten catalyst, (e) Linear chain of carbon atoms inside the nanotubes, (f) shows the amorphous regions of the wall structure due to presence of high density of structural defects, (g) shows herringbone (stacked cone) type nanotube, (h) and (i) shows the defects on the surfaces of the MWCNTs, (j) shows HRTEM image of broken wall structure, (k) clearly shows the variation of inner diameter of a nanotube in two different regions.

fault leads to sudden change in the inter-planar d-spacing indicated by regions α , β and γ , whereas region δ clearly shows the break in between the layers. Fig. 3-11(b) shows the amorphous carbon depositions on the outer walls of MWCNTs and surface terminated layers, i.e., broken outer walls and Fig. 3-11(c) shows the encapsulated fullerene (peapods). Fig. 3-11(d) show the metallic catalyst filled MWCNT. It indicates that the diameter of the MWCNTs changes during growth with the changing shape of the molten catalyst during growth leading to more strain in the graphitic structure locally. Fig. 3-11(e) shows the linear chain of carbon atoms inside the nanotubes and Fig. 3-11(f) shows the amorphous regions of the wall structure due to presence of high density of structural defects. Fig. 3-11(g) shows the herringbone (stacked cone) type nanotube. Fig. 3-11(h) and Fig. 3-11(i) show the defects on the surfaces of the MWCNTs. Fig. 3-11(j) shows HRTEM image of broken wall structure. Fig. 3-11(k) clearly shows the variation of inner diameter of a nanotube in the two different regions. Thus, it is evident from the HRTEM images that various kinds of structural defects are present in the as-received MWCNTs. These defects actually play a significant role in the oxidative stability of the MWCNTs. Point defects can easily anneal out during heat treatment. However, extended defects transform in a more complex way. Nevertheless, the overall structure of the nanotubes is expected to improve upon vacuum annealing.

3.4 Effect of High Vacuum Annealing

SWCNTs and MWCNTs both were annealed at various temperatures to investigate the optimum temperature for defect annihilation. The details of the annealing condition and sample code are given in Chapter-2, Section 2.4.3. The experimental results obtained from XRD, HRTEM, TGA and Raman spectroscopy was analyzed as below to understand the

effect of vacuum annealing on structural properties of CNTs. Spectroscopic signature defects especially in Raman spectra and EPR spectra has been studied using these vacuum annealed samples and are presented in Chapters-4 and 5. Here we have presented the detailed analysis of structural modification upon vacuum annealing.

3.4.1 XRD studies

X-ray diffraction studies were performed on vacuum annealed samples to monitor the structural changes, particularly strain and number of layers. Fig. 3-12 shows the XRD pattern of pristine, 300, 500, 700 and 1000 °C vacuum annealed SWCNTs (sample, SWCNT-A). These patterns were deconvoluted using Voigt line profile and the deconvoluted spectral parameters are summarized in Table. 3-5. Typical fitted spectra for pristine SWCNTs is shown by dotted curves in Fig. 3-12. Vertical lines are guide to eye for the change in the peak position with the annealing temperature.

The change in the peak position (2θ) and FWHM of SWCNTs with annealing temperature is shown in Fig. 3-13(a). The (002) peak monotonically up shifts to higher 2θ with increasing annealing temperature. This indicates that strain is released upon annealing. Variation in the FWHM indicates change in the disorders i.e rearrangement of C-atoms /defects in the lattice with the annealing temperature. At the temperature of 700 °C almost same FWHM is observed as that of pristine SWCNTs with higher 2θ value. This implies that at these temperature atoms at the defect sites diffuses to gain the energetically favorable position, leading to reduction in the lattice strain of hexagonal rings with comparatively fewer defects. The peak intensity of the (002) peak was found to monotonically decrease with the annealing temperature as shown in inset of Fig. 3-13(a). Parallel to this the intensity of the amorphous/ non-hexagonal carbon peak observed at ~

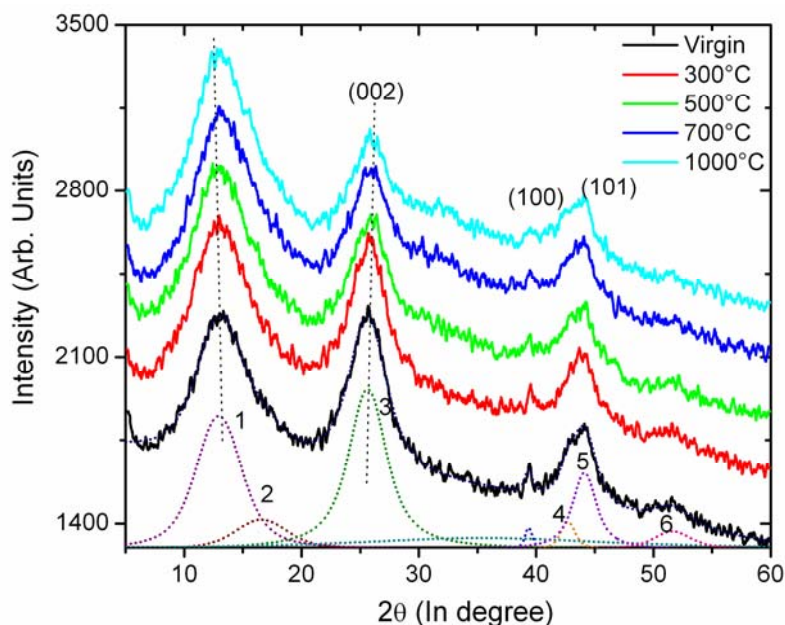


Figure 3-12: XRD spectra of SWCNT-A annealed at various temperatures. Typical deconvoluted spectra (using Voigt lineshape) is shown in dotted line for Pristine SWCNTs.

12.96 monotonically increases. This indicates increase in the number of non-hexagonal rings (pentagon, heptagon, pentagon-heptagon pairs) with annealing temperature. Such transformation is expected from transformation of vacancy and di-vacancy into formation of pentagon and pentagon-heptagon pairs. These changes are expected to lead to change in the diameter of SWCNTs, reflected by change in the RBM positions in the Raman spectra (discussed later). Fig. 3-13(b) and (c) shows the change in the diffraction profile of (100) and (101) peak with change in the annealing temperature. Although this shows a optimum temperature of ~ 300 - 500 °C for minimum strain in the sheet of nanotubes, but this is not as reliable as TGA and Raman spectra in case of SWCNTs. In SWCNTs, XRD intensity is too weak as compared to MWCNTs. This is due to comparatively smaller number of carbon atoms participating in scattering due to one dimensional monolayer cylindrical structure as compared to MWCNTs having multilayer structures. On the other hand,

intensity of (100) and (101) peak of MWCNTs is very weak for fitting along with (002) peak, for identical measurement conditions. Thus, change in the profile of (100) and (101) is not taken in account for drawing conclusion from XRD pattern.

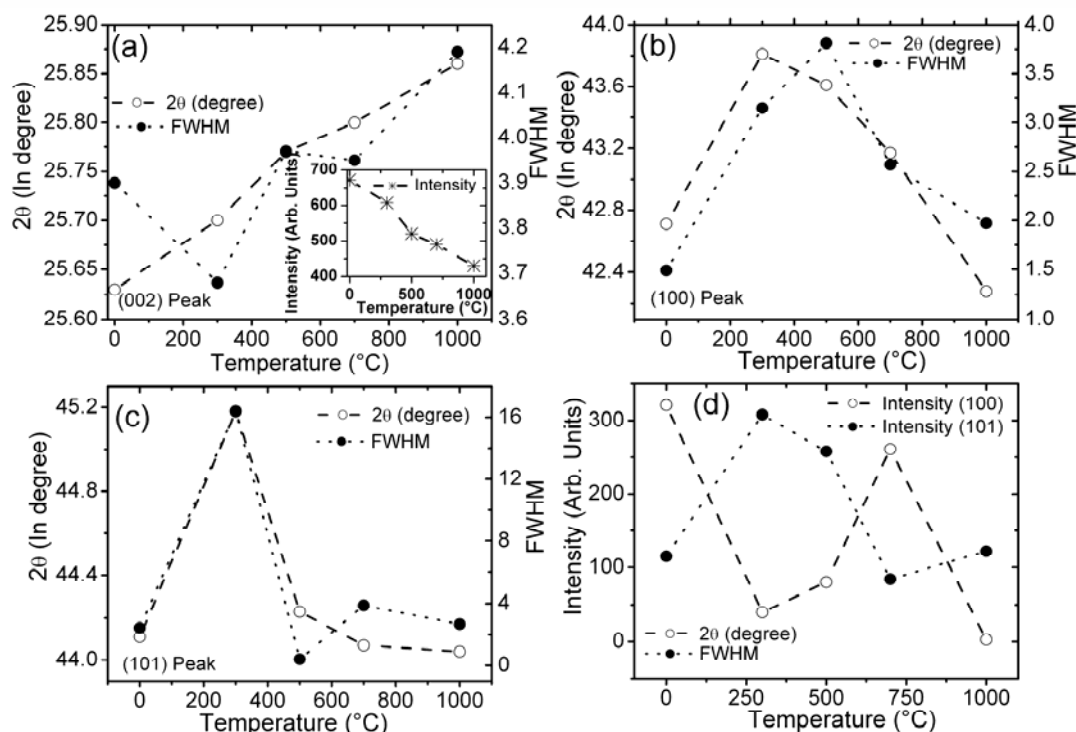


Figure 3-13: Fitting parameter of XRD pattern with Voigt line shape of vacuum annealed SWCNTs (a) Variation of 2θ and FWHM for (002) peak with annealing temperature. Inset shows change in intensity with annealing temperature. (b) and (c) Variation in 2θ and FWHM of (100) and (101) peaks with annealing temperature. (d) Variation in the intensity of (100) and (101) peak with the annealing temperature.

Fig. 3-14 shows the XRD pattern of MWCNTs (MWCNT-A) annealed at various temperatures between (300-1000 °C). Deconvoluted spectra of pristine MWCNTs is shown by dotted lines. Inset of the Fig. 3-14 shows the (002) peak plotted separately for visual inspection of change in the peak intensity and width with annealing temperature. Fig. 3-15 shows graphically the change in the diffraction profile of MWCNTs with

annealing temperature. In contrast to SWCNTs, (002) peak of MWCNTs required two Voigt peaks for deconvolution, named as peak-1 (lower angle) and peak-2 (higher angle). Fig. 3-15(a) shows the change in the diffraction profile of (002) peak-1 with the annealing temperature. This two peak structure (asymmetric peak) assigned to presence of different

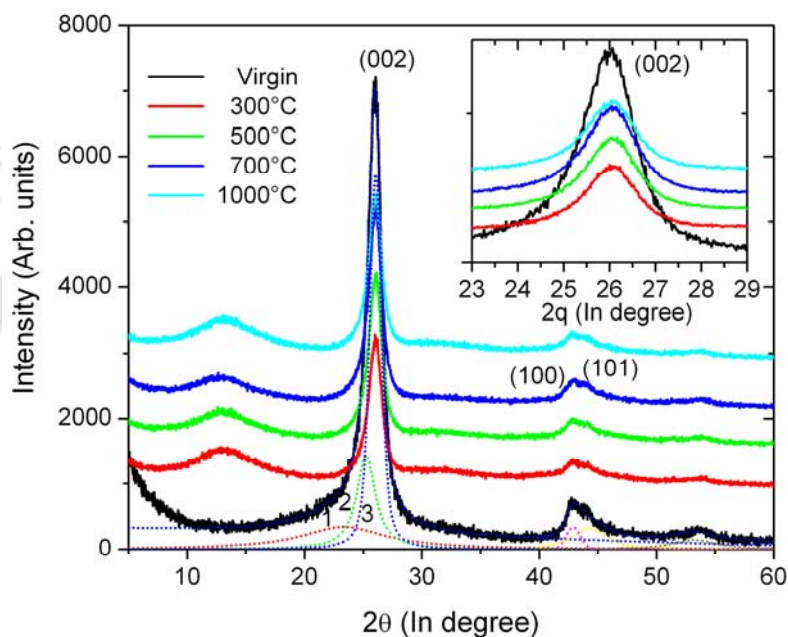


Figure 3-14: XRD pattern of MWCNTs annealed at various temperature. Typical deconvolution is shown for pristine MWCNTs. Magnified image of (002) peak is shown for better view of change in intensity.

crystalline species represent MWCNTs having two different extents of structural defects and hence different strain leading to different Bragg peaks. (002) peak-2 ($2\theta = 26.02^\circ$ to 26.09°) show comparatively lower change than the (002) peak-1 (from $2\theta = 25.22^\circ$ to 25.53°). This implies that peak-2 arises from a less strained structure and hence do not show much response to the annealing temperature. Interestingly the peak intensity of both the (002) peaks increases at 700°C , indicating increase in the order of coaxial arrangement in the MWCNTs. Similarly the diffraction profiles shown in Fig. 3-15(c) and

(d) indicates reduction in the lattice strain along (100) and (101) plane at 700 °C. Further increase in the annealing temperature (1000 °C) shows deterioration in the structure of MWCNTs. Thus the optimum annealing temperature for defective MWCNTs or, MWCNTs having small inner diameter is expected to be ~ 700 °C. Whereas, optimum

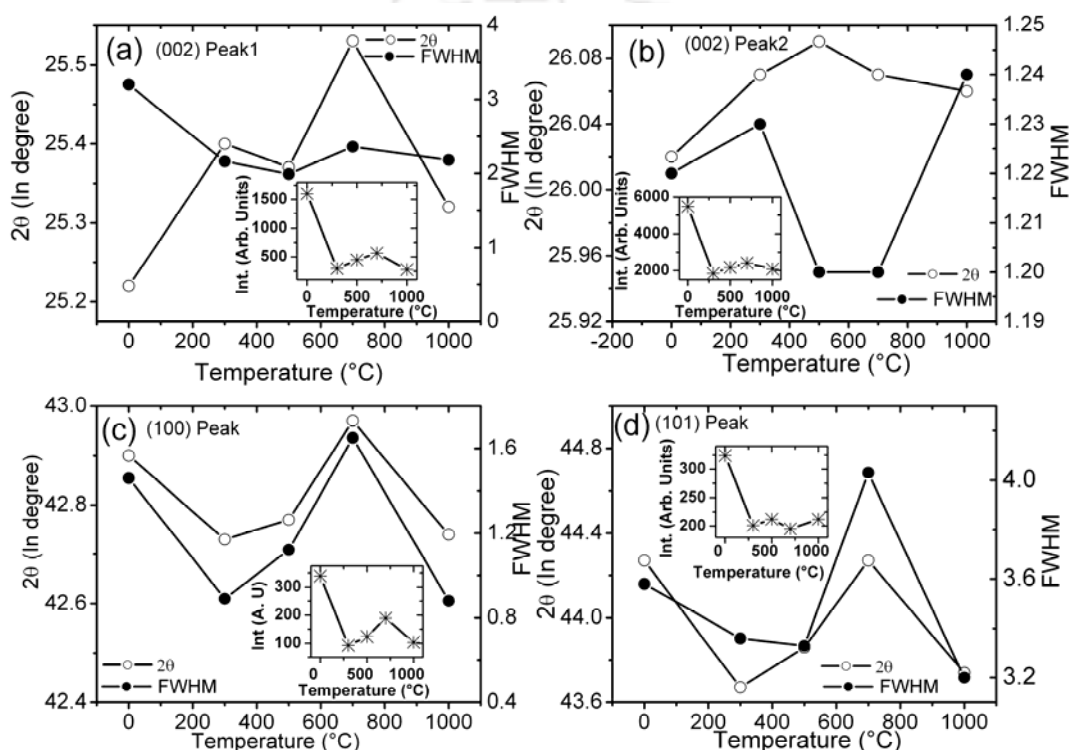


Figure 3-15: Variation of spectral parameters of diffraction peak of vacuum annealed MWCNTs. In case of MWCNTs samples (002) peak required two peaks contrary to SWCNTs, due to difference in strain in inner and outer walls. (a) and (b) shows change in the Bragg angle and FWHM of (002) peak-1 (lower angle) and (002) peak-2 (higher angle peak) respectively. Inset shows variation of their intensity. (c) and (d) shows variation in 2θ and FWHM with annealing temperature of (100) and (101) peaks respectively. Corresponding to change in temperature, change in the intensity is shown in insets.

annealing temperature for MWCNTs having fewer defects or, having comparatively large inner diameter is expected to be ~ 500 °C as reflected from the peak profile of (002) peak-

2, shown in Fig. 3-15(b). Fig. 3-15(b) shows that 2θ is maximum (least strained) and FWHM is minimum for the sample annealed at 500 °C, indicating requirement of only 500 °C for annealing of less defective/ less strained nanotubes i.e, higher inner diameter nanotubes.

Table-3-5: Parameters of fitted peaks for XRD pattern of vacuum annealed SWCNTs and MWCNTs.

Sample Name	Profile	Peak1	Peak2	Peak3	Peak4	Peak5	Peak6
Pristine SWCNTs	Centre	12.96	16.57	25.63	42.71	44.11	51.61
	FWHM	4.65	5.35	3.90	1.49	2.44	3.87
	Ampli.	559	125	672	115	321	76
SW-300 °C	Centre	12.79	15.81	25.70	43.81	45.18	51.75
	FWHM	5.00	6.06	3.68	3.15	16.40	4.26
	Ampli	615	134	607	308	40	73
SW-500 °C	Centre	12.80	15.67	25.77	43.61	44.23	51.76
	FWHM	5.32	6.28	3.97	3.81	0.41	1.84
	Ampli	649	145	520	258	80	52
SW-700 °C	Centre	12.94	16.47	25.80	43.17	44.07	51.02
	FWHM	5.18	6.31	3.95	2.57	3.88	7.34
	Ampli	682	196	490	84	261	76.9
SW-1000 °C	Centre	13.04	17.04	25.86	42.28	44.04	49.98
	FWHM	5.15	4.24	4.19	1.97	2.68	12.66
	Ampli	773	141.8	430	122	2.72	85
Pristine MWCNTs	Centre		25.22	26.02	42.90	44.27	53.23
	FWHM	----	3.20	1.22	1.46	3.58	4.58
	Ampli		1600	5471	339	324	143
MW-300 °C	Centre	13.14	25.40	26.07	42.73	43.67	53.62
	FWHM	6.38	2.16	1.23	0.89	3.36	2.31
	Ampli	447	295	1843	93	201	52
MW-500 °C	Centre	13.13	25.37	26.09	42.77	43.86	53.62
	FWHM	6.55	1.99	1.20	1.12	3.33	2.44
	Ampli	416	446	2167	124	212	65
MW-700 °C	Centre	12.90	25.53	26.07	42.97	44.27	53.44
	FWHM	6.13	2.36	1.20	1.65	4.03	3.54
	Ampli	374	566	2412	189	195	79
MW-1000 °C	Centre	13.24	25.32	26.06	42.74	43.74	53.51
	FWHM	6.42	2.18	1.24	0.88	3.20	2.68
	Ampli	457	277	2083	104	212	55
Assignments		Non-Hexagonal	(002)	(100)	(101)	(004)	

3.4.2 Thermo-gravimetric Studies

The effect of vacuum annealing on the oxidative stability of the SWCNTs and MWCNTs are further studied by TGA. Fig. 3-16(a) shows the TGA spectra of SWCNTs

vacuum annealed at different temperature in the range 300-1000°C. Vacuum annealing is expected to improve the structure of nanotubes by removal of defects in the nanotube structures. It is found that SWCNTs annealed at 700°C shows highest oxidation

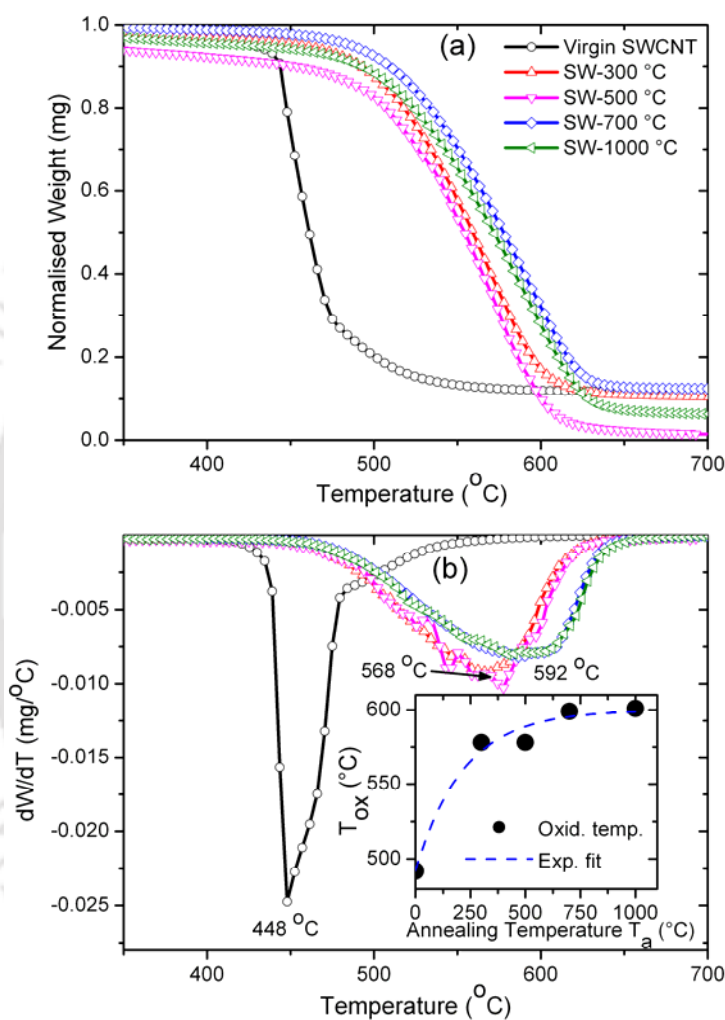


Fig. 3-16: (a) TGA spectra for SWCNTs vacuum annealed at four different temperatures. SWCNTs annealed at 700 °C shows highest oxidative stability. (b) DTA spectra for these samples showing a major improvement of oxidative stability (T_{ox}) due to annealing. T_{ox} increases from 448 °C to 592 °C due to annealing at 700 °C and above. Inset of Fig. 3-14(b) shows T_{ox} of SWCNTs as a function of temperature of vacuum annealing (T_a). Exponential fitting is shown with a dashed line.

temperature (T_{ox}). To evaluate contributions of different components in the TGA curves, TGA spectra of vacuum annealed samples were deconvoluted using reverse Sigmoidal function and the parameters are summarized in the Table 3-6. All the curves required three components to fit corresponding to the presence of three different species of carbon present in the sample.

Table-3-6: Oxidation temperature and relative weight % of different species present in the vacuum annealed MWCNT and SWCNTs, as obtained from deconvolution of TGA curves.

Sample name	Oxidation temperature (°C)					
	Peak1	Weight %	Peak 2	Weight %	Peak3	Weight %
Pristine SWCNT	456	72.11	476	8.38	492	19.50
SW-300 °C	374	5.07	539	62.90	578	32.02
SW-500 °C	389	14.86	538	49.40	578	35.73
SW-700 °C	449	4.12	552	63.39	599	32.47
SW-1000 °C	371	7.73	552	62.66	601	29.61
Pristine MWCNT	546	8.24	577	44.92	606	46.83
MW-300 °C	559	25.83	593	45.41	616	28.74
MW-500 °C	561	12.80	617	54.60	650	32.56
MW-700 °C	307	5.10	564	36.11	596	58.76
MW-1000 °C	548	17.97	581	49.78	604	32.24
Assignments	Defective SWCNTs		Perfect SWCNTs and defective MWCNTs		Perfect MWCNTs	

Corresponding DTA spectra for different samples are shown in Fig. 3-16(b). DTA spectra shows that pristine SWCNTs have T_{ox} of 448 °C and it increases to 568 °C after annealing at 300 and 500 °C. With the further increase of annealing temperatures to 700 and 1000 °C, T_{ox} raises to 592 °C. Note that the deconvoluted TGA spectral profiles of SWCNTs listed in Table 3-6 clearly shows a decrease of weight % of Peak 3 from 32.47%

to 29.61 % as the annealing temperature is increased from 700 to 1000 °C. This is due to structural degradation of SWCNTs annealed at high temperature (1000°C) under the high vacuum condition. Improvement in the oxidative stability of annealed nanotubes clearly indicate a structural improvement as well as strain relaxation during vacuum annealing that reduces the concentration of defects in nanotubes. In fact, powder XRD pattern (shown in Fig. 3-12) of annealed SWCNTs shows higher 2θ value as compared to pristine SWCNTs, indicating lower d-spacing as a result of annealing. It also shows a small decrease of linewidth in the XRD pattern clearly indicating a relaxation of strain upon annealing. In a recent study, we have attributed the XRD linewidth to strain and lattice distortion in the nanotubes [276]. The lattice distortion is considerably reduced after vacuum annealing. Thus, the optimum temperature of vacuum annealing for improved structure and improved oxidative stability of SWCNTs was found to be 700°C. Graph further shows that for major weight fractions of samples, vacuum annealing increases the T_{ox} from 456 °C to 578 °C. SW-700 °C shows 32.47 weight % of perfect MWCNTs (Peak3) as compared to 19.50 weight % observed in case of pristine SWCNTs. This is due to fusion of two SWCNTs forming higher diameter MWCNTs, as has been observed under HRTEM. With further increase of annealing temperature to 1000 °C, weight % of Peak 3 decreases indicating decrease of number of walls, which forms few walled MWCNTs or, finally SWCNT leading to increase in the weight percentage of Peak 2. In case of SWCNTs, relative changes in the weight % estimated for Peak 2 and Peak 3 indicates conversion from single walled structure to multiwalled structure or thickening of walls of SWCNTs upon vacuum annealing. Inset of Fig. 3-12(b) shows that T_{ox} for SWCNTs have an exponential recovery behavior with annealing temperature and follows the following empirical relation as obtained from fitting the experimental data:

$$T_{ox} = 600 - 107.5 \exp(-T_a / 221) \quad (3-5)$$

where, T_a is the vacuum annealing temperature. The first term (constant) in eqn. (3-5) represents the maximum oxidation temperature of annealed (up to 1000°C) SWCNTs. Note that this expression holds for heating rate of 5 °C/min and 40 sccm of air flow with SWCNTs. The constant in the exponential term represents a kind of relaxation temperature for the recovery of nanotube structure.

Effect of vacuum annealing on oxidation behaviour, i.e, TGA profile of MWCNTs is shown in Fig. 3-17(a) and DTA spectra is shown in Fig. 3-17(b). Pristine MWCNTs shows two DTA peaks at 574 °C and 602 °C due to presence of two types of species in the sample. In pristine MWCNTs, the rates of oxidation were comparatively much higher than the vacuum annealed nanotubes. MWCNTs annealed at 300 and 1000 °C shows T_{ox} of ~ 598 °C, whereas MWCNTs annealed at 700 °C shows T_{ox} at ~ 647 °C, as shown in Fig. 3-17(b). Various parameters of oxidative stability for MWCNTs obtained after deconvolution is listed in Table-3-6. It clearly shows that vacuum annealing leads to a major improvement in T_{ox} from 577°C to 617°C after 500°C annealing. Along with this major component, another component was found at 650 °C corresponding to the 32.56 weight % of sample. Further increase of annealing temperature to 700 °C and 1000 °C do not show any further improvement in T_{ox} . Instead, majority of MWCNTs was found to oxidize at 596 °C for 700 °C annealed sample and at 581 °C for 1000 °C annealed sample. Thus, in case of MWCNTs the optimum annealing temperature for removal of structural defects turned out to be 500 °C. Although 500 °C annealed MWCNTs shows highest T_{ox} , but a careful look at the derivative data shows that oxidation starts at much lower temperature as compared to other samples. This indicates presence of structural defects

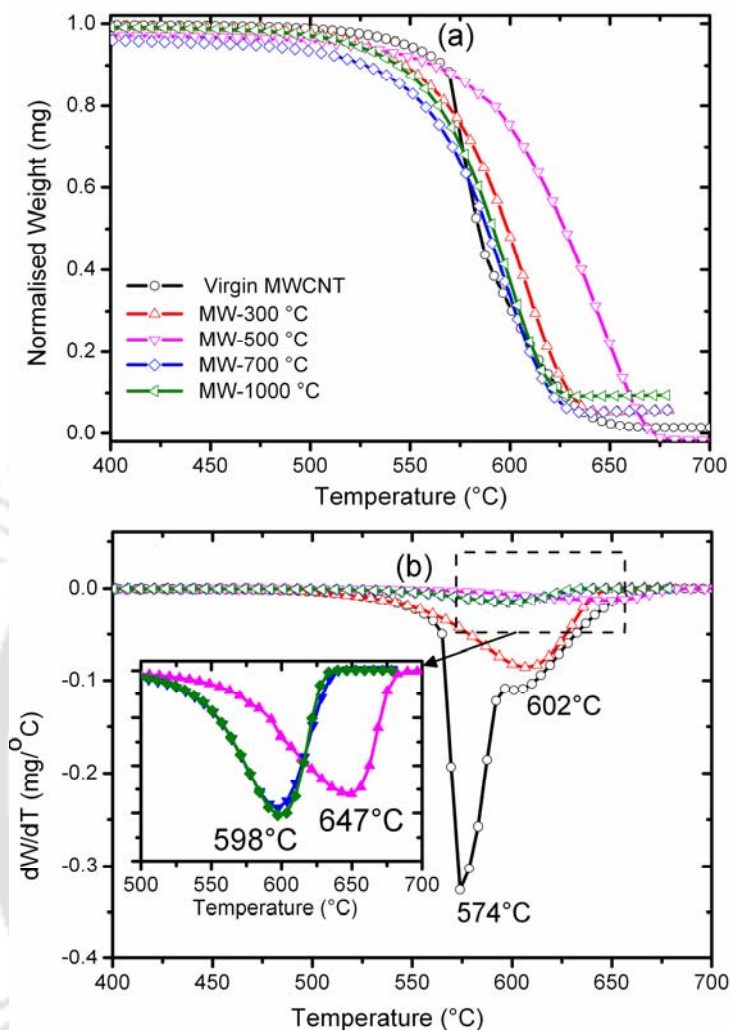


Figure 3-17: Effect of vacuum annealing on MWCNTs at various temperatures (a) TGA spectra shows MWCNTs annealed at 500 °C shows highest T_{Ox} . (b) DTA spectra show two peaks at 574 °C and 602 °C in case of pristine MWCNTs. High vacuum annealing at 500 °C leads to increase in $(dW/dT)_{max}$ to 649 °C and decreases to 598 °C after annealing at 700 °C and 1000 °C.

acting as sites of high reactivity towards oxidation [63, 61]. Also the DTA spectra shows comparatively large amount of amorphous carbon in case of MW-500 °C and MW-700 °C. Further, in MWCNTs the improvement in T_{Ox} after annealing is relatively low compared to that of SWCNTs. The improvement in T_{Ox} upon vacuum annealing is due

structural improvement via sp^3 to sp^2 conversion. This is similar to sp^3 to sp^2 conversion of carbon-carbon bonds observed upon vacuum annealing in the range 600-1000 °C in case of tetrahedral amorphous carbon [293]. We find that vacuum annealing increases T_{ox} of both SWCNTs and MWCNTs. However, the improvement is more pronounced in case of SWCNTs. The difference in the optimum annealing temperature found for SWCNTs and MWCNTs may imply that besides the high strain, the SWCNTs contain more structural defects than the MWCNTs. This is also consistent with the fact that the large diameter MWCNTs with lower inter-wall spacing have a more stable structure due to presence of too few defects. The structural defects observed in HRTEM images of Fig. 3-11 are expected to be responsible for lower oxidative stability of SWCNTs and MWCNTs. Similar to the graphite [294] edges, dangling bonds, vacancies, distortions etc. causes carbon nanotubes more susceptible towards oxidation. From these results, it can be concluded that the defects lowers the overall oxidative stability of both SWCNTs and MWCNTs. However, the T_{ox} in SWCNTs and low diameter MWCNTs is primarily decided by the strain, while the T_{ox} of large diameter MWCNTs with minimum strain are controlled by the defects.

3.4.3 Discussions

We have observed a clear diameter dependence of oxidative stability of SWCNTs and MWCNTs. It is seen that the lower the diameter of the nanotube, the lower is the oxidative stability. In case of unannealed SWCNTs, nature of the mass-loss curve in TGA spectra shows that not only the oxidation temperature is lower but also the rate of oxidation is faster in SWCNTs as compared to that in lowest diameter MWCNTs (See Fig. 3-16). Even in the lowest diameter MWCNTs, due to few wall structure, during oxidation first the

outermost layer is burnt and then it proceeds to outer layers and thus it results in higher oxidation temperature. In SWCNTs, both defects and strain play significant role in the oxidative stability as revealed from vacuum annealing studies. During annealing, besides the defect reduction there will be relaxation of structure that leads to strain relaxation. The angle between covalent bonds in the nanotube lattice is a function of curvature, being proportional to inverse of radius square. As the nanotube radius increases the bond angle approaches the expected 120° found in graphene. Further, due to high curvature of tube walls in low diameter nanotubes, defects are likely to be present in the walls of SWCNTs and oxidation proceeds relatively fast in such tubes compared to the MWCNTs. It is well known that oxidative stability of nanotubes depends on the method and temperature of growth of nanotubes. Given the fact that a comparatively low temperature is used in CVD synthesis compared to the growth temperature used in laser ablation or arc deposition and absence of electric field during growth results in higher defect density in CNTs leading to lower burn off temperatures [63].

In MWCNTs, the TGA results showed that after vacuum annealing at 500°C the oxidation temperature is increased considerably. However, it is observed that the mass-loss starts at relatively lower temperature than the case of pristine MWCNTs. This is possible if defects are present in the structure and after annealing these defects may form aggregates that may eventually leads to formation of fewer number of extended defects such as voids or holes in the nanotube wall. These holes acts as an efficient site for enhanced oxidation and due to their low density, initially the mass loss is very low. However, overall thermal stability of the structure improves upon thermal annealing and a higher T_{ox} is obtained upon annealing.

We have found that though the metal catalyst content is different in different diameter MWCNTs (diameters:15-80 nm), T_{ox} is not significantly different for these nanotubes. Thus the metal catalyst does not influence the oxidative stability of the MWCNTs in a significant way. This is consistent with previous studies [63]. In large diameter MWCNTs, the curvature induced strain is less and hence higher thermal stability is observed. Annealing studies show that improvement in thermal stability is considerably high in SWCNTs compared to MWCNTs. It may be due to the combined effect of strain relaxation and defect removal caused by annealing that leads to higher oxidative stability. From HRTEM studies, we have shown that interlayer d-spacing is considerably lower in large diameter MWCNTs. This is likely to be caused by higher ordering in graphitic stacking and diminishing defect density [295].

3.5 Conclusions

We have presented a systematic analysis of the diameter dependent spectral features in XRD pattern and Raman spectra of MWCNTs. XRD results showed exponential decrease in d_{002} inter-wall spacing with increasing diameter of the MWCNTs, which is fully consistent with the HRTEM observations. Decrease in FWHM of the XRD profile with increasing diameter is consistent with lower strain / curvature of larger diameter nanotubes. These results demonstrate the capability of XRD line profile analysis for understanding the intertube interactions for large diameter nanotubes and it further allows probing the strain and curvature effect for the small diameter nanotubes. This study further demonstrates the feasibility of nondestructive evaluation of average diameter and interwall separation in MWCNTs. In absence of any well defined tool for studying

MWCNTs and from the observed diameter dependence of various spectral features, we conclude that XRD is a very powerful tool to characterize MWCNTs.

Deconvolution of the Raman spectra for different diameter MWCNTs show gradual decrease of the semiconducting component of the G^- band frequency with increasing diameter that has been explained on the basis of intertube interactions. Our studies clearly show that phonon spectra of low diameter MWCNTs are similar to that of the SWCNTs and for large diameter nanotubes, intertube interactions becomes significant. These results demonstrate the capability of Raman line profile analysis for understanding the intertube interactions for large diameter nanotubes and it also allows probing of strain and curvature effect in small diameter nanotubes.

Through careful analysis of the TGA profile for MWCNTs of wide range of diameters, we have found a systematic diameter dependence of oxidative stability in MWCNTs. SWCNTs and low diameter MWCNTs show lower T_{ox} consistent with the high curvature and associated lattice strain. This is the first result where we have shown clear diameter dependence of the oxidative stability of MWCNTs of very wide diameter range (7-100 nm). For the data analysis, we have shown the superiority of reverse Sigmoidal fitting to the experimental TGA data as compared to the commonly used Gaussian fitting for estimating amount of different phases. SDTA profiles of MWCNTs shows two peaks at $\sim 420-470$ °C and at ~ 630 °C due to difference in lattice strain originating from different curvatures of inner and outer walls. Vacuum annealing studies reveal that optimum annealing temperature for strain relaxation and structural defect removal is 700 °C for SWCNTs and 500 °C for MWCNTs. The difference in the nature and concentration of structural defects between SWCNTs and MWCNTs may lead to different annealing temperatures required for defect annihilation.

VSM studies shows that magnetization measurement is a more sensitive tool compared to TGA for estimating the amount of metal residues present in the sample. It is also found that magnetic impurities do not influence the oxidative stability of MWCNTs.



Chapter -4

Raman Scattering and Photoluminescence Studies of Defects

4.1 Introduction

In this chapter, we have presented Raman scattering studies of SWCNTs and MWCNTs in the as-grown and processed conditions. A detailed analysis of RBM, D-band, G-band and G' band profiles has been carried out for large number of samples with wide range of diameters. Besides the commonly observed above bands, a number of additional Raman active modes appear in the intermediate frequency range ($500\text{-}1200\text{ cm}^{-1}$) and between the G and G' band and origin of these bands has been investigated. We have attempted to identify experimentally any characteristic Raman peak(s) of pentagon defects in the nanotube structures, as predicted theoretically. Further, we have used Raman spectroscopy to monitor structural improvement of SWCNTs and MWCNTs upon vacuum annealing. Fingerprints of defects in CNTs through Raman and photoluminescence spectra have been obtained and were correlated with various structural defects observed in HRTEM. A knowledge of defect related spectroscopic features of carbon nanotubes especially in Raman spectra will enable online monitoring of quality during device fabrication or, even for bulk characterization.

We have also studied the origin of visible photoluminescence (PL) from SWCNT and MWCNTs in pristine and chemically functionalized CNTs. Role of metal catalysts, amorphous carbon and carbon nanoparticles in the visible PL have been critically assessed.

4.2 Raman Scattering Studies of Defects

A typical Raman spectrum of SWCNTs (sample, SWCNT-A) with 632 nm laser excitation is shown in Fig. 4-1. It shows radial breathing modes (RBM), D, G and G' and 2G modes expected from CNTs. In addition, it contains a number of other modes like IFM

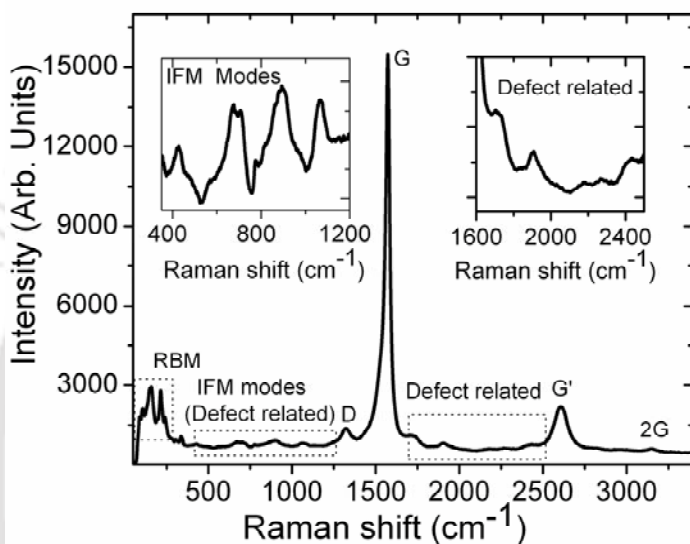


Figure 4-1: Raman spectra of SWCNT-A. Inset shows the spectra recorded separately in the 350-1200 cm^{-1} and 1600-2450 cm^{-1} with higher integration time. Raman spectra of (a) SWCNTs and (b) MWCNTs. Different bands are denoted by standard nomenclature. Intermediate frequency modes (IFM) are seen to be different in these two samples.

modes and a number of peaks between 1600-2400 cm^{-1} . Inset of the Fig. 4-1 shows IFM modes (left inset) and modes between 1600-2400 cm^{-1} (right inset) recorded with higher integration time. The origin of these modes is not established in the literature and recently it has attracted a great deal of attention in theoretical and experimental works. Though the origin of these bands is not clearly understood in the literature, these are believed to arise from defect allowed modes or combination modes of well known bands. One of the main focuses of this work is to identify the origin of these bands through a systematic Raman studies.

4.2.1 Origin of Intermediate Frequency Modes (IFMs)

To investigate the origin of IFMs, we have performed measurements for a number of pristine and processed samples like vacuum annealed, laser processed and ion-irradiated samples etc. Through systematic studies, we have attempted to distinguish the IFM modes originating from the combination modes and that originating from structural defects uniquely.

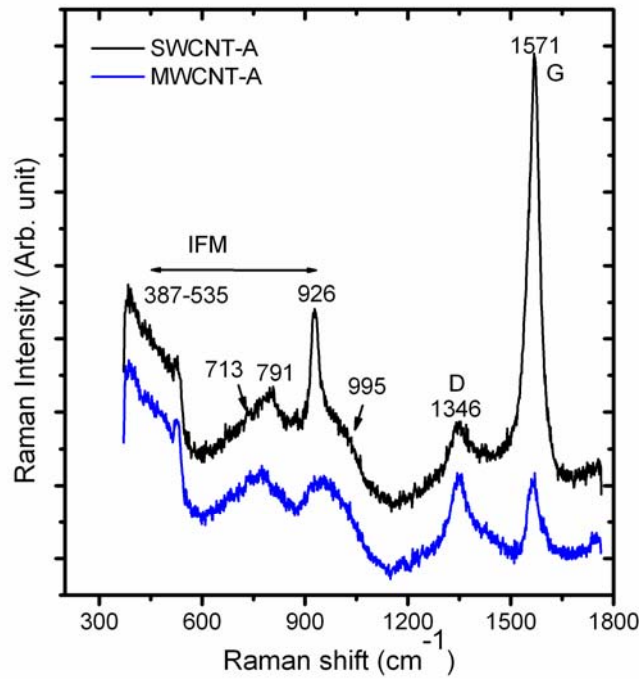


Figure 4-2: Raman spectra of SWCNT-A and MWCNT-A, showing IFM modes along with the D and G modes.

Fig. 4-2 shows Raman spectra of procured SWCNTs-A and MWCNTs-A recorded using 488 nm laser in the home-built Raman spectrometer. Raman spectrum of SWCNTs shows RBMs below 350 cm^{-1} , IFMs in the range 387-1200 cm^{-1} , and well-known D and G bands at ~ 1346 and ~ 1571 cm^{-1} . Intensity ratio of G band to D band is usually considered

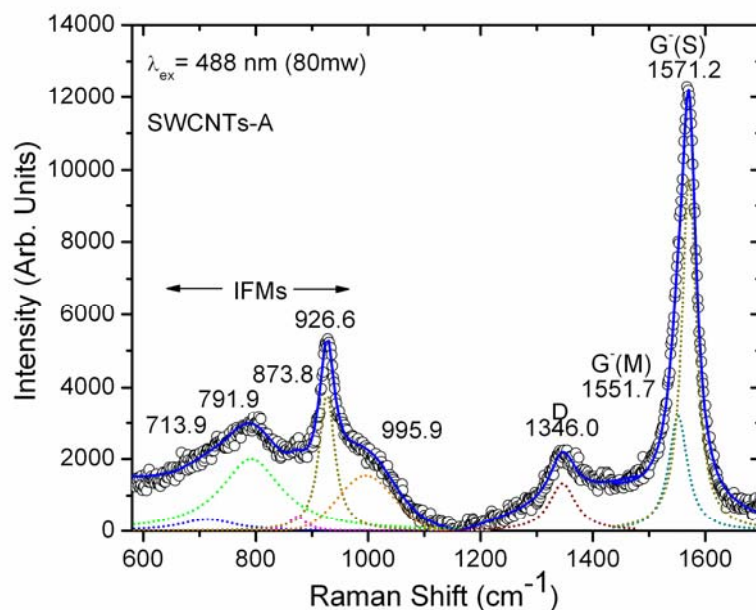


Figure 4-3: Deconvoluted Raman spectra of SWCNTs-A showing IFM modes along with the D and G modes.

as a measure of purity of the samples. We find a G/D ratio of ~ 10 in SWCNT samples. This is indicative of non-negligible content of disorder in nanotubes samples. Further, the presence of carbonaceous impurities, residual metal catalysts used during CVD growth of nanotubes and structural defects introduced during standard acid purification process are expected. In MWCNTs, the G band is relatively weak and thus the G/D ratio is very low. Fig. 4-3 shows the deconvoluted peaks of the SWCNTs-in the IFM, D-band and G-band region. It shows dominant IFM modes for SWCNTs at 743.5, 800.9, 869.8, 928.1, and 988.9 cm^{-1} , while that of MWCNTs at 676.6, 770.0, 936.9, and 1004.9 cm^{-1} , besides the common broad IFM feature in the range 387–520 cm^{-1} . For MWCNTs, the IFM modes are relatively broad and mode frequencies are different from that of SWCNTs. In SWCNT, the RBMs are relatively weak, due to the bundling of CNTs and low content of SWCNT in the sample. This is in agreement with the HRTEM analysis. In SWCNTs, the observed G band at 1571 cm^{-1} is close to the G^- band reported in the literature [33], and this is

attributed to the in plane vibration of the C-atoms along the circumferential direction. The relatively low intensity of 1551 cm^{-1} band indicates that our sample contains high percentage of semiconducting SWCNTs.

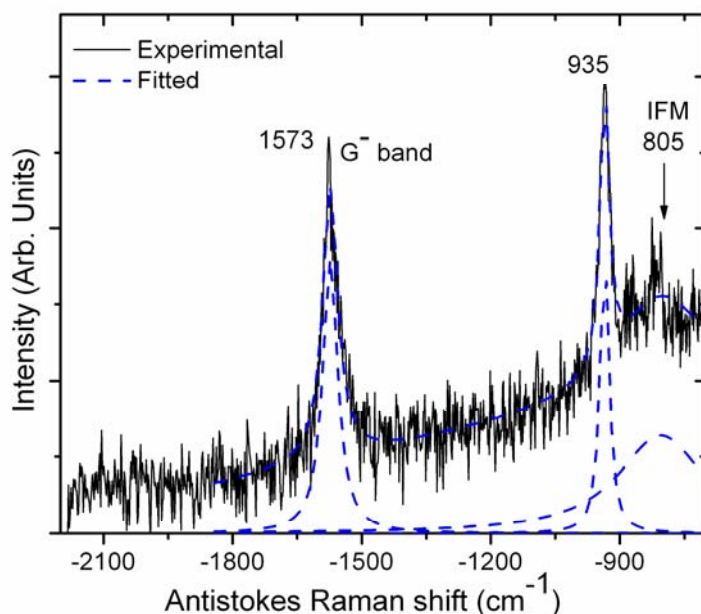


Figure 4-4: Anti-Stokes Raman spectra with IFM and G^- .

Fig. 4-4 shows the Anti-stokes Raman spectra showing G^- band at $\sim 1573\text{ cm}^{-1}$ and two IFM modes at $\sim 935\text{ cm}^{-1}$ and $\sim 805\text{ cm}^{-1}$, and a weak band at ~ 2100 . Thus, the IFM modes and the additional modes at higher frequency are present both in Stokes and Anti-stokes Raman spectra and characteristics of the nanotubes structure. Since the IFM frequencies are different in SWCNTs-A and MWCNTs-A samples, the intensity of the IFM modes are stronger than D-band in these sample and the peaks are broad, these peaks are likely to be related to structural defects in the nanotubes.

Figure 4-5 (a) shows the extended range Raman spectra for a different MWCNT sample (MWCNT2), where the metal catalyst content is extremely low (as evidenced from TGA analysis shown later (Fig. 4-21). We observe G' mode (overtone of D band) and 2LO

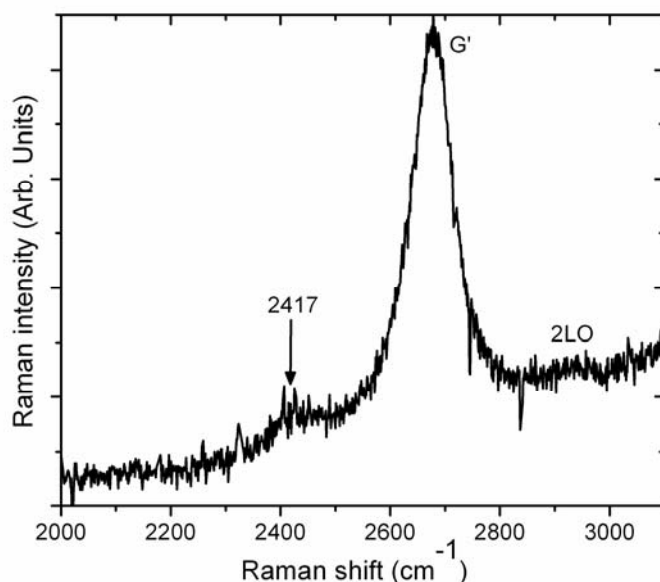


Figure 4-5: Stokes spectra for higher frequency range showing G' and 2LO modes and two new additional peaks at ~ 2417 and ~ 2135 cm^{-1} .

modes at ~ 2674 cm^{-1} and ~ 2927 cm^{-1} , respectively and additional new modes at ~ 2417 cm^{-1} . This new peak arises from the presence of pentagon defects [114], as expected from the large bent regions of the CNTs shown in the HRTEM (shown in Fig. 3-10).

Fig. 4-6 shows the Raman spectra of SWCNTs-A recorded using 488 nm and 632.8 nm lasers under identical conditions. Spectra recorded using 632.8 nm laser shows prominent IFM ($500\text{--}1200$ cm^{-1}) and defect induced feature in between $1650\text{--}2450$ cm^{-1} . With 632.8 nm excitation, the RBM feature appears to be much stronger than that recorded using 488 nm. The peak position of D band and G' band downshifts with lowering the laser excitation energy. Raman spectra with 632.8 nm laser show higher intensity due to resonance effect. A closer look at the G band shows a dominant semi-conducting component with the 632.8 nm laser.

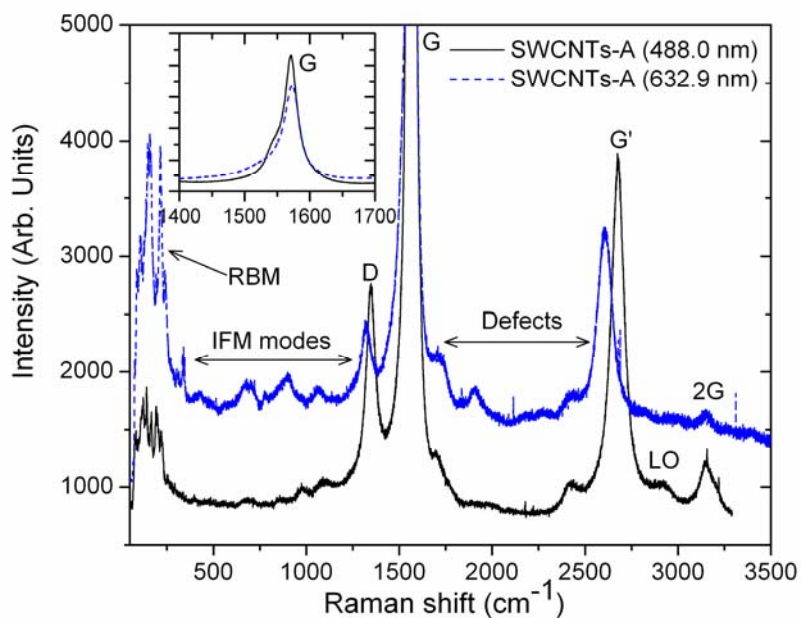


Figure 4-6: Raman spectra of SWCNTs-A with different laser excitations (488 nm and 632.8 nm). Inset of the figure shows characteristic G band.

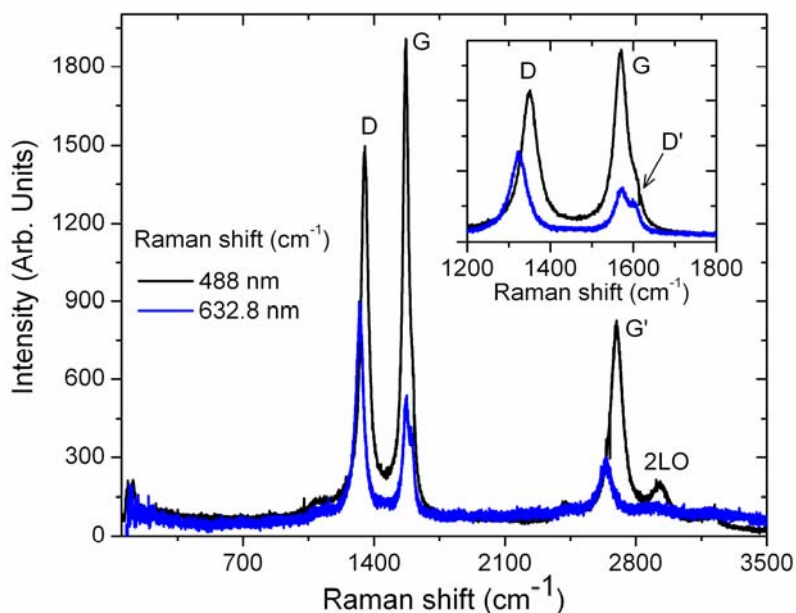


Figure 4-7: Raman spectra of MWCNTs-A with different laser excitations (488 nm and 632.8 nm).

Similarly, Fig. 4-7 shows the Raman spectra of MWCNTs-A for two different laser excitation: 488 nm and 632.8 nm. In contrast to the case of SWCNTs, MWCNTs shows lower Raman intensity when excited with 632.8 nm. Further, D-band intensity is higher than the G-band intensity with 632.8 nm laser. Another defect related peak D' is clearly observed at $\sim 1603 \text{ cm}^{-1}$ (shown clearly in the inset). The appearance of this extra mode is

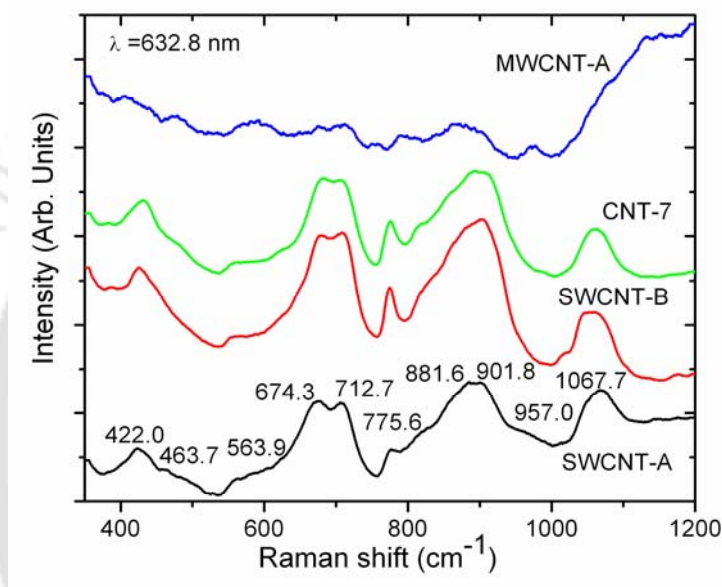


Figure 4-8: Shows the IFM modes of SWCNTs (SWCNT-A, SWCNT-B, grown in two different batches) and MWCNT (CNT-7, lowest diameter MWCNT (<7nm) and MWCNT-A having diameter in the range 10-20 nm).

because of break down of the $q = 0$ wave vector selection rule. D'-band has been observed for graphite samples with crystallite sizes less than 10 nm [296]. In case of MWCNTs it has been found as a disorder induced feature [297].

To identify IFM modes inherent to the SWCNTs, comparison of Raman spectra (IFM modes) of two different SWCNTs (grown in two batches), lowest diameter MWCNTs (CNT-7) and MWCNT-A, are shown in Fig. 4-8. Apparently a similar pattern is observed for all the samples except MWCNT-A having higher diameter and co-axial

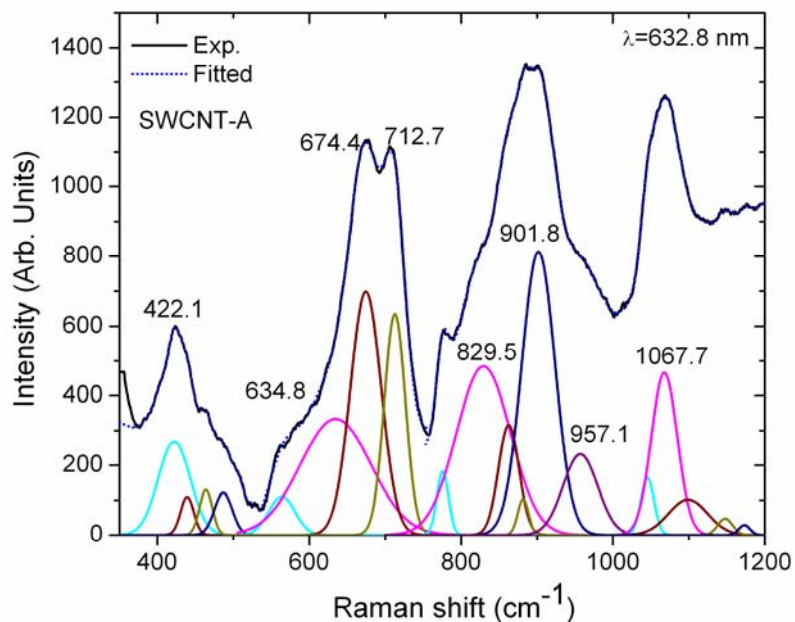


Figure 4-9: Shows the deconvoluted IFM modes (Gaussian line profile) of SWCNT-A.

multilayer structure. MWCNT-A shows broad and noisy spectra in comparison to the spectra from other samples. Broad structure observed in this case is due to combination of a number of peaks arising from individual layers. Fig. 4-9 shows the deconvoluted Raman spectra (IFM region) of SWCNTs-A. Gaussian line profile shows a better fit compared to the Lorentzian line profile. This is due to random distribution of variety of defects at different location in nanotubes.

Fig. 4-10 shows the IFM modes of various diameters MWCNTs. A closer look at the spectra shows the commonality of the major peaks at about 479, 704, 870 and 870 cm^{-1} . Since these modes are common, we account these peaks to be inherent to nanotubes. Apart from these peaks a number of other peaks have been observed specific to each sample, arising from the structural defects as predicted theoretically. Since the intensity of peaks are very weak and pattern is noisy it is difficult to assign the defect induced IFM

modes from Fig. 4-10. But this study clearly shows that IFM modes consist of band arising from defects and others inherently to graphitic tubular structure.

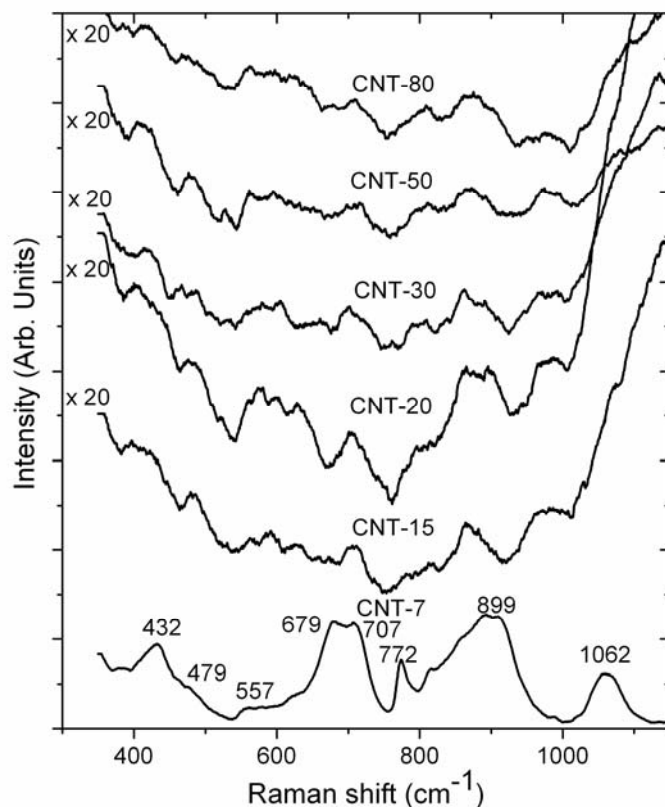


Figure 4-10: IFM modes of MWCNTs of various diameters, as the diameter of the CNTs increases, IFM gets broadened.

Further, to identify the defect induced IFM modes uniquely, we processed the SWCNT-A and MWCNT-A through thermal annealing, laser exposure and ion-irradiation. Fig. 4-11 shows the IFM modes of SWCNTs recorded with different laser wavelength and power. The peak position and width (FWHM) of each IFM peak is summarized in Table 4-1. With increase of the laser power from 30 mw to 250 mw sharp features evolves in the IFM region, which may be characteristics of structural defects. Since number of combination modes can not be so large, these mostly originate from structural defects.

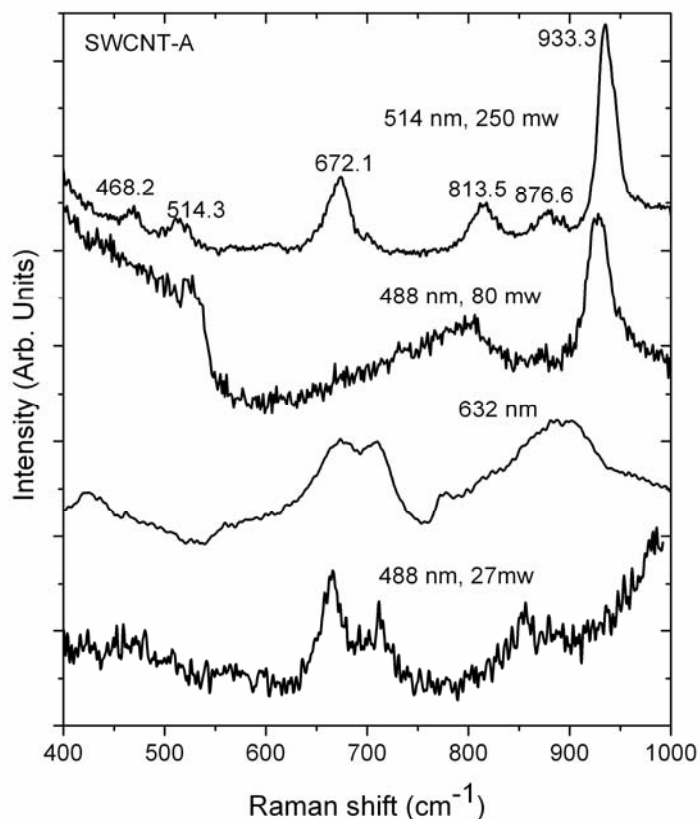


Figure 4-11: Modification of IFM modes of SWCNTs-A with laser energy and power.

Another experimental evidence about the origin of IFM modes from structural defects was obtained by studying effect of variation of laser power as shown in Fig. 4-12. These spectra were recorded using Ar^+ ion laser with varying power in the range 30 mw-160 mw at the laser output. Spectra have been recorded at 30 mw, 40 mw, 50 mw with a step of 10 mw upto 160 mw. Arrow marks shown in the Fig. 4-12 are guide to the eye for changes in the IFM modes observed. Peak observed at 668 cm^{-1} (Peak, 1) shows systematic variation in lineshape and width (FWHM) with variation in the laser power. It also shifts towards higher Raman frequency at an incident power of $\sim 100 \text{ mw}$ onwards. A small hump like feature associated with this peak disappears upon increasing laser power.

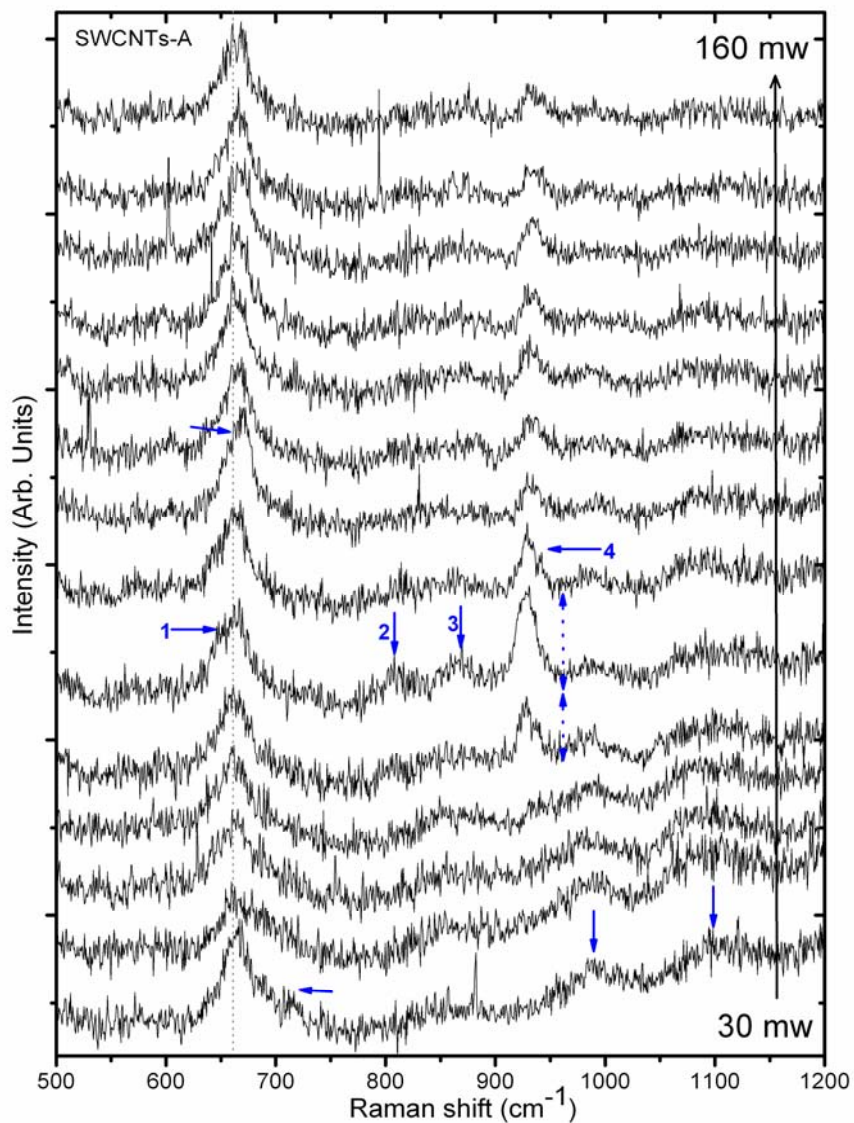


Figure 4-12: Laser power (at output) dependence of the IFM modes of SWCNTs-A. 488 Ar⁺-ion laser was used for this study.

Broad IFM bands in the region 750-900 cm⁻¹ evolve as two new peaks at 807 (Peak 2) and 867 cm⁻¹ (Peak 3) with a laser power of 80 mw. With further increase of laser power, this peak flattens up. Another new peak evolves at laser power higher than the 70 mw and above at 929 cm⁻¹ (Peak, 4), which shifts towards higher frequency side with increasing laser power. Even the peak intensity and line width of this peak varies with the change in

Table 4-1: Summary of the various IFM Modes experimentally observed.

Sample Name	Laser wavelength	Laser Power (P_{out})	IFM Modes (FWHM) in cm^{-1}
SWCNT-A	488 nm	80 mw (dispersive)	713.9 (120.0), 791.9 (133.0, 873.8 (37.5), 926.6 (33.2), 995.9 (115.7)
		30 mw (μ -Raman)	664.6 (21.0), 712.3 (55.3), 854.6 (22.0)
MWCNT-A	488 nm	80 mw (dispersive)	678.7 (25.1), 769.0 (172.7), 928.6 (86.1), 995.4 (112.5)
		30 mw (μ -Raman)	466.4 (95.7), 561.1 (42.8), 670.1 (63.2), 874.2 (188.2), 1096.9 (144.2)
SWCNT-A	514 nm	250 mw (μ -Raman)	468.2 (10.1), 514.3 (12.9), 590.4 (61.9), 672.1 (27.3), 813.5 (35.2), 876.6 (17.6), 933.3 (11.8), 942.6 (15.3), 974.7 (31.6)
SWCNT-A	632 nm	(μ -Raman)	422.1 (49.7), 439.1 (20.5), 463.8 (20.0), 486.8 (27.6), 563.9 (41.1), 634.8 (109.7), 674.4 (47.9), 712.7 (32.7), 775.7 (18.0), 829.5 (83.8), 862.6 (31.9), 881.6 (16.8), 901.8 (51.5), 957.1 (53.9), 1045.4 (20.5), 1067.7 (40.2), 1098.9 (60.1), 1147.9 (22.9), 1173.2 (17.2)
SWCNT-B	632 nm	(μ -Raman)	425.5 (21.3), 447.7 (41.4), 620.2 (38.5), 685.7 (69.3), 715.9 (22.7), 774.4 (12.9), 863.7 (106.9), 910.3 (56.9)
MWCNT-A	632 nm	(μ -Raman)	586.2 (81.2), 698.7 (56.8), 794.7 (19.3), 873.9 (67.3), 973.9 (9.4), 1114.9 (104.9)
CNT-7	632 nm	(μ -Raman)	658.2 (123.2), 679.2 (38.0), 713.3 (32.6), 774.4 (14.0), 818.5 (60.7), 859.9 (45.9), 904.9 (64.9), 1061.9 (45.6)

the laser power. Such change in the intensity and peak width is expected from the variation of defect density. Two broad peaks observed at ~ 999 and 1097 cm^{-1} flattens up with increasing the laser power. Thus from the above study, it is clear that some of the peaks in the IFM region are inherent to the SWCNTs while the other arises due to laser induced structural defects that evolves as a function of time / intensity during laser exposure.

Effect of vacuum annealing on the oxidative stability and structural defects has been discussed Chapter-3. The vacuum annealed samples were further studied with the

632.8 nm (He-Ne) laser to study the change in the IFM modes with defect concentration.

Fig. 4-13 shows the variation in the IFM modes with the annealing temperature. A number of peaks observed in the as-grown sample shows systematic variation in the intensity with

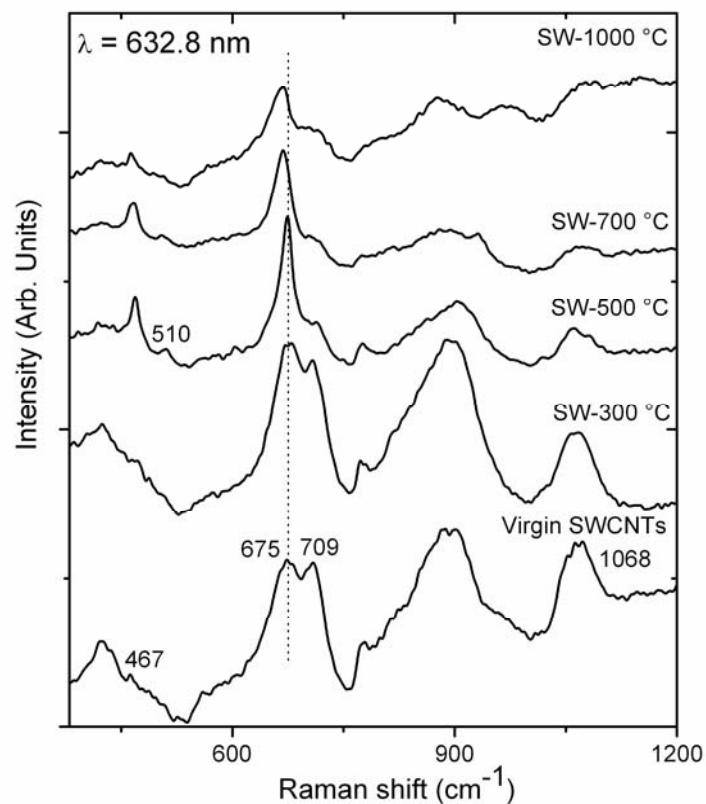


Figure 4-13: Variation in IFM modes of SWCNT-A upon vacuum annealing.

annealing temperature. Broad intense IFM bands observed in the region $400\text{--}550\text{ cm}^{-1}$ evolves as weak sharp peaks at 467 cm^{-1} and 510 cm^{-1} . Two peaks observed at ~ 675 and 709 cm^{-1} , shows a major change with the annealing temperature of $500\text{ }^{\circ}\text{C}$ and above. Peak observed at $\sim 675\text{ cm}^{-1}$ monotonically shifts towards lower frequency side while the other peak (709 cm^{-1}) shows rapid decrease in intensity with the annealing temperature. Broad Gaussian peak observed in the region $756\text{--}1011\text{ cm}^{-1}$ and 1068 cm^{-1} broadens and weaken further with the annealing. Such modification after high vacuum annealing is

clearly related to the annihilation of structural defects. Interestingly, from fig. 4-11, 4-12 and 4-13 it is clear that as the defect concentration increases upon laser exposure in air, IFM modes down shift. On the other hand, decrease in the defect concentration with the change in the annealing temperatures shows upshifts of these modes. These peaks intensify with the increase of defect concentration while with decrease in defect concentration these peaks weaken and get broadened. Thus, these IFM modes are attributed to defects in CNTs.

4.2.2 Additional Raman Modes (in the range 1600-2400 cm^{-1})

Besides the IFM modes, a number of bands are observed in the frequency range 1600-2400 cm^{-1} , i.e between first order G band and second order G' band. Fig. 4-14 shows the variation in the Raman spectra in this region for SWCNTs-A with change in the annealing

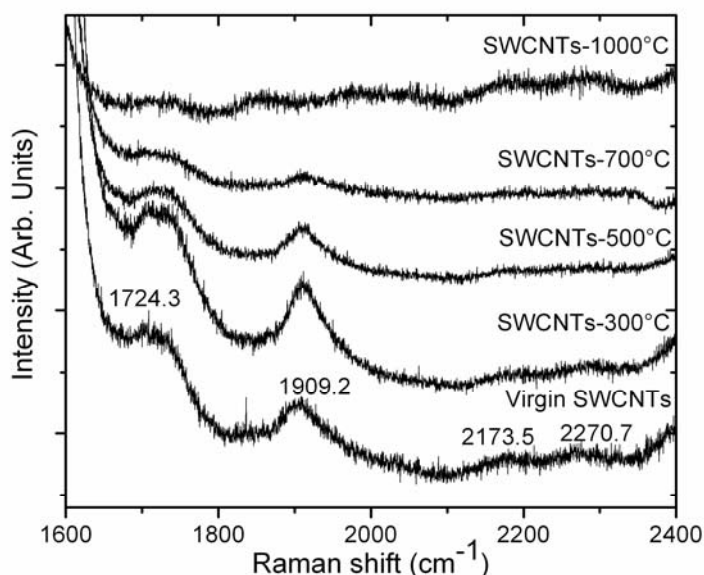


Figure 4-14: Change in Raman modes in the range 1600-2400 cm^{-1} with vacuum annealing at different temperatures. (Recorded with 632.8 nm laser at 30 mw)

temperature. In case of pristine SWCNTs (defective), it shows peaks at 1724.3, 1909.2, 2173.5 and 2270.7 cm^{-1} . The intensity of these peaks monotonically decreases with increasing the annealing temperature. Only for SWCNTs annealed at 1000 $^{\circ}\text{C}$, broad peaks in the region 2100-2400 reappears. This is consistent with the change in I_G/I_D ratio that showed a slight degradation with annealing at 1000 $^{\circ}\text{C}$, as discussed in Chapter-3. Thus, these additional modes are defect induced modes. Our results are in agreement with the theoretical predictions for Raman signature of pentagon defects and SW defects [108, 153].

The possibility of their origin from linear carbon chains is eliminated from the HRTEM studies (Fig. 3-10(a)). We have not observed presence of any such chains in SWCNTs-A, rather a number of sharp and smooth bents in CNTs (Fig. 3-10(b,)) indicating presence of a large number of non-hexagonal carbon rings like pentagons, heptagons and SW defects. These are unlikely to be combination modes since these peaks are relatively broad and changes with defect concentration.

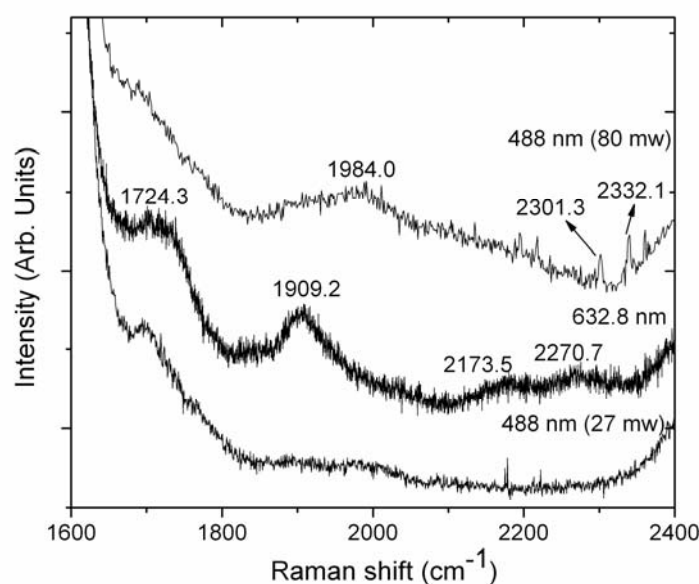


Figure 4-15: Effect of laser energy and power on the Raman modes in the range 1600-2400 cm^{-1} .

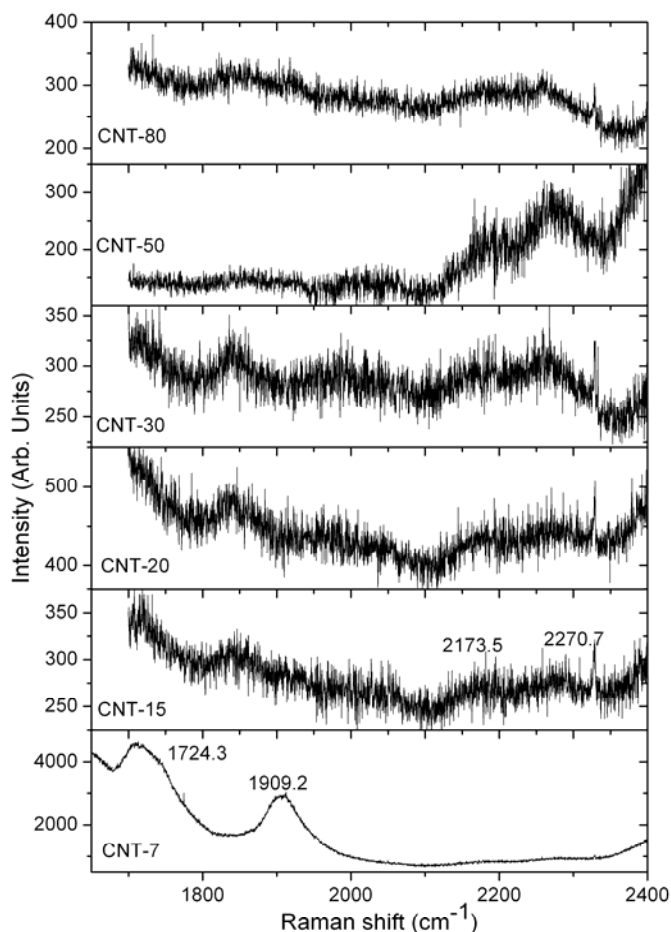


Figure 4-16: Defect induced modes of various diameter MWCNTs (in between 1650 – 1700 cm^{-1})

Fig. 4-15 shows Raman modes of SWCNTs-A recorded using different laser excitation and laser power. Similar to the IFM modes, spectra recorded with 488 nm excitation shows lower intensity than the spectra recorded with 632.8 nm excitation due involvement of resonant effect. It also indicates that these peaks arise from the nanotubes, not from the other carbonaceous impurities. Raman spectra recorded using 488 nm (dispersive Raman spectrometer) is also shown in Fig 4-15 (top curve). It shows peaks at 1984.0, 2301.3 and 2332.1 cm^{-1} which are different from 1724.3, 1909.2, 2173.5 and 2270.7 cm^{-1} peak observed using 632.8 nm laser. Raman spectra of various diameters

MWCNTs recorded in this region using 632.8 nm laser is shown in Fig. 4-16. The difference in spectral features is due to different amount of defects present in their structure as evident from the different I_G/I_D ratio shown in Table 3-3 (Chapter-3).

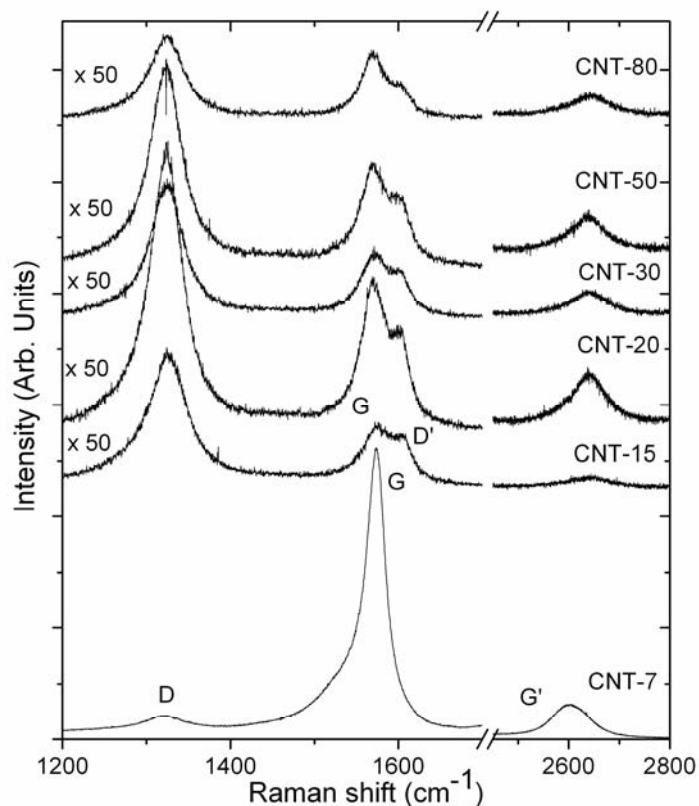


Figure 4-17: D, G and G' modes of various diameter MWCNTs along with defect induced D' mode. These spectra were recorded with 632.8 nm excitation in LabRam HR800. These defect induced D' bands were not observed / distinguishable when excited with 488 nm (Ar⁺ ion laser).

Fig. 4-17 shows the Raman spectra of MWCNTs of various diameters recorded using 632.8 nm laser. Apart from the characteristic D, G and G' mode, these spectra shows well resolved D' peak at $\sim 1602 \text{ cm}^{-1}$. This peak was not observed in case of SWCNTs-A and lowest diameter MWCNTs sample CNT-7. It is important to note that D' peak was not distinguishable with the 488 nm laser. This is due to the resonant effect expected with 632 nm excitation. Spectra recorded using 632.8 nm laser shows comparatively higher

intensity of D band compared to the G-band. While the spectra recorded using 488 nm lasers shows just the opposite behavior, higher intensity of G band compared to the D band intensity. This is due to the larger penetration depth of 632.8 nm laser as compared to the 488 nm laser.

4.2.3 Effect of Vacuum Annealing

Raman studies were performed to study the effect of vacuum annealing on the structural improvements in SWCNTs and MWCNTs. Fig. 4-18(a) shows the evolution of the low frequency RBM modes with annealing. Low frequency RBM (A_{1g}) modes are known to be inversely proportional to the diameter of SWCNTs. Virgin SWCNTs show prominent peaks at 92.8, 131.9, 171.9, 184.3, 229.7 and 307.7 cm^{-1} . 300°C annealed SWCNTs shows similar spectra with additional RBM features at 112.6, 162.0 cm^{-1} and a small down shift of the lowest frequency mode at 92.8 cm^{-1} indicating presence of higher fraction of SWCNTs perhaps due to formation of new SWCNTs and an increase in diameter, respectively. However, SW-500 °C shows reduction in intensity of RBM bands indicating possible degradation of SWCNTs. On the other hand, SW-700 °C sample shows improvement in the RBM features with a more intense band at 225.2 cm^{-1} . SW-1000 °C shows further increase in intensity of RBM modes with strong peaks at 93.4, 132.4, 177.8 (strongest), 225.2 and 308.7 cm^{-1} . Annealing induced changes in the Raman frequency and relative intensity of these RBM modes are indicative of the removal of structural defects that form near-perfect and higher fraction of SWCNTs in the sample. Fig. 4-18(b) shows the changes in the characteristics of D and G modes with vacuum annealing at different temperatures. D-band originates from asymmetry mode activated by loss of translational symmetry due to defects. This peak arises due to breathing modes of A_{1g} symmetry

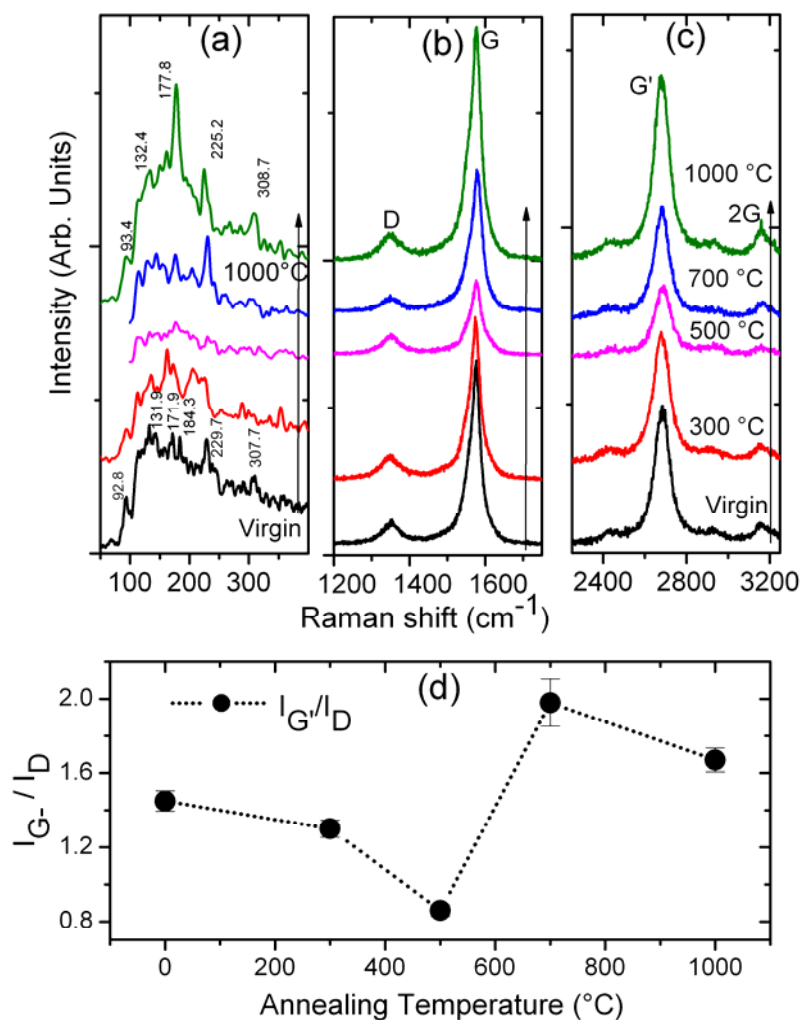


Fig. 4-18: Raman spectra of SWCNTs before and after annealing: (a) Changes in the Low frequency RBM modes with annealing temperature. (b) Modification of characteristic D-band and G-band (c) Variation of second order G' and 2G modes (d) Variation of intensity ratio of $I_{G'}/I_D$ a function of annealing temperature.

involving phonons near the K zone boundary (hexagonal corners of two-dimensional Brillouin zone) [149]. G mode is related to graphitic E_{2g} mode corresponding to tangential vibrational modes of carbon atoms. Changes in the second order Raman modes G'-mode, 2LO mode and 2G mode of SWCNTs are shown in Fig. 4-18(c). The G' mode corresponds to a two-phonon scattering process of phonons around the K point, and it is independent of

Table 4-2: Spectral line profile of first order Raman spectra of vacuum annealed SWCNTs.

Sample name	Spectral profile	Peak1	Peak2	Peak3	Peak4	I_G/I_D
VIRGIN SWCNT	Centre	1350	1560	1576	1585	8.69
	FWHM	50.7	20.7	27.0	81.4	
	Amplitude	132.3	189	1151	125.2	
	Fano (1/q)		-0.597			
SW-300 °C	Centre	1348	1557	1574	1596	7.50
	FWHM	58.8	22.9	28.8	89.1	
	Amplitude	140.7	141.7	1056	78.54	
	Fano (1/q)		-0.652	d		
SW-500 °C	Centre	1351	1563	1576	1608*	4.55
	FWHM	56	21.8	30.4	45.8	
	Amplitude	116	57.91	528	60.16	
	Fano (1/q)		-1			
SW-700 °C	Centre	1349	1561	1579		12.94
	FWHM	50.1	21.0	33.4	----	
	Amplitude	77.5	125.3	1003		
	Fano (1/q)		-0.696			
SW-1000 °C	Centre	1349	1557	1577	1620 *	10.22
	FWHM	58.0	22.5	31.7	235	
	Amplitude	156.4	262.8	1599	36.66	
	Fano (1/q)		-0.503			
Assignments		D-band	Fano	G'-band	G ⁺ -band / * Defects (D')	Ratio

presence of structural defects. D, G and G' modes of vacuum annealed SWCNTs were deconvoluted using combination of Lorentzian and BWF line shape. The spectral parameters obtained after deconvolution are presented in Table 4-2 and Table 4-3. In SW-300 °C, the intensity of the G band is lower compared to virgin SWCNT, whereas D band intensity is slightly higher. Further, with the increase in the annealing temperature to 500 °C, intensity of the G band drastically reduces along with the reduction in D band intensity. However, annealing at 700 °C shows an increase in the intensity of G band and

Table 4-3: Spectral line profile of Second- order Raman spectra of vacuum annealed SWCNTs-A.

Sample name	Spectral profile	Peak1	Peak2	Peak3	Peak4	I_G/I_D
VIRGIN SWCNTs	Centre	2436.3	2683.5	2929.7	3170.1	1.45
	FWHM	103.9	88.49	114.5	117.7	
	Amplitude	12.7	192.5	13.7	26.4	
SW-300 °C	Centre	2426.4	2679.9	2926.0	3166.9	1.30
	FWHM	117.7	94.9	132.1	134.0	
	Amplitude	13.9	182.9	14.2	24.8	
SW-500 °C	Centre	2436.3	2686.3	2929.9	3170.1	0.86
	FWHM	186.9	96.7	140.1	138.1	
	Amplitude	8.6	99.6	13.4	13.6	
SW-700 °C	Centre	2428.9	2680.8	2933.5	3171.1	1.98
	FWHM	143.7	88.2	130.5	107.6	
	Amplitude	10.8	153.4	9.2	22.4	
SW-1000 °C	Centre	2434.2	2680.8	2927.6	3165.9	1.67
	FWHM	140.6	87.8	112.0	102.3	
	Amplitude	17.9	260.5	17.7	40.9	
Assignments		Defect	G'	LO	$2G$	

simultaneous decrease in the intensity of D-band, which implies a structural improvement upon vacuum annealing at 700 °C and this is in agreement to our TGA results. Annealing at higher temperature (1000 °C) shows increase in the intensity of both D and G-bands. The optimum temperature of vacuum annealing for structural improvement can be decided by using the intensity ratio of D and G' band represented by I_G/I_D shown in Fig. 4-18(d). Sample purity is usually characterized using the intensity ratio of D/G band in the Raman spectra from SWCNTs, in analogy to the characterization normally done in carbon-based materials [298]. However, relative changes in the D-band and G' -band Raman spectra is usually used for material characterization to probe and monitor structural modifications of

the nanotube sidewalls that come from the introduction of defects. I_G/I_D ratio has been found to be comparatively more sensitive than I_G/I_D to changes in purity of samples [299]. In Fig. 4-18(d), 700°C annealed sample (SW-700 °C) shows largest value of I_G/I_D ratio. Thus, it is concluded that within the temperature range studied in this work, 700 °C is the most optimum temperature for vacuum annealing of SWCNTs to improve the thermal stability and structural property of SWCNTs.

Fig. 4-19(a) shows the Raman spectra of MWCNTs before and after vacuum annealing. Deconvoluted parameter of these spectras are presented in Table 4-4 (first order Raman spectra) and Table 4-5 (second order Raman spectra). In MWCNTs, low frequency RBM modes were not observed in the present study. In this case, besides the characteristic D, G and G' modes, another defect related mode (D') was observed at $\sim 1610 \text{ cm}^{-1}$ [297]. Note that, intensity of D' peak goes down drastically after annealing at 300 °C and above. Fig. 4-19(b) shows the variation in intensity ratio of I_G/I_D with vacuum annealing temperature. It is evident that 1000°C annealed sample show highest intensity ratio for MWCNTs and thus a relatively higher temperature annealing is essential for achieving improved structure of MWCNTs. Hence, in the range of temperature investigated, 1000 °C is the optimum temperature for defect annealing through vacuum annealing in case of MWCNTs. The correlation of Raman data with the TGA analysis show that samples having lower value of I_G/I_D ratio oxidize at lower temperature. Thus, apart from lattice strain associated with curvature of the CNTs, structural defect plays an important role in deciding oxidation kinetics of CNTs. Note that the Raman analysis on annealed MWCNTs shows the highest I_G/I_D ratio for 1000°C annealed samples, in contrast to the TGA results that show a lower T_{ox} in this sample. Raman analysis of strctural perfection in CNTs is

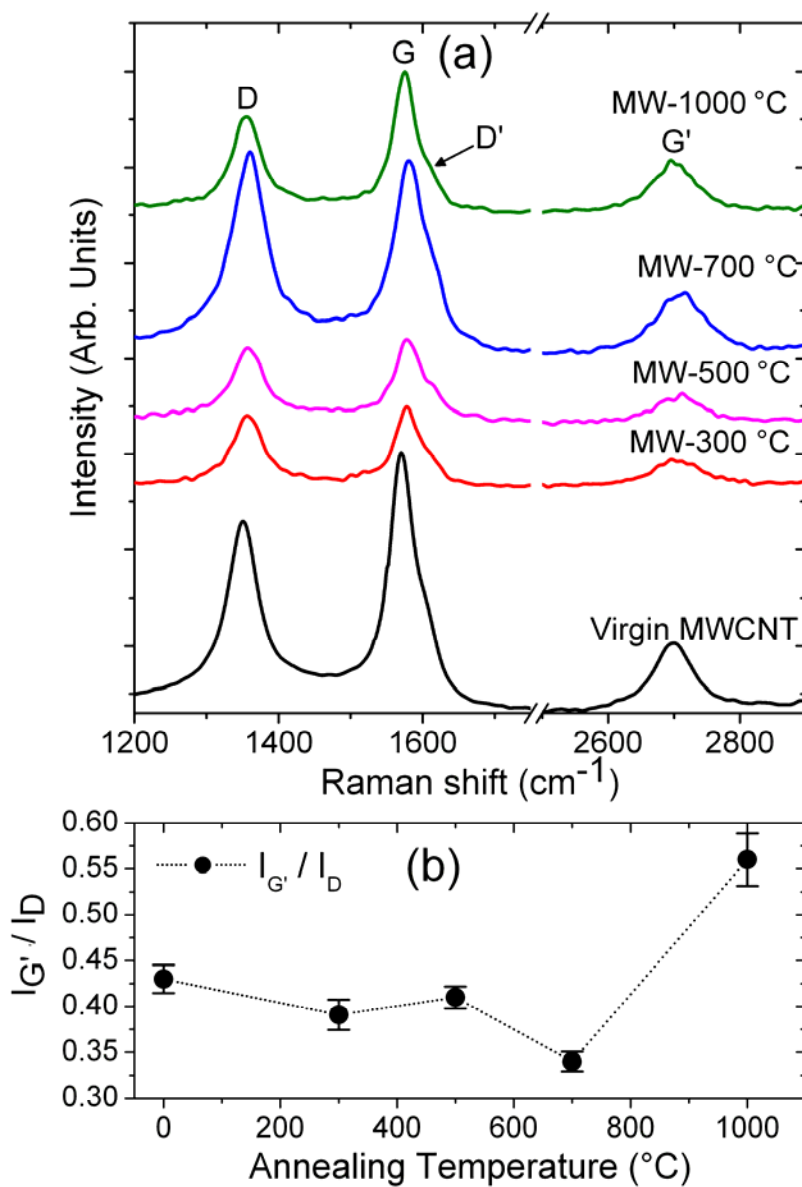


Figure 3-19: Effect of annealing on Raman spectra of MWCNTs of different diameters: (a) characteristic D-band, G band and the second order G'-band along with defect induced D' band. (b) Variation of intensity ratio of $I_{G'}/I_D$ as a function of annealing temperature.

considered to be reliable from the measure of $I_{G'}/I_D$ ratio. The apparent discrepancy can be understood in the following way. While TGA profile is expected to be strongly affected by

Table 4-4: Spectral line profile of first order Raman spectra of vacuum annealed MWCNTs.

Sample name	Spectral profile	Peak1	Peak2	Peak3	Peak4	Peak5	I_G/I_D
VIRGIN MWCNTs	Centre	1350	1362	1505	1570	1603	1.68
	FWHM	23.1	138.6	51.1	17.9	16.7	
	Ampl.	343.8	55.6	20.6	512.5	114.3	
MW-300 °C	Centre	1357			1578	1611	1.30
	FWHM	26.74	----	----	20.3	10.9	
	Ampl.	73.6			81.5	13.0	
MW-500 °C	Centre	1358			1580	1616	1.28
	FWHM	27.1	----	----	22.5	8.1	
	Ampl.	74.0			84.25	13.3	
MW-700 °C	Centre	1359			1581	1615	1.09
	FWHM	32.8	----	----	25.6	10.3	
	Ampl.	199.3			195.7	30.7	
MW-1000 °C	Centre	1355			1575	1609	1.62
	FWHM	25.3	----	----	18.1	9.3	
	Ampl.	98.8			147.1	18.2	
Assignments		D-band	Defects	Fano	G-band	Defects (D')	

all kinds of structural defects, intensity of Raman D-band may not reflect the actual content of extended defects such as holes or voids in the structure. D-band Raman signal primarily reflect the sp^3 carbon content in graphitic materials and the sp^3 signal has got about 50 times lower scattering cross section at visible excitation wavelength compared to that of sp^2 carbon bond. Since our Raman measurements were performed at 488 nm, the measured D-band intensity may not reflect the actual content of sp^3 carbon in these samples. Thus, TGA results are considered to be more appropriate for studying the defects content that decides the thermal stability of nanotubes more reliably. Diameter dependence

Table 4-5: Spectral line profile of Second order Raman spectra of annealed MWCNTs.

Sample name	Spectral profile	Peak1	Peak2	Peak3	Peak4	Peak5	I_G/I_D
VIRGIN MWCNTs	Centre	2425.2	2698.6	2831.3	2935.4	3168.2	0.43
	FWHM	137.5	74.4	29.3	170.7	192.2	
	Ampl.	11.3	149.4	5.8	26.9	11	
MW-300 °C	Centre	2438.3	2704.8		2933.6	3189	0.391
	FWHM	67.8	92.3		104.6	144.4	
	Ampl.	2.8	28.8		6.7	2.8	
MW-500 °C	Centre	2412.7	2708		2938	3211.8	0.41
	FWHM	374.9	88.4		157.9	180.2	
	Ampl.	4.4	30.4		7.6	4.0	
MW-700 °C	Centre	2458.5	2709.7		2934.2	3196.8	0.34
	FWHM	174.7	96.3		126.8	179.6	
	Ampl.	6.4	68.2		15.9	6.4	
MW-1000 °C	Centre	2438.5	2699.8		2927.1	3207.4	0.56
	FWHM	104.6	80.6		130.2	53.2	
	Ampl.	4.7	55.3		8.7	3.9	
Assignments		Defect	G'	Defect	2LO	2G	

of the I_G/I_D ratio show that defect concentration does not decrease systematically with increasing diameter, while the oxidative stability increases systematically with increasing diameter. Hence, observed diameter dependent T_{ox} is primarily caused by the curvature effects of nanotubes. At higher curvature, the CNTs are more strained and due to defects in the strained sites oxidation proceeds fast leading to a lower T_{ox} .

4.3 Photoluminescence Studies of Defects

4.3.1 Visible PL from SWCNTs and MWCNTs

Fig. 4-20 shows the PL spectra recorded at room temperature on SWCNT-A and MWCNT-A using 488 nm Ar^+ laser and dispersive Raman spectrometer. We have

recorded emission spectra only in the visible range of energy. The spectra show that besides the sharp peaks due to phonon modes (Raman) near 2.4 eV, both the samples show two broad PL emission bands in the visible region. For SWCNTs, the peaks are centered at 2.33 eV and 2.05 eV with full width at half maximum (FWHM) of about 0.22 eV and 0.40 eV, respectively. In MWCNT, PL emission peaks are centered at 2.34 eV and 2.05 eV having

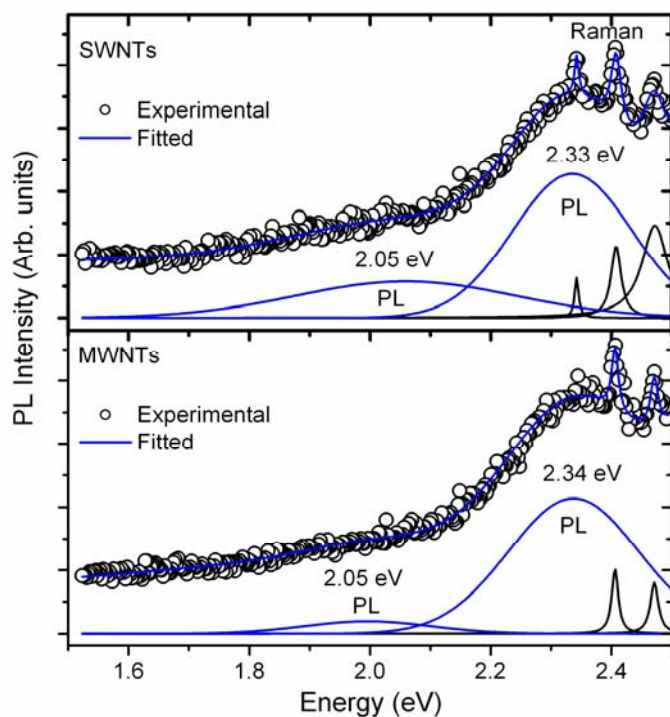


Fig. 4-20: PL spectra of SWCNT and MWCNT at room temperature. Experimental data points are shown in symbols and fitted spectra are shown solid line. Two broad PL peaks are common to both samples. The sharp peaks are due to Raman scattering.

FWHM of 0.25 eV in each case. These emission bands are far beyond the fundamental gaps of the semiconducting CNTs. Further, it is well known that aggregation of nanotubes into bundles otherwise quenches the PL emission through interaction with metallic tubes and substantially broadens the absorption spectra. Only the spectroscopy of isolated individual nanotubes gives rise to the expected band gap fluorescence from the

semiconducting SWCNTs. In MWCNTs such emission is not efficient due to the large outer diameter of the nanotubes.

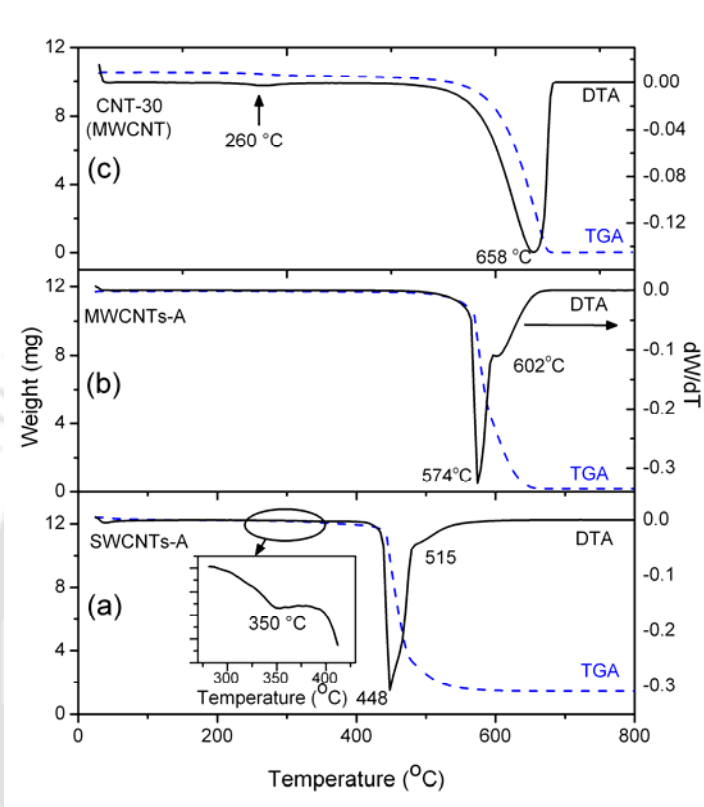


Fig. 4-21: TGA and differentiated TGA data for (a) SWCNT, (b) MWCNT1, and (c) MWCNT2 samples. Inset of (a) shows magnified view of low temperature peak. Peak positions (temperatures) are denoted in degree celcius unit.

In order to understand the role of metallic impurities in the visible PL, we studied these samples using TGA analysis. Figure 4-21(a) shows the TGA and differentiated TGA curves for SWCNT sample where residual impurity (metal) content is found to be 9.3% and Fig. 4-21(b) shows residual metal content of 1.1% for MWCNT1 and Fig. 4-21 (c) shows residual metal content of only 0.18% for MWCNT2 samples. The differentiated DTA data for SWCNT sample show a very low intensity peak at $\sim 350^{\circ}\text{C}$ (as shown in the inset of Fig. 4-21(a)) indicating very low content of amorphous carbon particles in the

SWCNT sample. On the other hand, DTGA curves of Fig. 4-21(b) do not show any low temperature peak indicating no measurable content of amorphous carbon particles in MWCNT1. Fig. 4-21(c) shows again a very low content of amorphous carbon particle as revealed from a peak at $\sim 260^{\circ}\text{C}$ in the DTGA data. The strongest peak in the DTGA curve is at 448°C , 574°C and 658°C for SWCNT-A, MWCNT-A and CNT-30 (MWCNT), respectively. The low temperature burning of SWCNTs is strongly indicative of defects in the nanotubes structure [63]. MWCNTs show relatively higher burning temperature depending on the metal content. Our results show that one with least metal content has highest burning temperature. The higher temperature small peaks at 515°C and 602°C are due to CNTs containing fewer defects.

With these observations, we would like to now address on the origin of the visible PL from both SWCNT and MWCNTs. Note that visible luminescence background has been found in several Raman studies reported earlier, though it has not been addressed properly in the literature. For example, Jorio et al. observed strong visible luminescence background above 1800 cm^{-1} in their Raman spectra [34]. Hence, our results are not particular to these samples, but it bears a generality to other nanotube samples with controlled or well-defined defects. The fact that PL features are identical in two different samples with different metallic content and different amorphous carbon content (as revealed from TGA analysis), the contribution of metallic impurity and carbon nanoparticles are ruled out as the possible origin of visible PL. In fact, it is well known that Fe, Co, Mo are good quenchers of PL in luminescent dyes, luminescent nanoparticles. Hence, any role of catalyst residues for the visible PL is completely ruled out. On the other hand, the additional IFM Raman modes, new Raman modes of Fig. 4-2 and low temperature peak in the DTGA (448°C for SWCNT and 574°C for MWCNT1) are strong

indicators of involvement of structural defects in the visible PL. Defective nanotubes are known to burn out at a lower temperature as compared to the pure nanotubes. HRTEM results clearly showed varieties of structural defects in the nanotube walls. Theoretical predictions suggest that the observed high frequency Raman modes are signature of pentagon defects in the bent nanotubes [108].

Efficient visible PL from very small diameter carbon nanotubes in zeolite template has been explained on the basis of dipole allowed transitions and photon emission [189]. However, higher energy emission at 2.6 eV has been attributed to nitrogen-defect states in the nanotubes. Polarized optical absorption spectra of single-walled 0.4 nm carbon nanotubes have shown 2.1 eV absorption band, which was attributed to dipole transitions between the Van Hove singularities [189]. Strain induced band gap change of CNTs due to hydrogenation or chlorination has been reported [37]. It is very likely that due to the large amount of defects in the nanotubes, these defects break the symmetry of the tube, leading to repulsion between crossing bands and thereby creating higher gaps. The presence of defects and impurities may change the local structure of the nanotubes and affect the optical properties. Theoretically the bond rotation defect has been found to close the gap in large-gap nanotubes, open gap in small-gap nanotubes, and increase the density of states in metallic nanotubes [36]. It has been shown that introduction of a pentagon-heptagon defects into a hexagonal lattice can change the helicity of the tube and alters its electronic structure [300]. Localized defect states has been observed in case of semiconductor-semiconductor nanotubes junctions [126]. Vacancy related band gap opening has been predicted theoretically in case of metallic carbon nanotubes [106]. Ab-initio pseudopotential calculations have shown formation of deep localized states caused by various vacancy-related defects in case of semiconducting tubes, which can behave as

recombination centers of electron and hole carriers [92]. Interestingly midgap luminescence at ~1235 nm has been observed in case of SWCNTs upon UV-illumination [152]. Thus band gap opening is quite likely from the defective nanotubes and it may extend to visible region of energy. A very large line width of the PL spectra is also typical of emission from extended defect states with a broad distribution of energies. Due to bundling of the nanotubes, the efficiency of radiative emission from the defect states is low at room temperature and thus low intensity of PL is observed.

4.3.2 Visible PL After Aniline Functionalization

Chemical modification of CNTs has been attempted by many authors to tailor its physical [301-303] and chemical properties [304]. Chemical modification of CNTs was performed for their dissolution in aromatic amines, details as discussed in Chapter-2. We have followed the method reported by Y. Sun and others for SWCNTs [186], and changes in their chemical, structural and optical properties has been studied. We have functionalized SWCNTs and MWCNTs both for a comparative study of effect of aniline functionalized on the type of nanotube. In particular, changes in the structural, chemical and optical emission and absorption properties are discussed in below.

Structural studies: SEM, TEM, XRD results

As obtained functionalized carbon nanotubes were characterized by SEM, HRTEM, powder XRD and FT-IR spectroscopy. Fig. 4-22 shows the electron micrographs of carbon nanotubes before and after functionalization. SEM image of SWCNTs before functionalization is shown in Fig. 4-22(a), whereas after functionalization it is shown in Fig. 4-22(b)-(c). Most of the CNTs were found to be aggregated after aniline

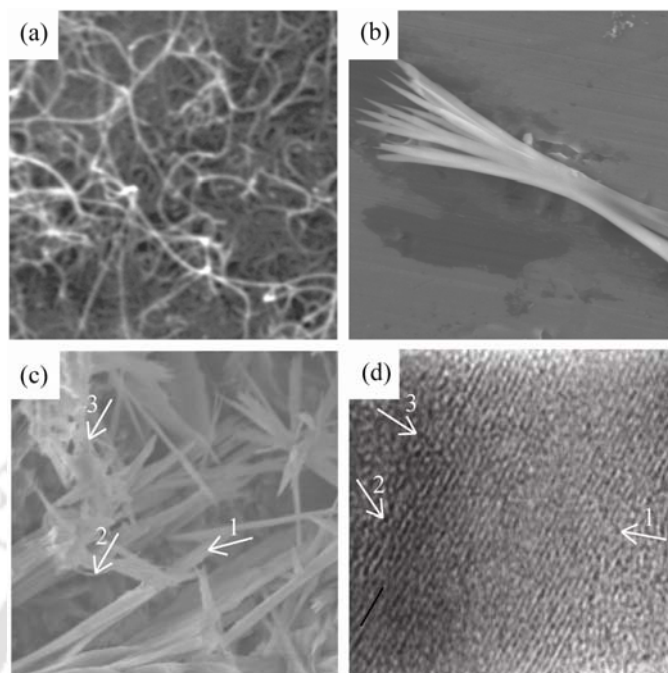


Figure 4-22: SEM images of SWCNT-A before functionalization, (b) after NH_2 functionalization (c) magnified image of a portion of functionalized SWCNTs sample shows 1- bundled nanotubes, 2-individual nanotube, 3-aggregated nanotube bundles. (d) HRTEM image of MWCNTs-B- NH_2 , showing damaged outer walls (indicated by arrows 1-3) after aniline functionalization.

functionalization as shown in Fig. 4-22(b). Enlarged image of a portion of functionalized sample is shown in Fig. 4-22(c). Region-1 shows bundled tubes, region-2 shows a dispersed single CNT, while region-3 shows aggregated bundled portion. Fig. 4-22 (d) shows the HRTEM image of a aromatic amine functionalized MWCNT sample. It shows damaged outer wall structure as indicated by arrows (regions1-3). This shows that aniline is attached to defect sites after reflux. Fig. 2-28 shows the XRD pattern of pristine and aromatic amine functionalized SWCNTs. Presence of characteristic (002) peak in the filtered solution confirms the presence of dissolved aniline functionalized SWCNTs. It also indicates that aniline groups are attached at the defect sites, but the tubular graphitic structure remains intact.

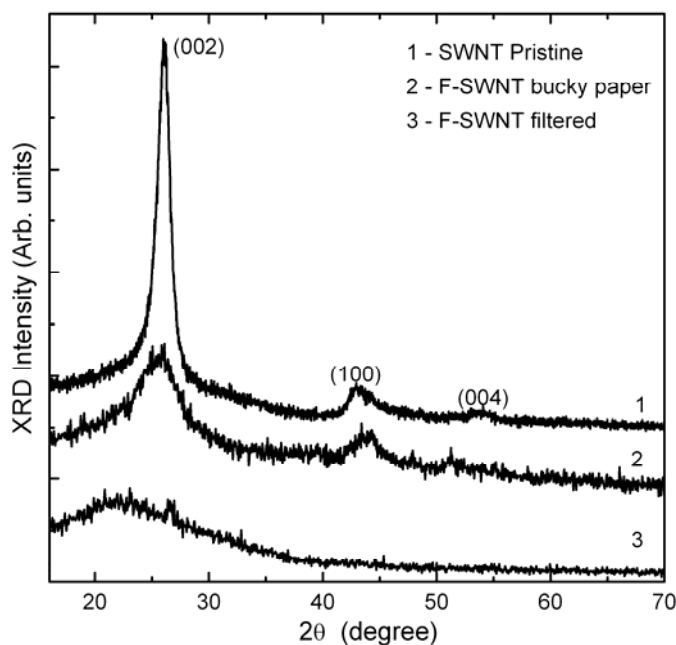


Figure 4-23: Shows XRD pattern of pristine SWCNT-A and SWCNTs-NH₂ (aromatic amine functionalized SWCNTs). Presence of (002) reflection in the solution confirms presence of functionalized SWCNTs.

FTIR studies:

Fig. 4-24 shows the FTIR spectra of SWCNT-A before and after aniline functionalization. FTIR spectra of pristine samples (prior to functionalization, upper curve) show several bands, such as C-O stretching (1022), C-H deformation (1392), C-C stretching (1627), CO₂ (2358), C-H stretching (2917) and moisture related bands (3436). Due to long exposure in atmosphere, these samples show hydrogen and oxygen related bonds, besides the expected C-C band. Though energy dispersive X-ray (EDX) spectra do not show any impurity content such as oxygen and hydrogen, FTIR spectra show presence of these impurities in the nanotubes. Lower spectrum in Fig. 4-24 shows the FTIR spectra after functionalization. The spectrum shows several additional bands related to grafted aniline (chemical group). The strong absorption peaks at 1603 and 3358 are due to N-H

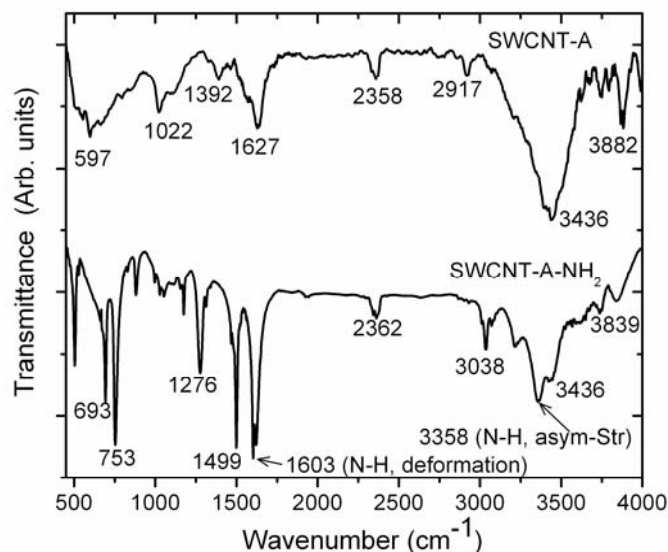


Figure 4-24: FTIR spectra of SWCNT-A before (upper curve) and after functionalization (lower curve).

deformation of primary amine and N-H stretching (asymmetric) vibrations, respectively. Small peak at 1053 is due to C-N stretching modes. Therefore, the amino group appeared to graft onto the surface of SWCNTs. This group is believed to change the surface properties of the CNTs that in turn drastically changes the optical properties of the SWCNTs as observed in fluorescence and optical absorption measurements.

UV-Vis Absorption studies:

Pristine SWCNTs dispersed in common solvents (e.g. ethanol, methanol, acetone etc.) do not show any optical absorption Uv-Visible region at room temperature. However, after functionalization strong optical absorption peak below 350 nm and a relatively broad absorption bands in the visible range are found. Fig. 4-25 shows the absorption spectra of aniline functionalized SWCNTs and MWCNTs diluted with ethanol. These spectra were deconvoluted using Gaussian lineshape to determine the exact absorption peaks as shown

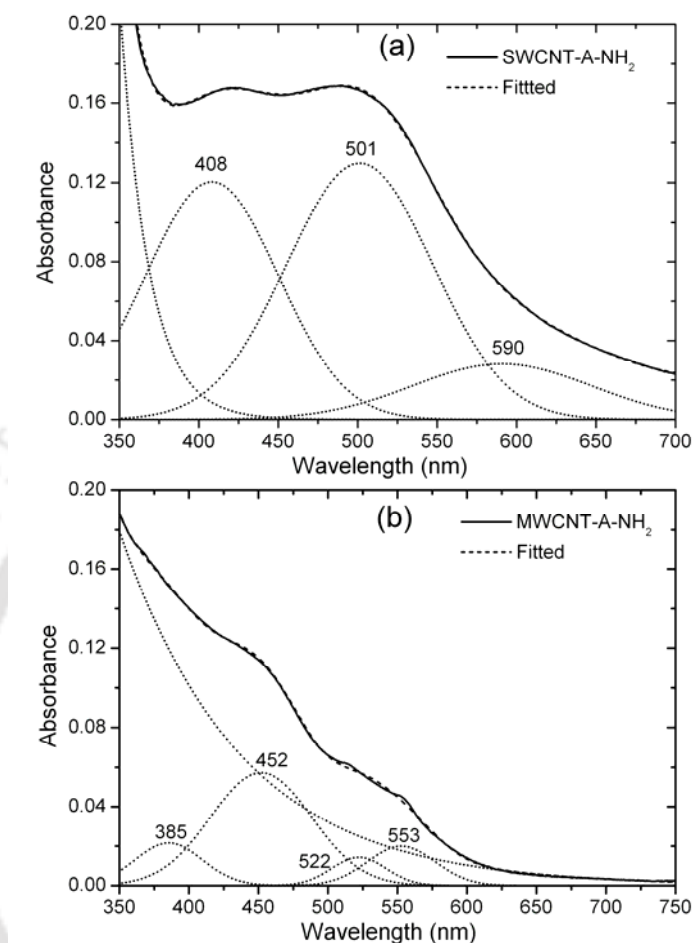


Figure 4-25: UV-VIS absorption spectra (a) Aniline functionalized SWCNTs (SWCNT-A-NH₂) showing prominent absorption peaks at 408 and 501 nm (b) Aniline functionalized MWCNT-A (MWCNT-A-NH₂), peaks at 385, 452, 522 and 553 nm.

by dotted lines. SWCNT-A-NH₂ shows the absorption peaks at 408nm, 501 nm and broad hump at 590 nm, while MWCNT-A-NH₂ shows a number of absorption peaks at 385nm, 452nm, 522nm and 553 nm. Increasing concentration of functionalized SWCNTs and MWCNTs in ethanol shows increase in the intensity of these peaks, supporting that these peaks genuinely arise from the functionalized CNTs. Dilution of functionalized nanotubes (SWCNT-A-NH₂) with another solvent acetone shows stronger absorption peak at ~440 nm as shown in Fig. 4-26(a). With further dilution using acetone the peak position do not

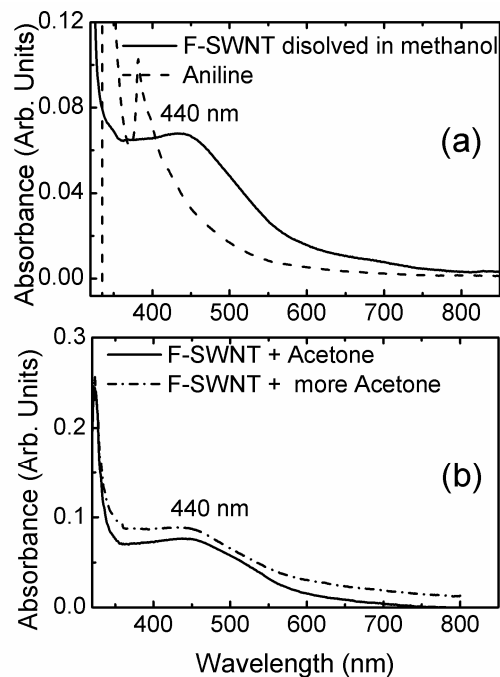


Figure 4-26: UV-Vis absorption spectra of SWCNT-A-NH₂ in different solvents.

show any shift as shown in Fig. 4-26(b). Absorption spectrum of aniline solution is shown for comparison, since aniline was used for functionalization. The broad peak in the range 400-450 nm is attributed to the formation of an aniline-SWCNT charge transfer complex [186, 305]. Carbon nanotube is expected to be a good electron acceptor while aniline is a fairly good electron donor [176, 187]. At elevated temperature ($\sim 184^\circ\text{C}$), CNTs and aniline may form a charge-transfer complex in its ground state as evidenced by the appearance of new absorption peak in the visible region. SWCNT-aniline solution diluted with toluene and chloroform shows maximum absorption at wavelength 301 nm and dilution in acetone showed peak absorption at 323 nm. Intensity of absorption in SWCNT-aniline diluted with toluene and chloroform is found to be much higher than the dilution with acetone. A mechanism proposed by Sun et al. [186] for attachment of alkyl amine with carbon atoms of nanotubes is likely to operate during the reflux reaction performed in

the present study. Results of our FTIR studies confirm such a reaction where C-H and C-N bonds are found after reaction. In general, nanotubes have a strong tendency to aggregate, which is one of the reasons they are insoluble in common solvents.

PL Studies:

Pristine samples do not show any measurable PL signal in the visible region. However, after functionalization, strong visible PL emission is observed from SWCNTs.

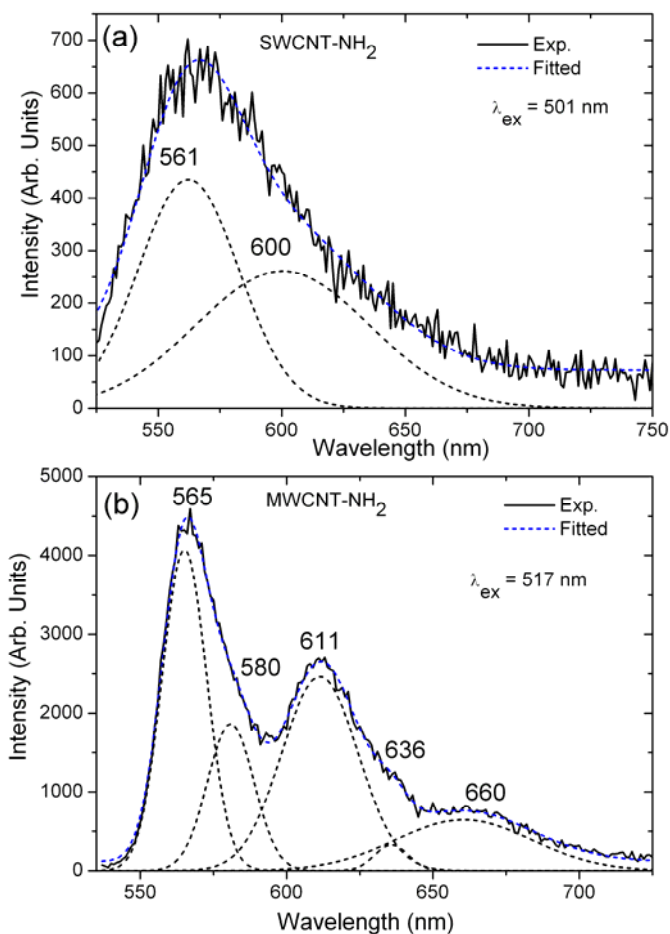


Fig. 4-27: (a) PL from aniline functionalized SWCNT-A (SWCNTs-NH₂) showing emission at 561 and 600 nm, when excited at 501 nm (b) Emission at 565, 580, 611, 636 and 660 nm from aniline functionalized MWCNTs (MWCNT-A-NH₂).

Emission spectra of aniline functionalized CNTs in ethanol are shown in Fig. 4-27. SWCNT-A-NH₂ shows emission at 561 and 600 nm respectively (shown in Fig. 4-27(a)) while MWCNT-A-NH₂ shows emission at 565, 580, 611, 636 and 660 nm (Fig. 4-27(b)). In this case a large number of emission peaks is consistent with its multiple absorption bands.

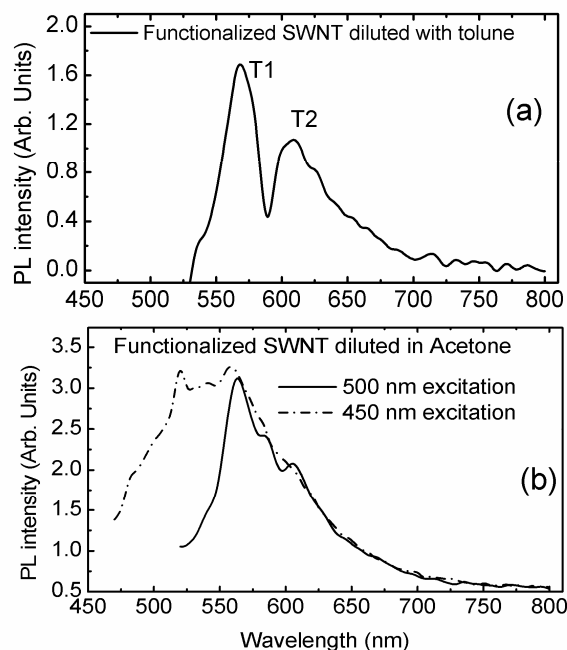


Figure 4-28: Room temperature PL spectra of SWCNT-A-NH₂. (a) Excitation with 500 nm, (b) Excitation with 450 nm and 500 nm light. Peaks at ~565 nm and ~611 nm are common to F-SWCNTs diluted with various solvents.

Fig. 4-28 shows PL spectra of the functionalized SWCNT samples diluted with two different solvents toluene and acetone. Fig. 4-28 (a) shows two strong fluorescence peaks at 568 nm and 608 nm from functionalized SWCNTs. The spectrum is obtained after subtracting the background due to toluene. Similar spectrum is obtained when acetone is used for dilution. Fig. 4-28 (b) shows that fluorescence spectra are dependent on excitation wavelength. Higher the energy of excitation, additional higher energy or low

wavelength peaks are observed in fluorescence spectra, which indicates that functionalized nanotubes have broad electronic density of states.

PL Excitation Studies:

Fig. 4-29 shows the Photoluminescence excitation (PLE) spectra of the aniline (aromatic amine) functionalized SWCNTs and MWCNTs. Excitation spectra is an analogue of the absorption spectra, with a small difference for optically not allowed

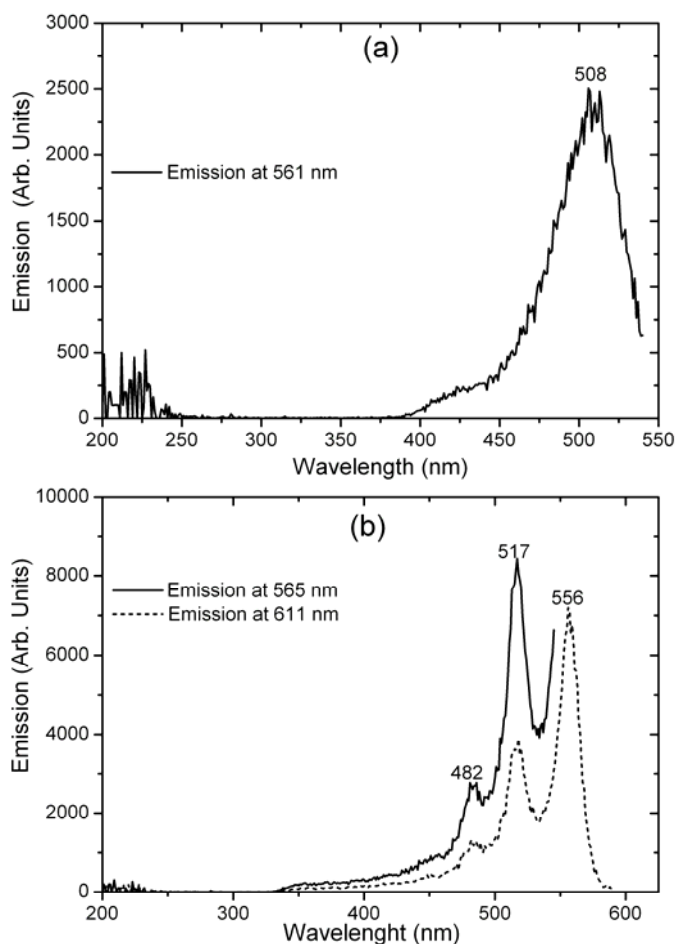


Fig. 4-29: (a) PL excitation spectra of SWCNT-A-NH₂. It shows prominent absorption at 508 nm for emission at 561 nm. (b) PLE showing common three peak absorption profile at 482, 517 and 556 nm for emissions at 565 nm and 613 nm.

transitions. Excitation spectra represent the optical band structure of a material. Fig. 4-29 (a) shows the excitation spectra of SWCNT-A-NH₂ for emission at 561 nm (prominent peak in the emission spectra, Fig. 4-27(a)). It shows a prominent peak at 508 nm (absorption band) along with a hump at ~ 425 nm. This is close to the absorption peak at 501 nm experimentally observed, while corresponding to the prominent absorption peak at 408 nm only a small hump like excitation peak is observed at ~ 425 nm. This shows that absorption at 501 nm primarily contributes towards the visible PL observed experimentally after aniline functionalization. Fig. 4-29(b) shows the PLE spectra for MWCNT-A-NH₂ for 565 and 611 nm emission peaks. Interestingly, it shows common sharp excitation peaks at 482, 517 and 556. These peaks are close to the broad absorption peaks observed at 452, 522 and 553 nm shown in Fig. 4-25. Slight difference in peaks position are due to broad feature of the absorption spectra contrary to the excitation spectra and comparatively lower spectral resolution of the absorption spectrophotometer than the emission spectrophotometer used for recording the excitation spectra. The common excitation peaks for emission at 565 and 611 nm indicates their origin from the similar band states. This is possible with the creation of intermediate energy levels due to slight difference in the nature of structural defects.

Further, these samples were studied using time resolved photoluminescence (TRPL) spectroscopy and the results are shown in Fig. 4-30. These decay curves were fitted with exponential decay function to determine the PL decay time and the possible channels of decay i.e possible number of pathways. TRPL spectra of SWCNTs shown in 4-30(a) requires two exponentials for deconvolution with time constants of 0.21 ns and 1.42 ns and amplitudes of 93.5 % and 6.5 % of the decay channels respectively for 565 emission and 505 nm (picoseconds pulsed diode laser) excitation. MWCNT-A-NH₂

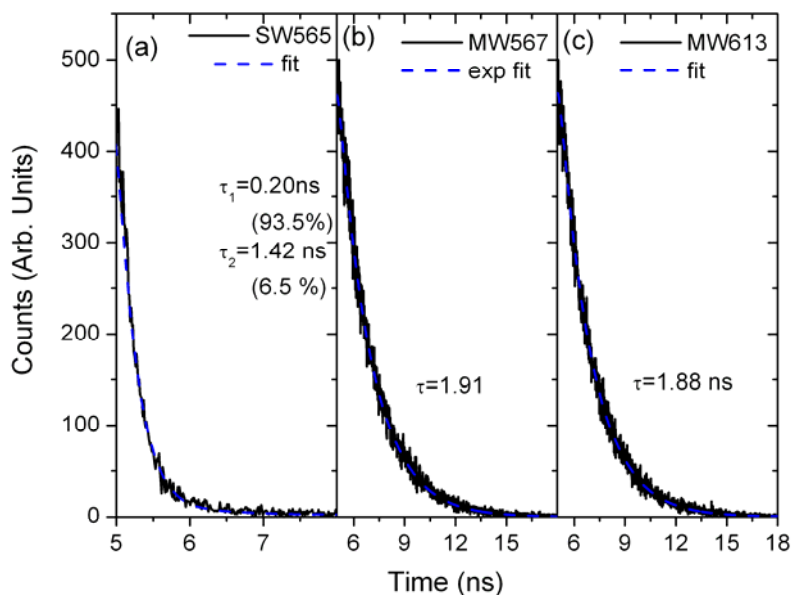


Fig. 4-30: Time resolved PL spectra. of aniline functionalized CNTs. (a) PL decay spectra of SWCNT-A-NH₂, showing decay times of 0.2 ns (for 93.5%) and 1.42 ns (for 6.5%) for 565 emissions peak. (b) PL decay spectra of MWCNT-A-NH₂ showing single exponential decay constant of 1.91 ns for 565 nm and (c) PL decay spectra of MWCNT-A-NH₂ s showing single exponential decay with time $\tau = 1.88$ ns for 613 nm emission peak. Both the spectra were recorded using 505 nm picoseconds pulsed diode laser excitation.

requires single exponential fit for the TRPL spectra corresponding to decay constants of 1.91 ns and 1.88 ns for 565 nm and 613 nm respectively with 505 nm (picoseconds pulsed diode laser) excitation. Almost similar time constants of 1.91 and 1.88 ns for 565 and 613 nm emission channels is in agreement with the similar excitation profile observed for both the emission peaks of MWCNT-A-NH₂. This is another evidence of our understanding that both the emission peaks have a common origin. Different lifetimes observed in case of SWCNT-A-NH₂ and MWCNT-A-NH₂ indicate different extent of surface damage and nature of defects created during functionalization, giving rise to unique emissions in case of SWCNTs and MWCNTs. Origin of such visible PL from naturally NIR emitting CNTs is only possible through defect that modify the band structure.

The FTIR spectrum of SWCNT-A-NH₂ confirmed several additional bands related to grafted aniline (chemical group), as shown in Fig. 4-24, indicating presence of grafted amino group on the surface of SWCNTs. This functional group drastically modifies the optical properties of CNTs as observed in fluorescence and optical absorption spectroscopy. This is in contrast to the possible physical adsorption of impurities on the nanotube which may not alter electronic properties of the material. It is likely that a new chemical species is produced on heating SWCNT in aniline, and that photoexcitation of this species leads to a luminescent charge separated state (exciplex). In polymer bound CNTs, Riggs et al. suggested that the luminescence might be due to the trapping of the excitation energy at defect sites [187]. Another factor that might enhance the PL efficiency is their large molecular size, which would inhibit deactivation through molecular motion.

It is well known that pristine SWCNTs emit in the near IR range due to their small bandgap. However, functionalization modifies the surface of the CNTs and higher energy transitions are allowed due to possible opening of the bandgap. Visible PL could be mediated by the defects at the nanotube surface after functionalization as seen in HRTEM (Chapter-2, Fig. 2-27(d)). Modification of nanotube surface is also apparent from broadening of the XRD pattern after aniline functionalization (Fig. 4-22). Such high PL yield of SWCNT-A-NH₂ can be exploited for applications involving visible light emitting devices and as biomarkers.

4.4 Conclusions

In conclusion, Raman scattering studies on SWCNTs and MWCNTs grown by CVD method and processed through laser irradiation and vacuum annealing show new IFM modes and additional feature that are signature of structural defects in the nanotubes.

Room temperature PL studies show two broad PL peaks centered at ~2.05 and ~2.33 eV

for both the samples. Our results strongly indicate that structural defects in the nanotubes are responsible for the broad visible PL at room temperature and most of the IFM modes are related to the structural defects in the nanotubes. Results from Raman studies are consistent with TGA studies (presented in Chapter-3), showing higher thermal stability of large diameter MWCNTs is primarily due to low lattice strain and low defect density. Studies on vacuum annealed sample shows that structural defects and strain influence the oxidative stability of SWCNTs in a stronger way than that of MWCNTs.

SWCNTs show different optical properties in comparison to MWCNTs after aniline functionalization. PL excitation spectroscopy shows creation of a broad energy state in case of SWCNTs, while sharp energy states in case of MWCNTs after aniline functionalization. Visible PL arises from the band gap opening due to structural defects created during reflux reaction.

Chapter -5

Electron Paramagnetic Resonance Studies

5.1 Introduction

Electron paramagnetic resonance (EPR) is a very sensitive probe for electronic structure in materials and it monitors effective g-value for both conduction and localized (defect) electron states in materials in which unpaired electrons exist. It has been utilized for studying paramagnetic defects and localized electron states in CNTs. In this Chapter, we have studied the EPR of SWCNTs and MWCNTs before and after vacuum annealing in order to understand the signature and role of structural defects in the EPR spectra of CNTs. Further, the effect of diameter of the MWCNTs on the EPR spectral line profile has been studied systematically for diameters in the range 5-100 nm. The temperature dependence of EPR spectra have been performed in the temperature range 150 - 300 K to understand the origin of various peaks observed experimentally at the room temperature.

5.2 ESR Studies of SWCNTs and MWCNTs

Fig. 5-1 shows EPR spectra of as-received SWCNTs and MWCNTs. Both SWCNT-A and MWCNT-A samples show almost identically broad EPR spectra, as shown in Fig. 5-1(a) and (b) respectively. However, CNT-30 (MWCNT of diameter 30 nm) sample which contains almost negligible metal content show additional sharp feature, besides the broad feature in the ESR data, as shown in Fig. 5-1(c). Sharp feature in the range (300-340 mT) i.e., near free electron g value (g_e) are characteristic of CNTs. To determine the exact g-value of the broad EPR peaks, spectral deconvolution was performed using combination of a Dysonian line and two Gaussian lines, as shown in Fig. 5-2 for CNT-30. Deconvolution of ESR spectrum may require more number of lines depending upon sample purity, amount of defect and metallic impurity content. The high

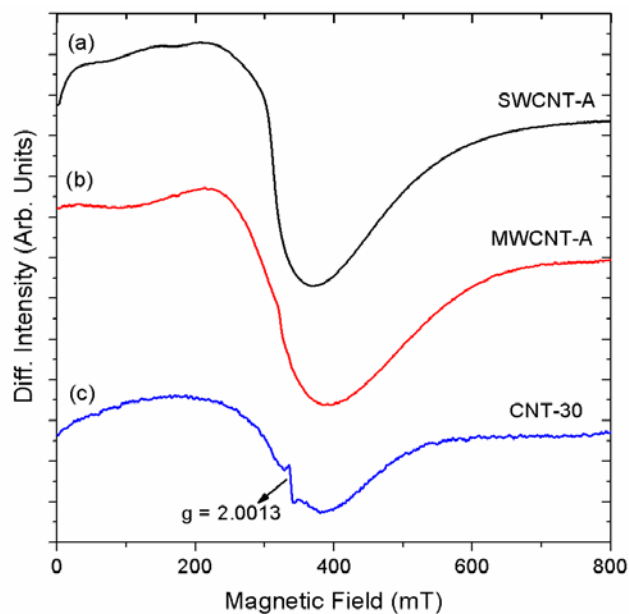


Figure 5-1: ESR spectra of (a) SWCNT-A (b) MWCNT-A and (c) CNT-30. Broad absorption feature arises from metallic catalyst nanoparticles. Characteristic sharp peak is observed only in case of CNT-30, which contains very low amount of metallic impurity.

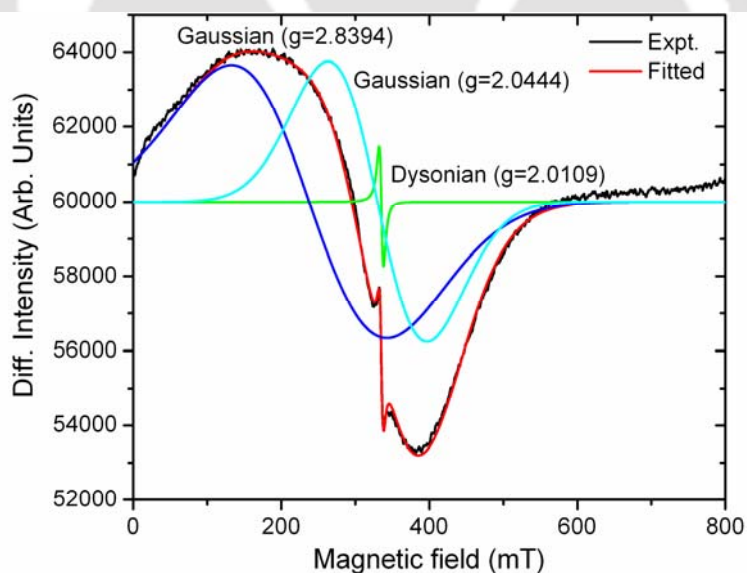


Figure 5-2: Deconvoluted EPR spectra of a MWCNT consisting of two Gaussian peaks and one Dysonian peak using Matlab.

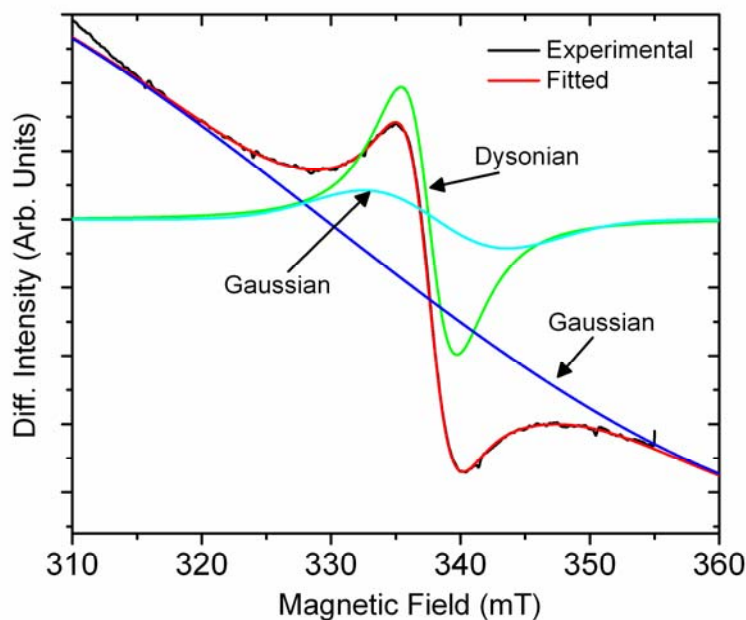


Figure 5-3: Deconvolution of the sharp peak recorded with higher integration time and small scan range using combination of a Gaussian and Dysonian peak profile.

'g' value ~ 3.0 is attributed to magnetic impurities present in the samples. The 'g' value of ~ 2.0 (broad and asymmetric peak) is assigned to the interaction between the conducting electrons in the nanotubes trapped at defects or magnetic ions site, known as conduction electron spin resonance (CESR) peak. However, electrons localized at the defect sites on the nanotube walls give rise to a comparatively sharper peak, generally located at a lower g-value than the CESR peak. CESR peaks are expected to show Pauli like behavior i.e. no change in the susceptibility (χ) with variation in temperature, while defect induce peaks are expected to show Curie like behavior ($\chi \propto 1/T$). But it is difficult to assign exact g-value for the characteristic CESR and defect induced peaks separately by visual inspection, for samples containing even very low amount of metallic impurities. Interestingly, a closer look at Fig. 5-2 shows the requirement of another weak peak near the Dysonian peak. In this case, our attempt to deconvolute it further with an additional

Lorentzian/ Gaussian peak was not feasible due to its very low intensity. Hence we recorded separately the spectra only for the sharp peak region (310-360 mT), as shown in Fig. 5-3 with higher integration time and amplification factor. Deconvolution of the spectra shows that it requires a very weak Gaussian / Lorentzian component along with a strong Dysonian component. We have studied the change in the line profile of characteristic peaks and broad ferromagnetic resonance (FMR) peak after deconvolution of spectra. We have also studied the temperature dependence of the g-value for these peaks, presented later.

5.3 Diameter Dependence of EPR Line Profile

Fig. 5-4 shows the EPR spectra of MWCNTs of various diameters. These measurements were performed with microwave oscillator frequency of ~ 9.5 GHz, modulation width 0.35mT and the modulation amplitude 500. Constant weight of each sample was taken for ESR measurement equal to 2.1 mg. Calibration was done using standard Mn^{2+} marker. All the samples show a broad ESR spectrum that was deconvoluted using combination of Gaussian and a Dysonian components using Matlab. Any sharp peak expected from the paramagnetic defects / impurities was masked under the broad FMR peak. However, CESR peak was distinguishable only in case of CNT-20 and CNT-30, which contains very small amount of metallic impurities as confirmed from TGA and VSM studies.

Diameter dependent variation in EPR line profile was analyzed in terms of shift in g-value, FWHM and the microwave absorption intensity. Deconvolution of spectra in this region (310-360 mT) requires a Gaussian component (at $g \sim 2.009$) along with an asymmetric Dysonian component (at $g \sim 2.000$), as expected from a paramagnetic defects

and from conduction electrons residing on the nanotubes. Such Dysonian line shape arises when the length of the sample along the propagation direction of microwaves is larger than the skin depth, resulting into damping of microwave field within the sample.

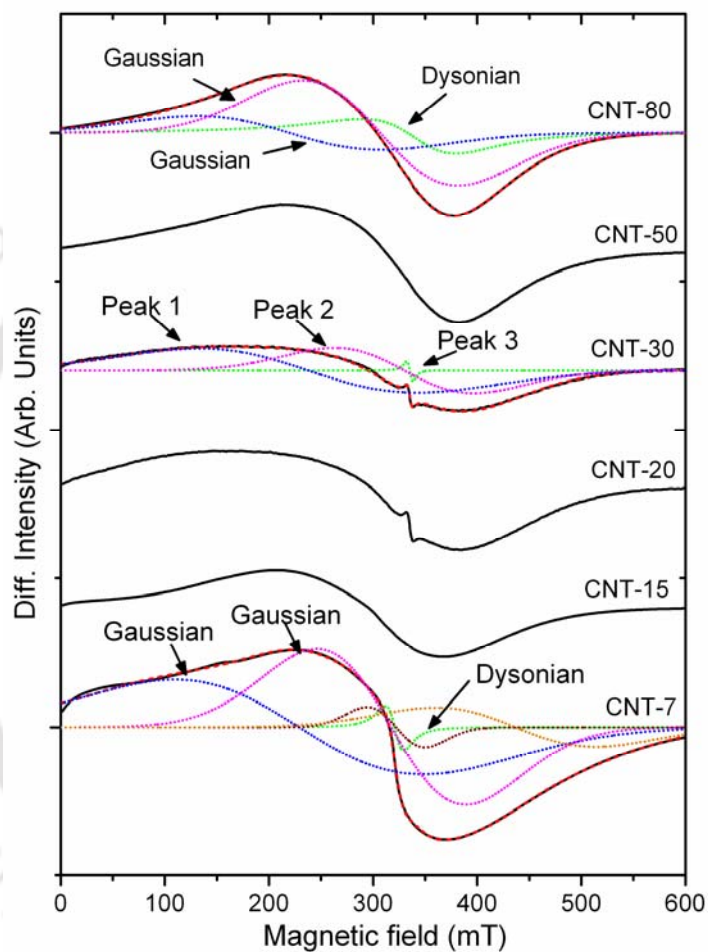


Figure 5-4: ESR spectra of MWCNTs for various diameter MWCNTs. Deconvoluted spectra of CNT-7, CNT-30 and CNT-80 are shown with dotted line. Broad Gaussian components, peak 1 and peak 2 arise from Ferromagnetic impurities and a narrow Dysonian component due to conduction electrons of CNTs.

Dysonian lineshape is expressed in terms of combination of dispersive and absorptive components. For the observed broad spectra, Gaussian peak profile gives better fit than the Lorentzian profile. Non-interacting electronic spins are responsible for Gaussian like

resonance shapes, whereas motional effects distort the resonance line towards a Lorentzian one [214]. Diameter distribution of MWCNTs in our samples contributes towards observed Gaussian line shape. Deconvoluted EPR line shape parameters for different diameter MWCNTs are summarized in Table 5-1. The calculated g -values and the fitting parameters are plotted as a function of the average diameter of MWCNTs in Fig. 5-5. Peak 1 in Fig. 5-5(a) shows a large g -value and is likely to be caused by magnetic impurities. The g -value of this peak varies from 2.945 (CNT-7) to 2.362 (CNT-15), 3.660 (CNT-20), 2.839 (CNT-30), 2.659 (CNT-50) and 3.076 (CNT-80) for different diameter

Table 5-1: Deconvoluted EPR line profile parameters for various diameter MWCNTs.

Sample Name	Line profile parameters	Peak1	Peak2	Peak3	Peak4	Peak5
		Gaussian	Gaussian	Dysonian	Gaussian	Gaussian
CNT-7	g -value	2.9451	2.1258	2.0100	2.0954	1.5447
	FWHM (mT)	280.9	168.2	30.1	27.8	76.6
	Assym. (α)			0.1821		
CNT-15	g -value	2.3629	1.8716	2.0720		
	FWHM (mT)	208.5	79.9	130.1		
	Assym. (α)			1.7310		
CNT-20	g -value	3.6607	2.1335	2.0102		
	FWHM (mT)	184.4	178.0	11.3		
	Assym. (α)			0.3532		
CNT-30	g -value	2.8395	2.0444	2.0109		
	FWHM (mT)	247.25	157.49	10.17		
	Assym. (α)			0.2826		
CNT-50	g -value	2.6595	2.1412	1.9944		
	FWHM (mT)	234.4	161.1	146.0		
	Assym. (α)			0.3813		
CNT-80	g -value	3.0764	2.1983	1.9471		
	FWHM (mT)	208.1	175.2	152.3		
	Assym. (α)			0.7345		
Assignments		FMR (g_1)	CESR (g_2)	FMR	CNTs	---

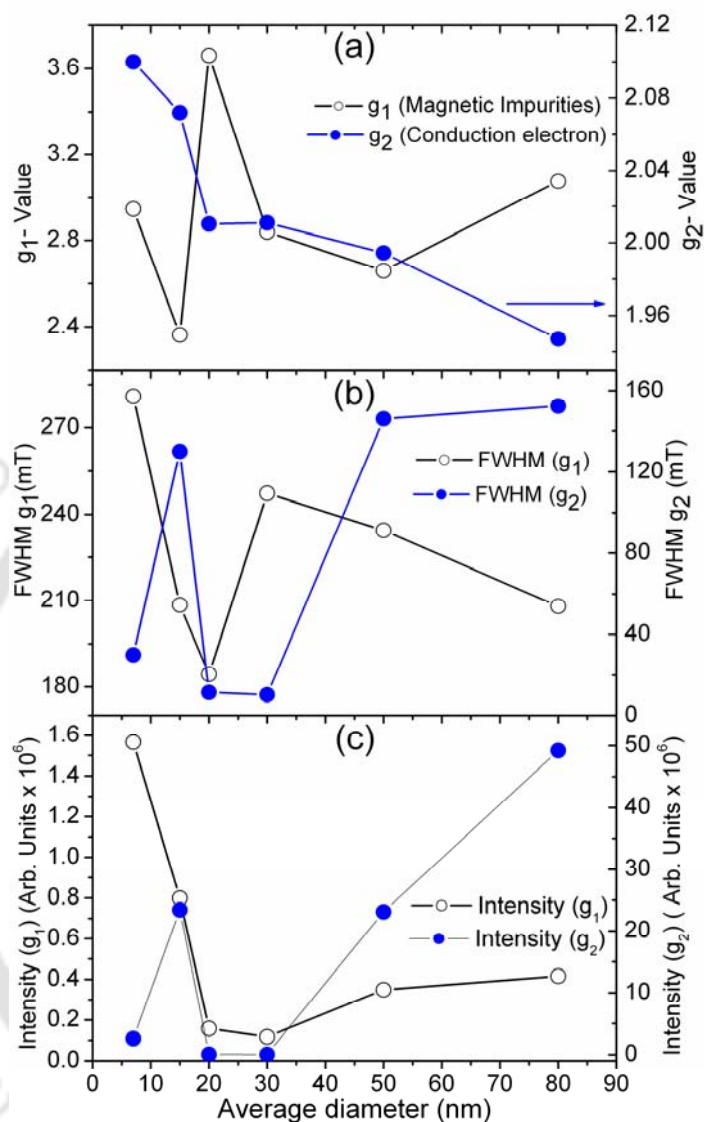


Figure 5-5: Diameter dependence of Gaussian deconvoluted ESR parameter for MWCNTs: (a) g component corresponding to peak 1 shifts to higher g -value in case of samples containing lesser metallic impurities, Whereas g_2 corresponding to peak 2 monotonically upshifts from $g = 2.01363$ to 2.15002 with increasing diameter of MWCNTs except for CNT-80 (b) Variation of EPR peak width with average diameter of MWCNTs. FWHM of peak 2 monotonically decreases due to quantum size effect. (except CNT15 which has wider diameter distribution range) (c) Variation of EPR peak intensity with average diameter of MWCNTs.

samples. Interestingly, sample with smaller g -value corresponds to peak 1 having higher metal catalyst content, as evident from TGA and VSM studies. As the catalyst content

decreases, g-value is found to increase. The peak 1 is attributed to the ferromagnetic impurities, called as FMR peak.

Peak 2 corresponds to a 'g-value' close to that of free electron 'g-value'. It shows a systematic decrease from 2.099 to 1.947 as the diameter of the nanotube increases from 7nm to 50nm. For CNT-80, it shows again a downshift. Note that CNT-80 has lesser purity as found from SEM imaging. The change in g-value for peak 2 is different from that of peak 1 and it is not correlated with the magnetic impurity content of the sample. Thus, 'g-value' of the peak 2 depends on the CNT diameter. Peak 2 arises from interaction of conduction electrons of CNTs and metallic catalysts. Interestingly, the diameter dependence of this peak can be taken as a measure for estimating the diameter of MWCNTs using EPR spectroscopy. Third peak is again assigned to the FMR structure. Such two-line pattern EPR response observed in our samples is typical for magnetic NPs ensemble consisting of particles of different sizes and shapes [306]. Such two-peak FMR structure has been observed even in case of Ni nanoparticles encapsulated in as grown SWCNTs bundles [307]. The two peaks FMR feature arises from unblocked (super-paramagnetic) and blocked (ferromagnetic) nanoparticles. More details about the temperature variation of line width and position of these peaks are presented in section 5.5.

In case of sample having very low amount of metallic impurity, particularly CNT-20 and CNT-30 broad third peaks was not observed, rather a sharp feature was observed as expected from pure CNTs. So the third peaks is identified in terms of two peak FMR structure (broad feature) in case of sample containing high metallic impurity and peak from CNT (sharp feature) is distinctly observed only when the sample contains very low amount of metallic impurity.

The origin of diameter dependence of the CESR peak (g_2) can be understood from folding of graphene sheets. When the magnetic field is parallel to the graphene planes, g -factor has a minimum value 2.0026 slightly higher than free electron value due to the small spin-orbit coupling with carbon atoms [210]. This special property of the graphite arises due to the position of the Fermi level near the π bands crossing at K points of the hexagonal Brillouin zone [259]. When a magnetic field is applied perpendicular to the plane, electrons condense on the $N = 0$ Landau level, which induces this unusual anisotropic behavior [260]. When the field is parallel to the planes, no closed orbits are accessible and the effect disappears. In case of CNTs, this picture is modified due to cylindrical wrapping especially when the tube radius is small compared to the cyclotron radius (r_c); then closed orbits can not form. Usually average 'g value' 2.0012 of pure CNTs is different from the 'g value' of graphite 2.0018. It is expected that g shift would decrease with the tube diameter since it becomes more and more difficult to form Landau levels [201]. This agrees with the experimental observation of diameter dependence of the CESR g_2 peak. ESR spectra of CNT-20 and CNT-30 that showed a sharp Lorentzian peak at $g = 2.0127$ and CNT-7 at 2.0987, as shown in Fig. 5. This sharp feature with a g -value lower than that of the broad line, is assigned to paramagnetic impurities or defects. This sharp feature is close to the sharp EPR peak at $g = 1.9798$ observed in case of pure graphite powder (Fluka).

The diameter dependence of line width or, FWHM of these two peaks is shown in Fig. 5-5(b). The line width of ESR spectra depends on the relaxation time of the spin state under study. The FWHM of Peak 1 follows the same pattern as I_G/I_D ratio as well as metal catalyst content for different diameter MWCNTs (see Fig 3-8, chapter 3). i.e. MWCNTs having higher impurity content shows higher FWHM for peak 1. This implies an

interaction between the metallic impurities and the conduction electron that gives rise to large FWHM for peak 1. FWHM of Peak 2 also shows a nice correlation with the metallic residue and structural defects. Samples having a lower FWHM contains lesser metallic impurities (as estimated from TGA studies Table 3-4) and lesser structural defects (estimated from I_G/I_D ratio, Inset of Fig. 3-8).

The line width of the first derivative EPR signal is related to the spin relaxation time T_s and is given by following equation $T_s = 2[\Delta H_{pp} g \gamma_e k]^{-1}$, where, g = g-factor (Lande' factor), $\gamma_e = 1.42 \times 10^7 \text{ G}^{-1}\text{s}^{-1}$ is the Gyromagnetic ratio and k is a constant depending upon the line shape (usually taken as 5.44 for a Lorentzian line shape). Presence of metallic impurities or nanoparticles may provide an efficient and faster path for spin relaxation leading to decrease in the FWHM proportionally with the amount of metallic impurities present. Similarly, lower defect density causes slower damping of the vibrations of lattice, resulting into slower spin-lattice relaxation time causing line broadening. Thus, nanotubes having lesser defects show narrower line width for the CESR peak 2, accounting for lower FWHM of peak 2 in CNT-50 and CNT-80. CNT-20 shows deviation from systematic behavior compared to other samples due to presence of several carbon phases, as observed in DTA spectra. Thus, the relaxation of CESR (FWHM of Peak 2) is decided by two competing factors: metal nanoparticle and defects.

Intensity variation of ESR absorption with diameter is shown in Fig. 5-5(c). Intensity of the peak 1 is consistent with the metallic impurities content in the sample, as evidenced from magnetization (emu/gm) and TGA measurements. It shows high intensity for CNT-7, CNT-50 and CNT-80 which contains higher amount of metallic impurities while samples CNT-15, CNT-20 and CNT-30 shows comparatively lower intensity due to relatively lower metallic content. Intensity of peak 2 scales with the defect density and

amount of metallic impurities present in the sample. Peak 2 intensity scales with I_G/I_D ratio. The higher I_G/I_D ratio i.e., less defects leads to lesser localization of charge carriers resulting into weaker absorption intensity, except CNT-7 where comparatively much higher amount of metallic impurities shows very strong FMR peak and masks the CESR signal, reflected from the very small intensity of the peak 2.

Variation of FWHM with diameter (as shown in Fig. 5-5(b)) can be interpreted in terms of quantum size effect. This effect has been studied in case of metal nanoparticles [308]. The resonance position, or g-shift, the ESR linewidth, the saturability of the resonance or longitudinal relaxation time (T_1) and the integrated intensity, all these factors are expected to change when the discreteness of electron level spectrum becomes apparent at low temperature, or where the average level spacing is large compared to the magnetic field. The peak to peak line width (H_{pp}) of the bulk derivative ESR spectrum can be expressed in terms of the electron spin relaxation time τ_s , for bulk metal or large particles, T_s can be expressed by Elliott relation using $\Delta H_{pp} \approx (\gamma_e T_s)^{-1}$,

$$\frac{1}{T_s} = \frac{1}{T_r} (\Delta g_\infty)^2 \quad (5-1)$$

For particles with diameter d , smaller than the RF skin depth, one expects to see an effect of the resistivity scattering rate, $1/T_r$

$$\frac{1}{T_r} = \frac{v_F}{d} + f(T) \quad (5-2)$$

The regime for which eqn (5-2) holds is that for which the spin diffusion length is greater than the particle diameter, $d \ll d_s = [(v_F \lambda) T_s / 3]^{1/2}$, where λ is the electronic mean free path. For pure metals d_s may be typically a number of micrometers. This gives a picture

suggested by Dyson [309] where the conduction electron is scattered by the surface of a particle with the probability of a spin flip given simply by $(\Delta g_{\infty})^2$. Including both bulk and surface terms the temperature dependent linewidth becomes:

$$\Delta H_{pp} \approx \gamma_e^{-1} [F(T) + \nu_F / d] (\Delta g_{\infty})^2 \quad (5-3)$$

Eqn. (5-3) shows that one would expect broader ESR line shape for smaller particles [308] in agreement with the broad EPR line shape for peak 1 in for CNT-7, having very small diameter of the CNTs used during growth.

Broad component, peak 2, is not located exactly at the theoretical g value ($g_{th} = 2.0023$), as the angular momentum is not completely quenched. The deviation of the resonance line position is controlled by the spin orbit coupling λ , and by the energy difference ΔE between the corresponding electronic levels belonging to the same wave vector [204]. For a real system, the particle size distribution leads to a distribution of shifts and widths that produce inhomogeneous broadening of the ESR line as observed an anomalous behavior for CNT-20 experimentally than other samples.

5.4 Effect of Vacuum Annealing

ESR spectra of pristine and vacuum annealed SWCNTs are shown in Fig. 5-6. Equal weight of all the samples were used for EPR measurements for the comparison of intensity of the peaks. SWCNT-A, MWCNT-A and CNT-20 was vacuum annealed at various temperatures. Sample details and conditions of vacuum annealing are described in Chapter-3. Inset of the Fig. 5-6 shows the spectra for a specific range. Besides the broad (FMR) feature, we can see the small CESR and paramagnetic peak in the range 280-350 mT. These spectra were deconvoluted using combination of Gaussian and Dysonian peaks.

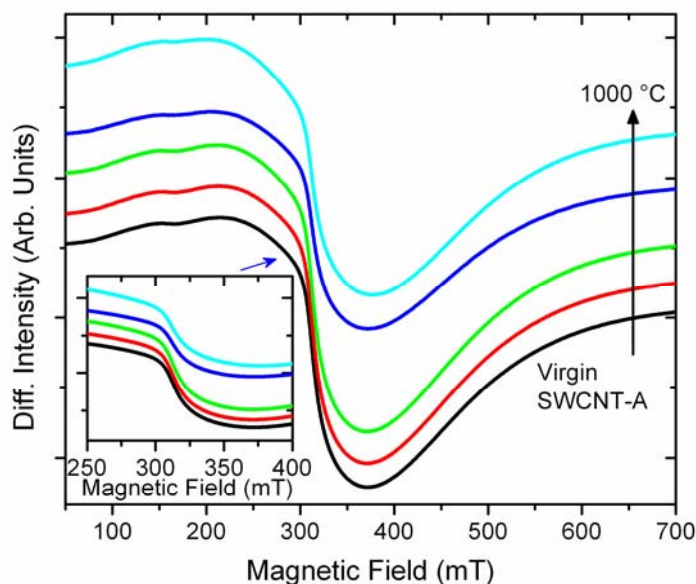


Figure 5-6: ESR spectra of SWCNT-A before and after vacuum annealing. It shows change in the absorption intensity with annealing temperature especially at 700 and 1000 °C. Inset shows magnified image of a portion of the spectra.

Fig. 5-7 shows the deconvolution of spectra of SWCNT-A (before annealing). Deconvoluted EPR spectra contains five peaks: a super paramagnetic resonance (SPR) peak, a gaussian FMR peak and a broad dysonian (~ 107 mT) CESR component arising from residual metallic catalysts, and two other relatively sharp peaks in the region (250-380 mT) arising from conduction electrons of CNTs and localized electrons at the defects. Although it is apparently difficult to distinguish the characteristic peaks of CNTs in presence of FMR peak arising from metallic residues, in some cases using deconvolution it is feasible to estimate the position, peak width and intensity of the characteristic CESR and defect peaks in CNT. In this sample, our attempt to experimentally record the sharp features was not successful to visually distinguish the two peaks, which arises in SWCNT-A. Broad and FMR peaks observed in this case are in agreement with the TGA results,

which shows 9.3 % metallic impurity. Peak-2 arising from defects enlisted in Table 5-2 shows

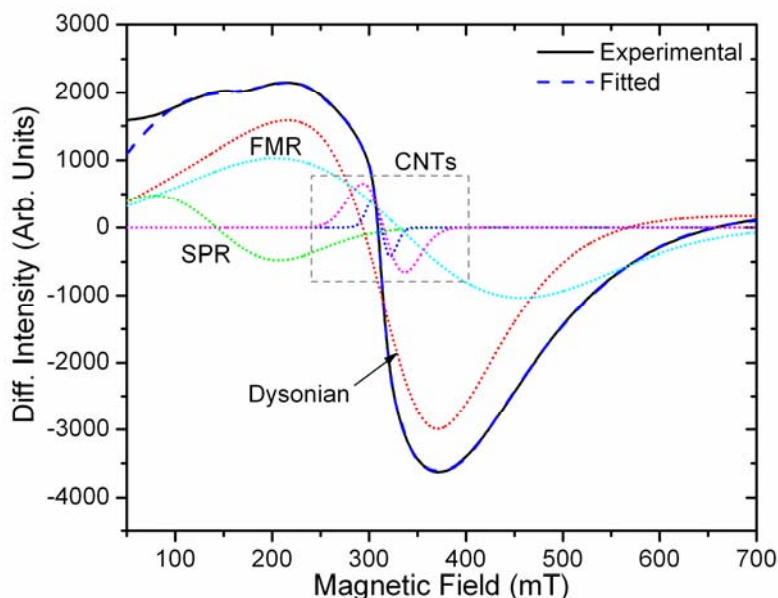


Figure 5-7: Deconvoluted EPR spectra of virgin SWCNT-A containing FMR and broad dysonian (~ 107 mT) component arising due to residual metallic catalyst and a relatively sharp peak in the region (250-380 mT) arising from CNTs. This CNT peak is expected to contain two peaks a Dysonian arising from CESR from CNTs and a Gaussian / Lorentzian component from defects. Here it was not possible because FMR peak masked it. Even the attempt to record separately did not help to distinguish the two peaks arising from SWCNT-A. Broad and FMR peaks observed in this case are in agreement of TGA results showing high metallic content.

reduction in the intensity after annealing at 700 °C. With 1000 °C annealing it shows further increase in the intensity for the defect peak. This is consistent with our TGA and Raman studies presented in Chapter-3 and Chapter-4, showing 700 °C annealing to be the optimum for defect removal in SWCNTs. Also the SPR and FMR peaks showing reduction in the intensity due to reduction in the amount of metallic nanoparticles by evaporation at 700 °C and 1000 °C. Change in the resonance field (g-value after vacuum annealing) indicates structural modification due to defect annihilation, consistent with the

change in (RBM) frequencies observed in the Raman spectra of vacuum annealed samples, presented in chapter-4.

Table 5-2 Deconvoluted EPR line profile parameters for vacuum annealed SWCNTs.

Sample	Profile	Peak1	Peak2	Peak3	Peak4	Peak5
SW-virgin	g-value	4.73377	2.15735	2.14229	2.04062	1.94367
	FWHM	150.6	21.3	50.9	298.59	147.3
	Ampli	50140	6251	23270	216000	50780000
	Asym.					1.034
SW-300 °C	g-value	4.62654	2.15797	2.14222	2.05985	1.94081
	FWHM	131.8	21.5	51.9	301.9	150.2
	Ampli	37010	6576	24820	208000	54220000
	Asym.					1.035
SW-500 °C	g-value	4.63297	2.15731	2.14225	2.07827	1.93416
	FWHM	122.4	21.7	52.5	308.0	152.0
	Ampli	31080	6923	25720	230900	53570000
	Asym.					1.105
SW-700 °C	g-value	4.75782	2.15822	2.14381	2.14723	1.94258
	FWHM	137.4	21.4	51.1	300.0	147.8
	Ampli	28750	4556	16980	197400	36500000
	Asym.					1.063
SW-1000 °C	g-value	4.6596	2.15907	2.14534	2.20134	1.93271
	FWHM	117.5	21.3	51.6	302.8	152.1
	Ampli	21580	4880	18780	258100	41810000
	Asym.					1.06
Assignments		SPR	Defects	CESR (CNTs)	FMR-1	CESR

The EPR spectra of MWCNTs before and after vacuum annealing are shown in Fig. 5-8. Similar to SWCNTs, equal weight (2.1 mg) of virgin and annealed samples were used for EPR measurements. Visibly is clear that the MWCNTs annealed at 500 °C shows comparatively lower absorption intensity. A closer look at the spectra in the region 280-350 mT clearly shows monotonic decrease in the intensity with increasing annealing

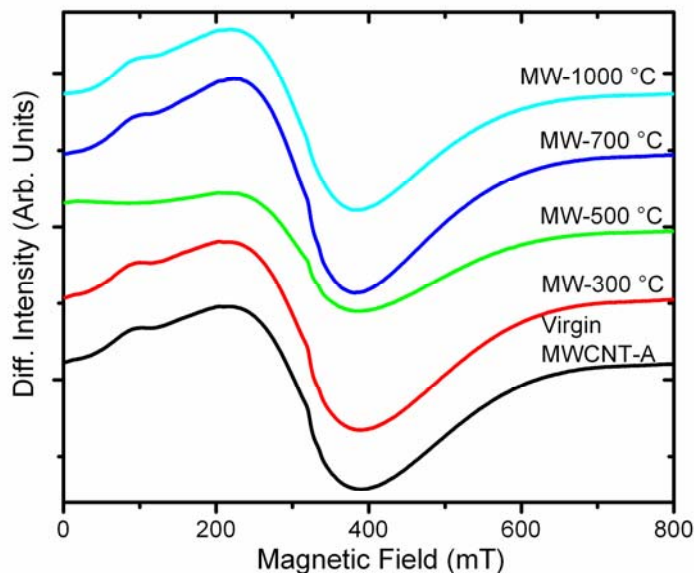


Figure 5-8: ESR spectra of MWCNT-A before and after vacuum annealing. It shows change in the absorption intensity with annealing temperature, especially at 500 °C.

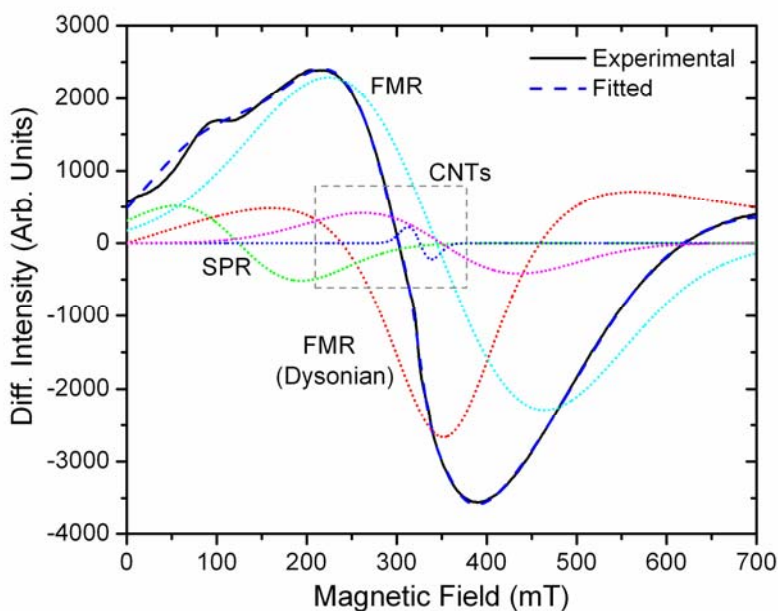


Figure 5-9: Deconvolution of ESR spectra of MWCNT-A. It consists of two peaks arising due to catalyst nanoparticles called as FMR peaks and small and relatively sharper feature (in the enclosed box) arising from CNTs. Due to Strong FMR peak, features from CNTs are enveloped.

temperature for the characteristic sharp peak from CNTs. As the annealing temperature is increased, spectra becomes more symmetric, clear from visual inspection and also the asymmetry parameter (α) obtained on deconvolution. Fig. 5-9 shows the typical deconvoluted spectra of the MWCNT-A before vacuum annealing. Similar to the SWCNTs, it requires one SPR peak, two FMR peak (one Gaussian component and another Dysonian component) along with two other sharp features closer to the free electron g-value. The deconvoluted parameters of EPR spectra for MWCNT-A before and after

Table 5-3: Fitting parameters for EPR spectra of vacuum annealed MWCNTs.

Sample	Profile	Peak1	Peak2	Peak3	Peak4	Peak5
MW-virgin	g-value	5.4392	2.0725	1.9605	1.9325	1.9160
	FWHM	163.9	30.6	282.3	204.4	160.9
	Ampli.	59230	4772	452200	59890	34340
	Asym.					1856
MW-300 °C	g-value	5.6159	2.0745	1.9901	1.9370	1.9166
	FWHM	167.5	32.4	281.6	213.2	160.6
	Ampli.	68290	5381	469200	63350	89370
	Asym.					692.6
MW-500 °C	g-value	5.7915	2.0665	1.9950	1.9277	1.9427
	FWHM	208.4	28.9	298.8	185.8	151.8
	Ampli.	69550	2683	299900	67740	69090
	Asym.					519.2
MW-700 °C	g-value	5.5601	2.0661	1.8766	1.8024	1.9358
	FWHM	96.3	26.2	307.8	168.4	149.8
	Ampli.	16920	3795	368700	114200	18890000
	Asym.					4.508
MW-1000 °C	g-value	5.5851	2.0882	1.9664	1.8700	1.9567
	FWHM	87.2	17.9	304.5	165.3	150.1
	Ampli.	11820	1176	356600	98750	6766000
	Asym.					9.037
Assignments		SPR	Defects	FMR	CESR (CNTs)	CESR

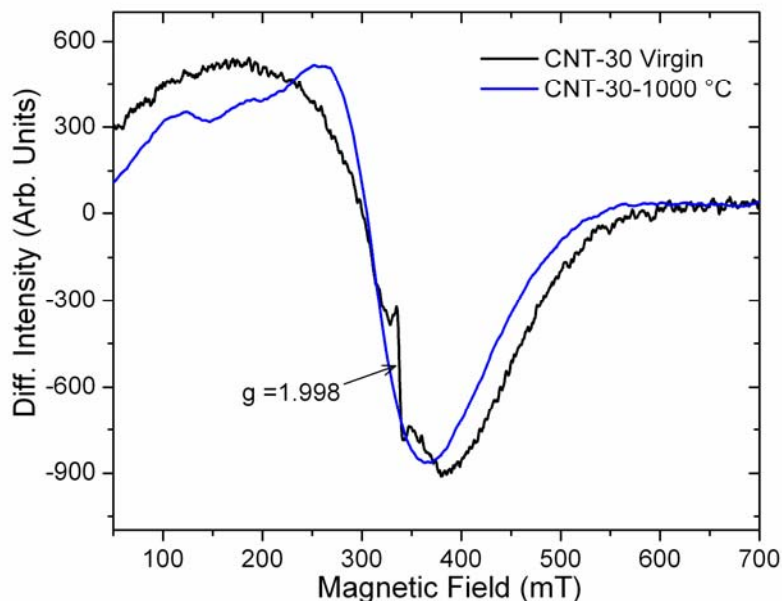


Figure 5-10: ESR spectra of CNT-30 (MWCNT sample, containing low metallic impurities) before and after vacuum annealing at 1000 °C. The characteristic sharp features disappears after vacuum annealing indicating its origin as structural defects.

vacuum annealing is summarized in Table 5-3. It shows a reduction in the defect peak intensity at 500 °C and 1000 °C, in agreement with our TGA and Raman studies discussed in chapter-3 and chapter-4, respectively.

Fig. 5-10 shows the comparison of EPR spectra of CNT-30 (MWCNTs sample containing very low amount of metallic impurities) before and after vacuum annealing. The sharp absorption feature absorbed at $g = 1.998$ disappears after vacuum annealing at 1000 °C. This is one of the important experimental finding, which clearly shows that very sharp spectral feature in the EPR spectra of CNTs (at room temperature) indeed arises from the structural defects. Also it shows reduction in the intensity of the SPR peak (low magnetic field region) and reduction in the broad feature due to decrease in the metal residue content after evaporation of metal nanoparticles during vacuum annealing. Metal

nanoparticle can evaporate even at much lower temperature than its bulk melting point due to size confinement effect.

5.5 Temperature Dependence of EPR Spectral Profile

Temperature dependent (low temperature) studies were carried out to understand the origin of various EPR peaks experimentally observed. Fig. 5-11 shows the EPR spectra of SWCNT-A recorded in the temperature range 153.3 to 303.3 K. Inset of the Fig. 5-11 shows the EPR spectra recorded at two extreme temperatures 303.3 K and 153.3 K for better visualization of effect of temperature. It shows change in the peak intensity

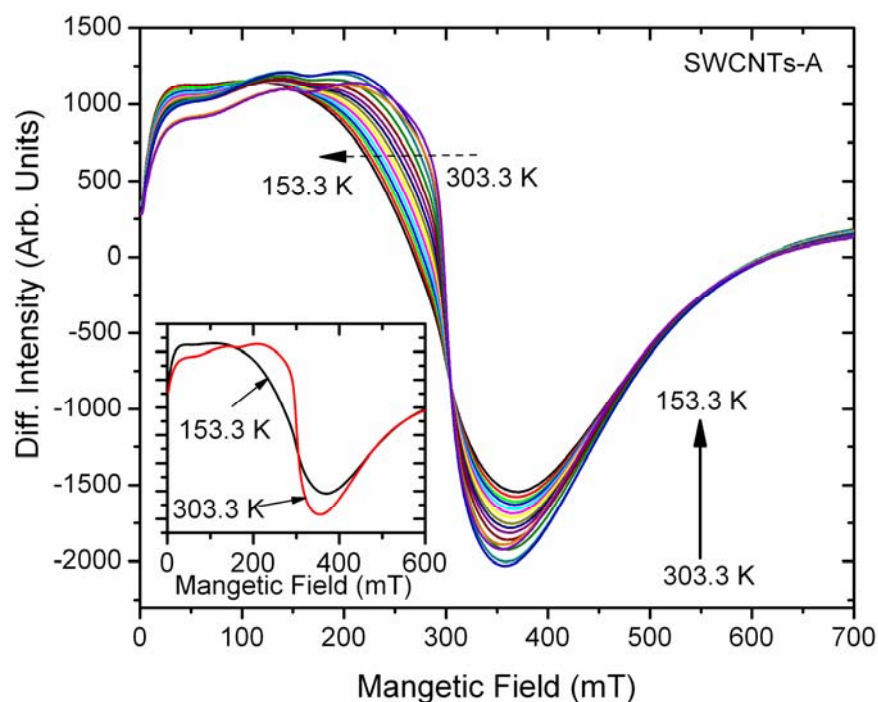


Figure 5-11: Temperature dependent EPR spectra of SWCNT-A. It shows variation in the FMR lineshape with temperature. No sharp peak was observed in this case due to strong FMR absorption.

and asymmetry with the temperature. These spectra were deconvoluted to monitor the systematic change in the spectral line profile with temperature. A typical deconvoluted spectrum for SWCNT-A recorded at 303.3 K is shown in Fig. 5-12 Deconvoluted spectrum consists of two peaks structure of FMR,

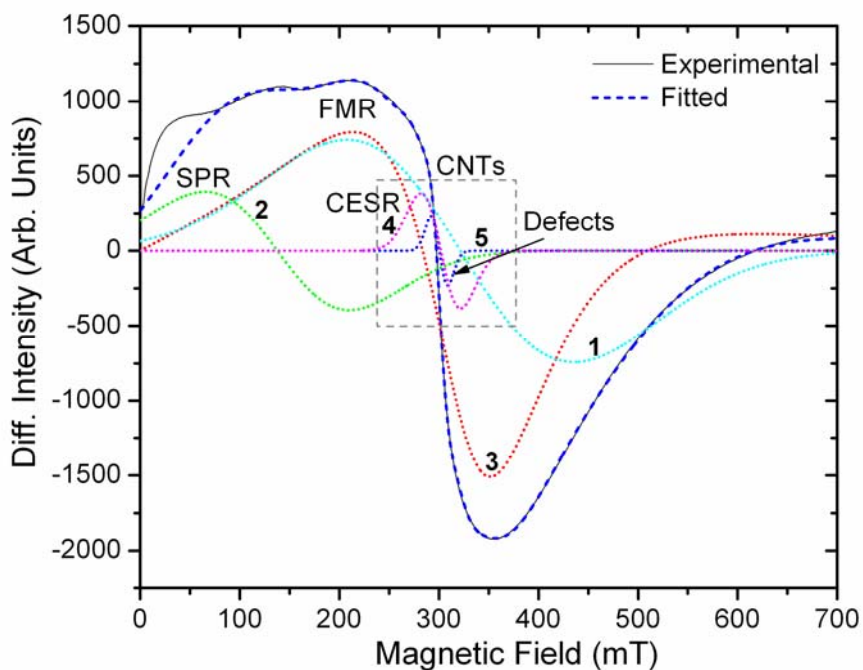


Figure 5-12: Shows the deconvoluted EPR spectra of SWCNT-A (Temperature 30 °C). It shows characteristic CCSR and defect related peaks from CNT. It also shows SPR and FMR peaks arising from residual metallic nanoparticles.

namely SPR and FMR1 (Dysonian), FMR2 and two peaks of weaker intensity originating from CNTs. The variation in the line profile of these peaks is shown in Fig. 5-13 to 5-15. Fig. 5-13 shows fitting of four peaks (SPR, FMR, CESR & defects) for the SWCNT. Temperature dependence of g-value for different peaks are presented. FMR1 and SPR peak shows complimentary behavior to each other in terms of g-value as a function of temperature. FMR1 and SPR peaks shows minimum and maximum g values at $\sim 50^\circ\text{C}$, as shown in Fig. 5-13(a) and 5-13(b). FMR peak 2 shows slight variation in the g-value from

(2.1588 to 2.1472) with temperature. Significant increase in the error bar values at low temperature is due to heavily reduced intensity at such low temperatures.

Fig. 5-14 shows the FWHM variation of broad features of SWCNT-A with temperature. Fig. 5-14(a) shows the variation of FWHM of Dysonian component of FMR

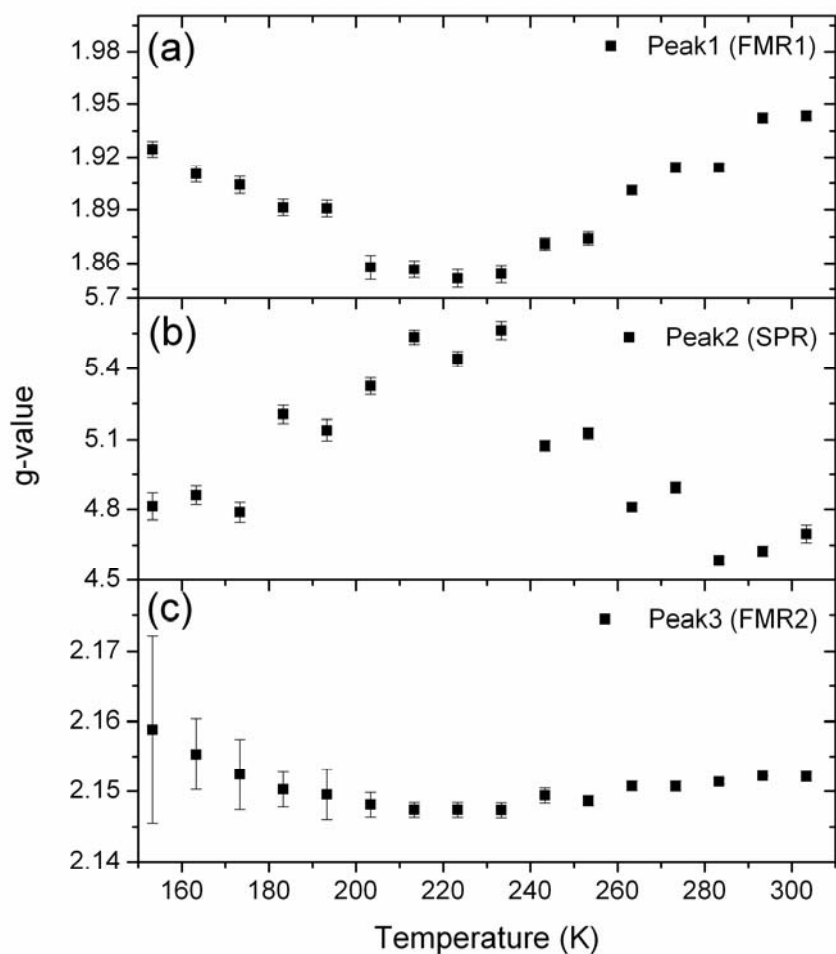


Figure 5-13: Shows the variation in the g-value of FMR and SPR peaks with change in temperature (153.3 K to 303.3 K). Dysonian FMR peak 1 and SPR peaks shows complimentary behavior, while gaussian component of FMR peak i.e FMR-2 shows comparatively very small shift as shown in Fig. 5-13(c).

peak 1, Fig. 5-14(b) shows the variation of the FWHM of SPR peak observed due to unblocked nanoparticles and Fig. 5-14 (c) shows variation in the FWHM of gaussian component of FMR peak (peak 2) as a function of temperature. The FWHM of Dysonian component (peak 1) shows gradual increase with decreasing temperature. Similarly, the SPR peak gets broadened with lowering of temperature. In contrary, two Gaussian components of the FMR peak show a different behavior. At ~ 213.3 K and above it shows slight decrease in FWHM with increasing temperature, while below

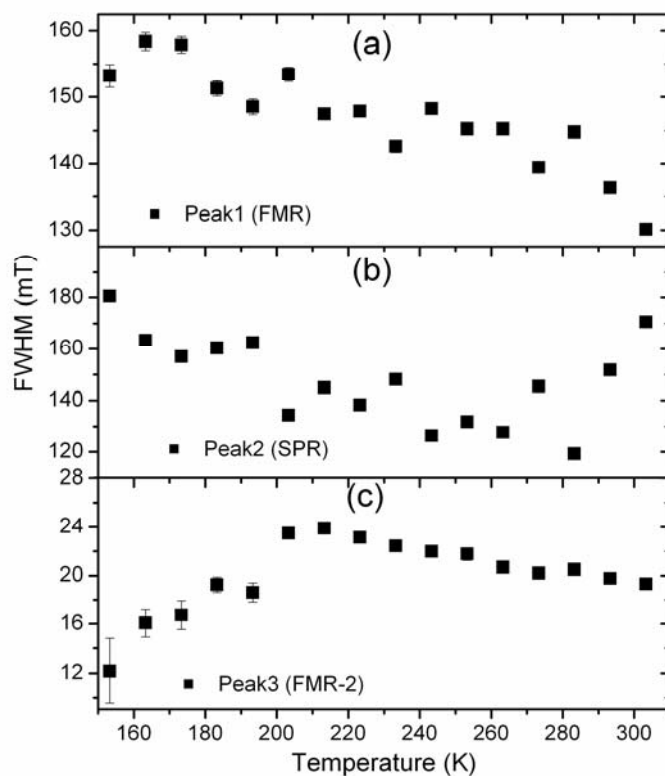


Figure 5-14: Variation in the FWHM of FMR peak and SPR peak with temperature

this temperature, it shows very fast decrease in FWHM. Note that the conduction electron peaks (Peak 1, FMR) is expected to shows temperature independence, according to the

Pauli paramagnetism. The temperature dependence of the resonance line width, ΔH_{pp} is given by

$$\Delta H_{pp}(T) = \Delta H_{pp}^0 + \alpha_H T^m \quad (5-4)$$

Where, ΔH_{pp}^0 and α_H are constants and equals to $m = -\frac{1}{2}$ for conduction electrons scattered by an interaction through the spin-orbit coupling of impurity atoms [210, 310], $m = 0$ for non-interacting graphene sheets [311] or, $m = \frac{3}{2}$ for conduction electrons scattered by the lattice vibrations below the Debye temperature [312]. It has been proposed that Curie like temperature dependence of conduction electron may arise from the introduction of localized states near the Fermi level due to pentagon defects or edges [311, 313]. In case of graphene, the density of states is zero at the Fermi energy, and rises linearly and symmetrically above and below the Fermi energy. For the calculation of density of states for the graphene sheets, a small band gap is taken into account due to hybridization of the crossing bands at the Fermi level due to the curvature of the sheets. Disorder and finite size of the systems also shows the similar effect. These considerations results into the following expression for paramagnetic susceptibility [311]

$$\chi(T) = A \left[k_B T \ln \left(\exp \frac{\Delta}{k_B T} + 1 \right) - \Delta \right] + \frac{C}{T} \quad (5-5)$$

Where, the first part of the expression accounts for the Fermi tail activation of Pauli susceptibility over the gap of $2\Delta = 0.1$ eV into the linear density of states. Second term accounts for the Curie like contribution arising from localized (narrow peak) density of states near the Fermi energy. Existence of such localized states is quite possible in our case due to large curvature effects (induced by folding the graphene sheets into cylinder)

and existence of variety of defects (mostly pentagon-heptagon reflected from number of bents in HRTEM studies). The double integral of the ESR spectrum S , is proportional to the static spin susceptibility (χ) of the sample. For a symmetric Lorentzian / Gaussian line shape, there is a simple relationship between S and the resonance line parameters [214]

$$S = KI H_{pp}^2 / mA \quad (5-6)$$

Where, K is the line shape factor (constant for Lorentzian or Gaussian line), I is the

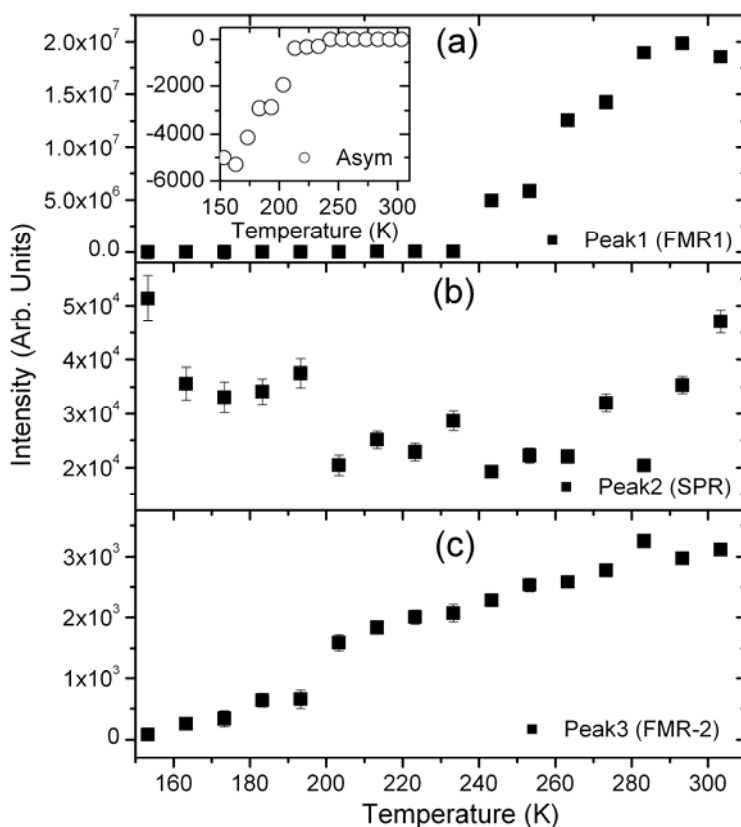


Figure 5-15: Temperature dependence of deconvoluted broad peaks in SWCNT-A. (a) Intensity change of dysonian component of FMR peak with temperature. Inset shows variation in the asymmetry with temperature. (b) Variation in the intensity of SPR peak and (c) variation in the intensity of Gaussian component of FMR peak.

resonance line intensity and ΔH_{pp} the peak to peak resonance line width (FWHM), m is the mass of the sample and A is the spectrometer gain. Thus from equations (5-5) and (5-6), its clear that temperature dependence of CESR of CNTs arises from the curvature or defect induced localized states near the Fermi energy.

The temperature dependent variation of the peak intensity of deconvoluted peaks of SWCNT-A is shown in Fig. 5-15. The intensity of the Dysonian component of the FMR peak arising from the metallic nanoparticles decreases with decreasing temperature. It decreases at a fast rate as the temperature decreases from 303.3 K down to 233.3 K and then remains very low. The SPR peak does not show any systematic change with temperature as shown in Fig. 5-15(b). Intensity of the Gaussian component of the FMR

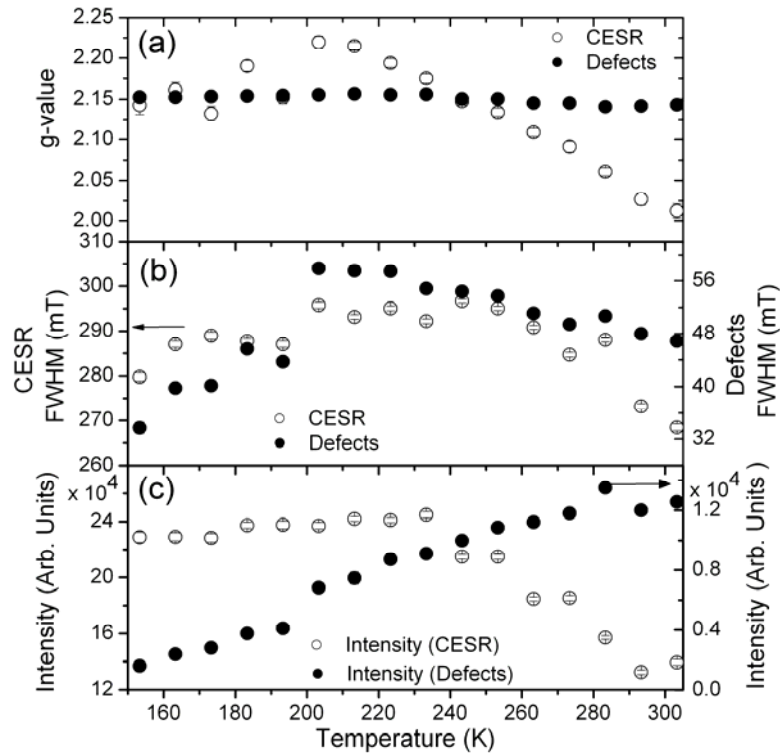


Figure 5-16: Temperature dependent variation of the characteristic sharp feature arising from CCSR and structural defects (a) change in the g-value with temperature (b) variation in the FWHM with temperature and (c) temperature dependent intensity of CCSR and defect peak.

peak (FMR-2) monotonically decreases with decreasing temperature.

Temperature dependence of the CESR peak parameters from CNTs is shown in Fig. 5-16. The change in the g-value with temperature is shown in the Fig. 5-16(a). With the lowering of temperature, the g-value of the CESR peak shift away from the free electron g-value ($g_e = 2.002318$) having maxima at ~ 213.3 K and with further decrease in temperature its value is lowered. On the other hand, defect related peak does not show any change in g-value with temperature. Although the conduction electrons are not expected to shows temperature dependence (Pauli paramagnetism), but in case of CNTs they can show temperature dependence due to presence of curvature induced gaps and presence of localized density of states near the Fermi level [311]. In most cases, there exists a strong interaction between the itinerant and conduction electrons known as bottleneck regime. This leads to temperature dependence of the g-factor of electrons delocalized over nanotubes mathematically expressed as [314, 315]

$$g(T) = \frac{g_l C + g_i \chi_i T}{C + \chi_i T} \quad (5-7)$$

Where, subscripts l and i represents the localized and itinerant electrons, χ is the corresponding susceptibility and C is the Curie constant. Such interactions also contribute to the temperature dependence of the CESR peak profile experimentally observed in our case (Fig. 5-16 (a)). Both the deconvoluted peaks show temperature dependent FWHM, as shown in Fig 5-16(b). The FWHM of both the peaks first increases with decrease in temperature from 303.3 K to 203.3 K and with further decrease of temperature it again decreases. The variation of the intensity of these peaks is shown in 5-16(c). The intensity of the CESR peak gradually increases as the temperature goes down to 233.3 K and with further decrease in temperature it shows slight decrease in the intensity. In contrast, the

intensity of the defect related peak shows monotonic decrease in the intensity with decreasing temperature as shown in Fig. 5-16(c).

Since the characteristic sharp peak of CNTs in case of SWCNTs was masked under the intense and broad FMR spectra, we further studied the temperature dependence of EPR spectral line profile for CNT-30, which contains very small amount of metallic impurity. Fig. 5-17 shows the temperature dependent EPR spectra of CNT-30 for the temperature range 153.3 to 283.3 K. It is clear that as the temperature is reduced the intensity of the peak decreases and the spectra shows modification in the lower field range, i.e. in the expected SPR range. At high temperatures all the magnetic dipole moments are unblocked and only the SPR spectrum is observed (intense Peak). The SPM spectrum vanishes conversely at sufficiently low temperature, where all the magnetic dipole moments are blocked and only the FM spectrum is observed [307].

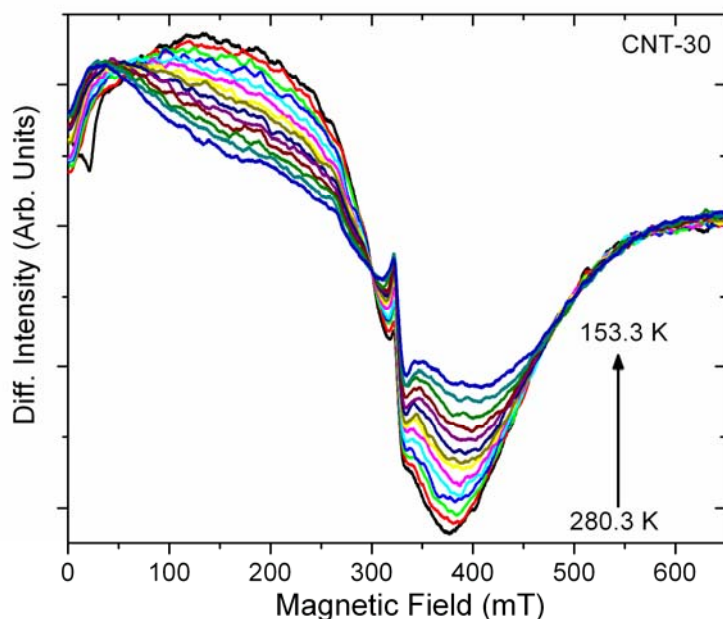


Figure 5-17: Temperature dependent EPR spectra of CNT-30 (MWCNT sample, containing low metallic impurities). It shows variation in the FMR lineshape with temperature.

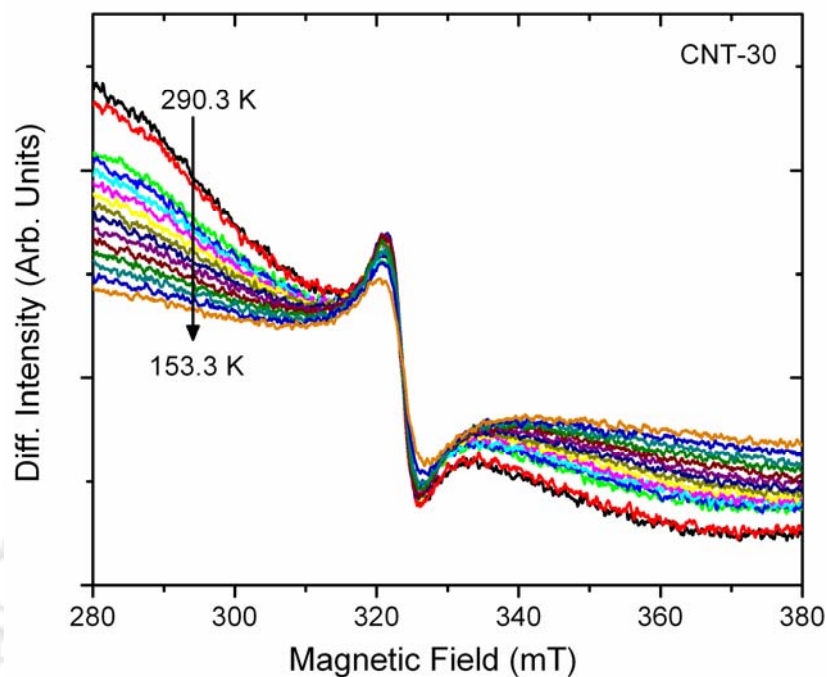


Figure 5-18: Temperature dependence of characteristic sharp feature of EPR spectra of CNT-30, recorded with higher integration time and for a small spectral window separately.

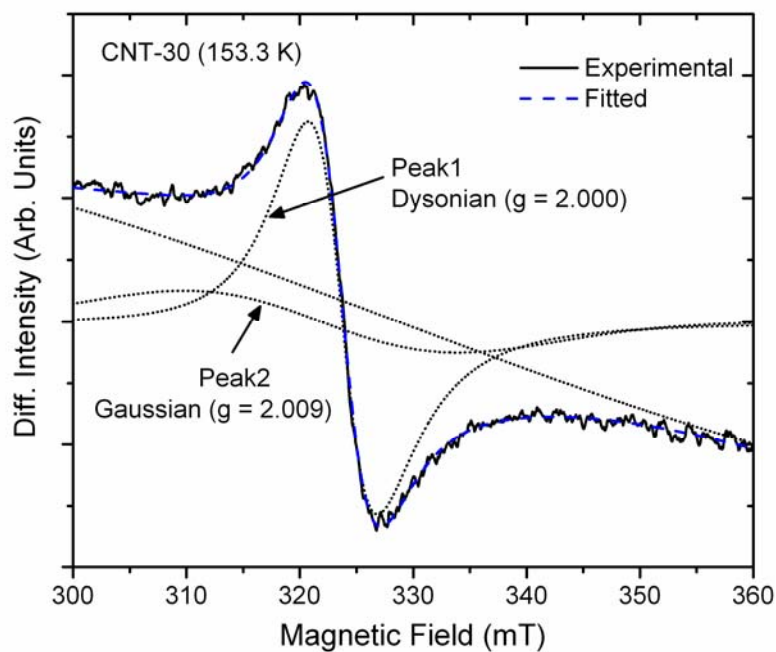


Figure 5-19: A typical deconvoluted EPR spectra of CNT-30 showing a defect related Gaussian component and Dysonian peak from CESR from CNTs.

The temperature dependence of sharp peak was analyzed by recording the spectra for a small range (280-380 mT) with higher integration time as shown in Fig. 5-18. Deconvolution of this peak requires combination of a Gaussian peak ($g=2.009$) along with a Dysonian peak ($g=2.000$) as shown in Fig. 5-19. Gaussian peak is expected to arise from

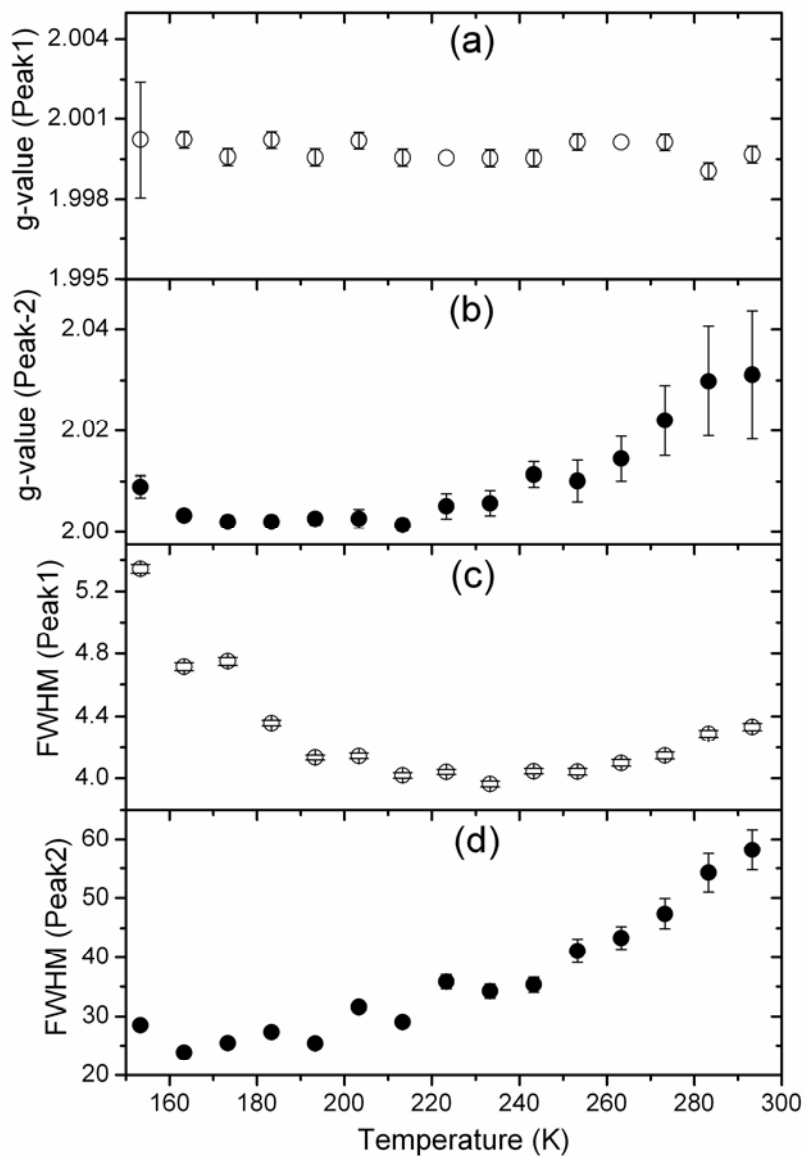


Figure 5-20: Shows temperature dependent (a) Change in the g-value of the peak 1 (CESR peak) (b) Change in the g-value of the Peak 2 (Gaussian) (c) variation in the FWHM of CESR peak (d) FWHM of defect related peak 2 (Gaussian component).

the localization of electrons at the structural defects, whereas Dysonian peak arises from the conduction electrons.

Fig. 5-20 shows temperature dependence of the EPR spectral parameters for CNT-30. Peak 1 do not show any change in the g-value with temperature, as expected for the conduction electrons (shown in Fig. 5-20(a)). Absence of temperature dependence of CESTR peak shows a weaker coupling between the conduction electrons and localized electrons and a weak interaction between concentric graphene sheets [212]. However, the defect related peak 2 shows temperature dependence. In fact, it shifts closer to the free

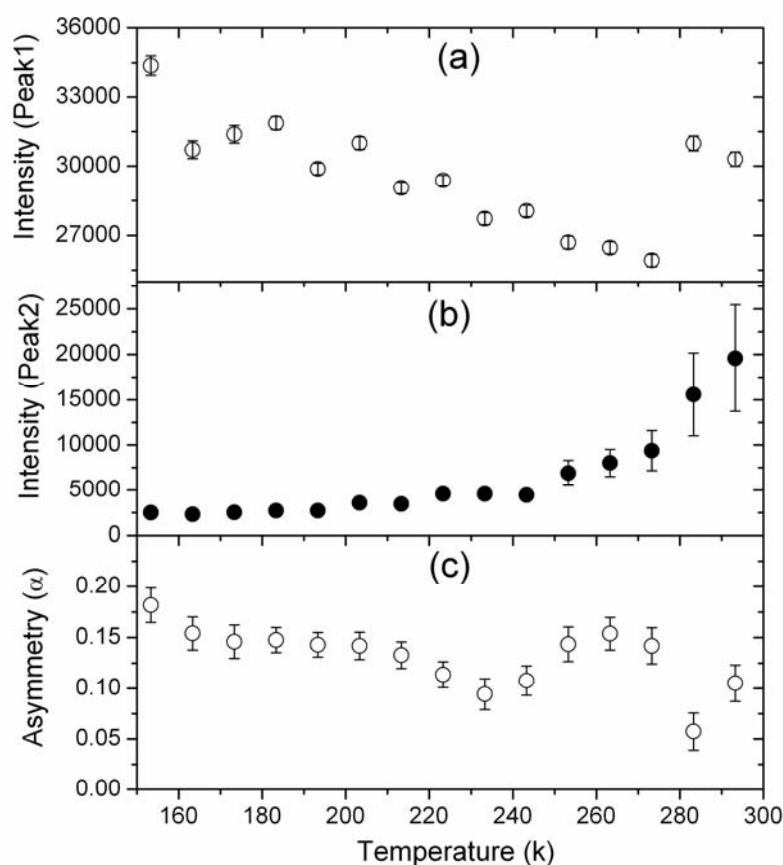


Figure 5-21: Shows the temperature dependent variation in the intensity of sharp EPR features of CNT-30 (a) Changes in the intensity of CESTR peak 1 (b) variation in the intensity of defect peak and (c) shows variation in the asymmetry parameter (α).

electron g -value (g_e) with decreasing temperature, as shown in Fig. 5-20(b). The FWHM of conduction electrons follows the T^3 dependence as expected for conduction electrons above Debye temperature, as shown in Fig. 5-20(c). The FWHM of the peak 2 monotonically decreases with decreasing temperature, as shown in Fig. 5-20(d). Fig. 5-21 shows the variation in the intensity and asymmetry with temperature of peak 1 and peak 2. Intensity of the peak 1 (CESR peak) increases with decreasing temperature, while the intensity of the peak 2 (defect peak) decreases with decreasing temperature as expected for defect related peaks [214]. Fig. 5-21(c) shows the variation in the asymmetry parameter with temperature. With decreasing temperature the asymmetry of the CESR peak increases as reflected from the α value. This is due to the decrease in contribution of the defect related peak and the dominance of the conduction electrons at lower temperature, as also reflected from temperature dependent intensity plot for these peaks.

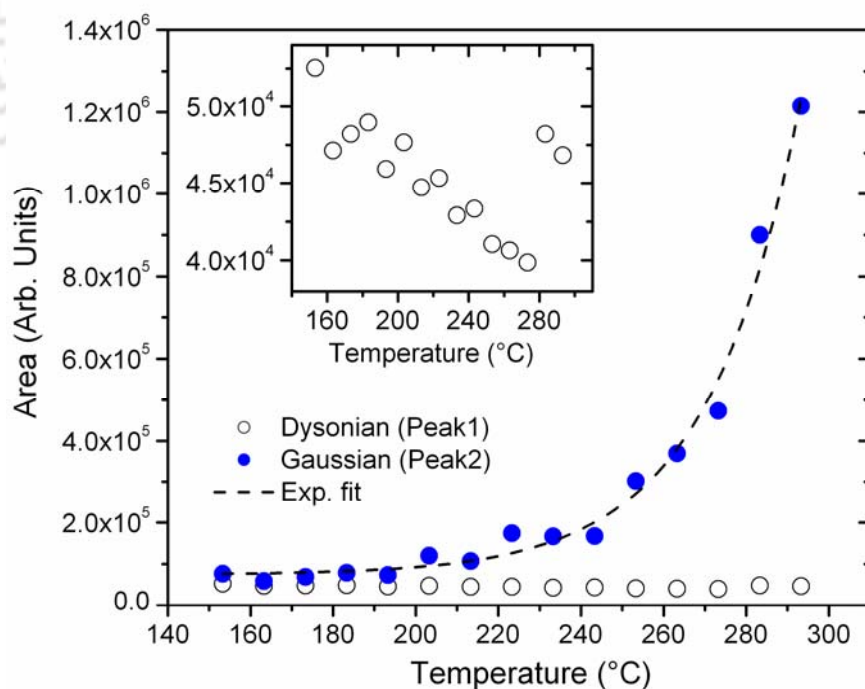


Figure 5-22: Variation in the peak area of deconvoluted Dysonian and Gaussian components of EPR peaks of CNT-30.

Fig. 5-22 shows the variation in the double integral of the deconvoluted peak 1 (CESR) and peak 2 (defects). The double integral of ESR peak is proportional to the static spin susceptibility given by eqn. 5-6. Inset of the Fig. 5-22 shows variation in the area of CESR peak with temperature. Defect peak shows monotonic increase in the area with temperature. The experimental data follows the exponential growth as shown by dotted curve in Fig. 5-22. It's clear from the Fig. 5-22 that the variation in the susceptibility (area) of the CESR peak (Peak 1) is negligible to the defect peak for the temperature range studied as expected for conduction electrons [208]. Although for the temperature range 273.3 K to 153.3 K it shows very small monotonic increase in the area probably due to the very weak but not negligible interaction between the conduction and localized electrons.

5.6 Conclusions

We have found systematic diameter dependence of g-values of MWCNTs. Broad ESR spectra of MWCNTs on deconvolution shows diameter dependence in terms of change in g-values from $g = 2.099$ to 1.947 . This component has contribution from interaction between conduction electrons residing on nanotubes and conduction electron of metal nanoparticles. The g-value of the FMR peaks shifts away from the free electron g-value with increase in the metal residue content. Thus the higher g-value of the FMR peaks represents higher metallic residue content in the sample. The origin of diameter dependence of the g-value of CESR peak is understood in terms of folding of graphene sheet to form CNTs. The FWHM of FMR peak increases with the structural defects, while FWHM of Peak 2 shows a nice correlation with the metallic residue and structural defects both. Similarly the intensity of the FMR peak scales with the amount of the metallic

impurity content and the intensity of the CESR peaks is influenced by combined effect of structural defects and metallic impurities.

To quantify the relative contributions from metallic impurities and characteristic features of CNTs in EPR spectra, we have carefully analyzed the spectra by proper deconvolution. ESR studies on the vacuum annealed samples confirm that the 700 °C and 500 °C to be the optimum temperature for defect annihilation for SWCNTs and MWCNTs respectively. Disappearance of sharp feature near g_e after vacuum annealing confirms its origin from structural defects. A systematic study on the temperature dependence of two different samples having different amount of metal residues allow us to distinguish the characteristic EPR features of CNTs and the features arising from the FMR originating from metal nanoparticles. Our studies confirm that a Dysonian like sharp feature at $g = 2.000$ arises from conduction electrons residing on the nanotube walls, while paramagnetic defects gives rise to a gaussian like feature at $g = 2.009$. We Confirm the presence of structural defects from EPR studies (curie like sharp absorption feature near g_e), which corroborates our understanding of the origin of visible photoluminescence from structural defects in pristine SWCNTs and MWCNTs.

Chapter -6

Defect Engineering Using Ion-irradiation

6.1 Introduction

In this chapter, we have presented a detailed study on the effect of Hydrogen, Carbon, Nitrogen and Argon ion-irradiation at low energies (30 keV and 80 keV) on SWCNTs and MWCNTs. Ion-irradiation with different ion species, energies and fluences are expected to influence the structure and properties of CNTs in different ways. We have studied samples irradiated at three different doses 10^{12} ions/cm² (*low dose*), 10^{13} ions/cm² (*intermediate dose*) and 10^{14} ions/cm² (*high dose*). Irradiated samples are investigated using High resolution transmission electron microscopy (HRTEM), XRD (X-ray diffractometry), Raman spectroscopy and EPR (Electron paramagnetic resonance) spectroscopy. Some of the SWCNTs samples have also been investigated using UV-Vis-NIR absorption spectroscopy, FT-IR spectroscopy and X-ray photoelectron (XPS) spectroscopy to explore the change in band structure and hybridization states. We also present results of in-situ modification of CNTs with electron beam under HRTEM. Details of the samples studied and irradiation parameters are presented in Chapter-2. These results enable us to isolate the spectral features specific to defects in Raman and EPR spectroscopies. It also provides the knowledge of optimum dose and ion species to be used for structural improvement of CNTs containing defects.

6.2 SRIM Calculation

SRIM calculations were carried out using SRIM2010 [275] to estimate the respective electronic and nuclear losses in the graphitic system. Calculation were performed for estimating the amount of energy loss in graphite of accelerated hydrogen (H⁺), Carbon (C⁺), Nitrogen (N⁺) and Argon (Ar⁺) ions in the energy range 1 keV-10

MeV. Results are shown in Fig. 6-1 with the energy scale on the horizontal axis adjusted for better visualization and comparison of electronic versus nuclear energy loss. Dotted line in Fig. 6-1 shows the energy at which the experiment has been performed (i.e 30 and 80 keV). Fig. 6-1(a) shows the energy loss of accelerated H^+ ions. H^+ ions show mainly electronic energy loss at 30 keV, while C^+ ions at 30 keV show both electronic and nuclear energy loss. Change in energy from 30 keV to 80 keV leads to competing effects of

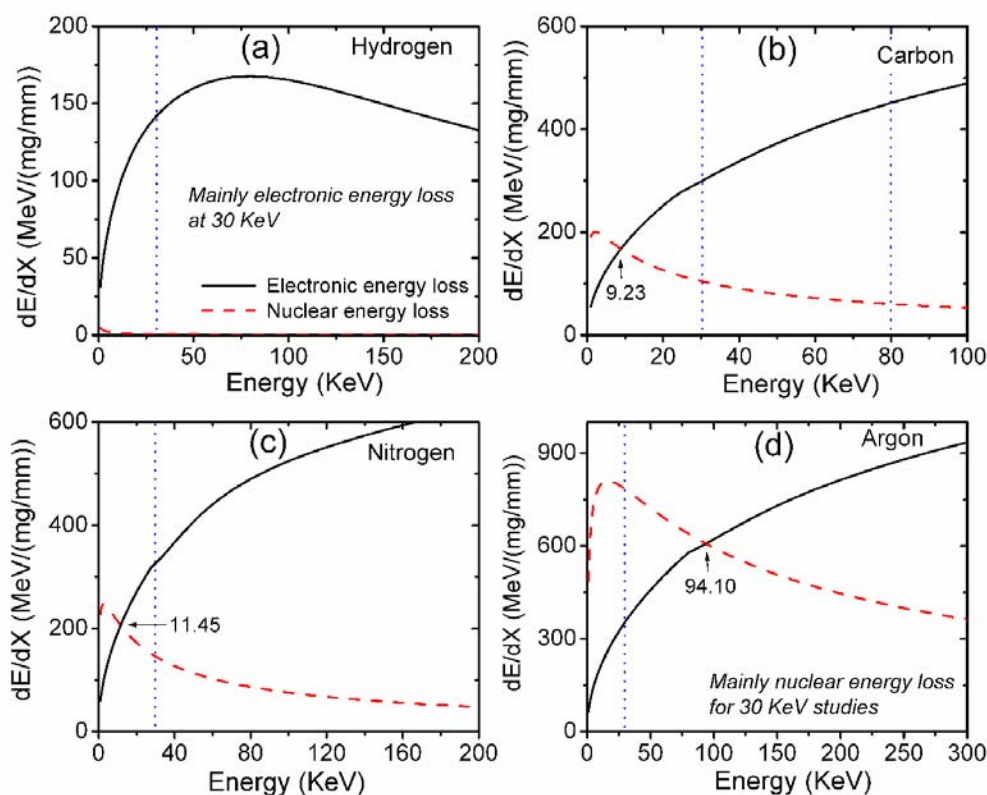


Figure 6-1: SRIM simulations of the electronic and nuclear energy loss in graphite of (a) Hydrogen (H^+) showing mainly electronic energy loss at 30 keV (b) Carbon (C^+) has combined effect of electronic energy loss and nuclear energy loss at 30 keV and 80 keV with relative changes in the nature of energy loss at the two energy investigated (c) Nitrogen (N^+) shows combined effect of electronic energy loss and nuclear energy loss at 30 keV and (d) Argon (Ar^+) ions shows mainly nuclear energy loss at 30 keV.

electronic energy loss versus nuclear loss. Similarly Nitrogen ions show combined effect of electronic energy loss and nuclear energy loss, as shown in Fig. 6-1(c). In case of Argon ions, nuclear energy loss dominates over the electronic energy loss at 30 keV as shown in Fig. 6-1(d). Thus, these four ions were selected depending upon the relative changes in the contribution of electronic energy loss and nuclear energy loss, as we move from light ions H^+ to heavy ions Ar^+ . Although this gives a theoretical estimate of the losses and resulting effects, experimental results on CNTs include a number of factors like type of the nanotube SWCNTs or MWCNTs, curvature effect i.e., effect of diameter, defects and relative orientation of CNTs with the beam. Hence experimental investigation on the effect of these ions needs spectroscopic studies for controlled introduction of defects and modification of CNTs through defect engineering using ion beams.

6.3 Effect of H^+ Ion Irradiation

6.3.1 HRTEM Studies

HRTEM images of SWCNT-A before and after irradiation is shown in Fig. 6-2. Virgin SWCNTs are straight and long with very few point defects, as shown in Fig. 6-2(a) and (b). A low dose H^+ ion-irradiation leads to increase in the density of point defects as shown with arrow mark in Fig. 6-2(c) and (d). Irradiation at intermediate dose leads to formation of multiple vacancies finally leading to collapse of the CNTs and formation of amorphous carbon, as shown in Fig. 6-2(e). At high dose, it leads to increase in the amount of amorphous carbon as shown in Fig. 6-2(f).

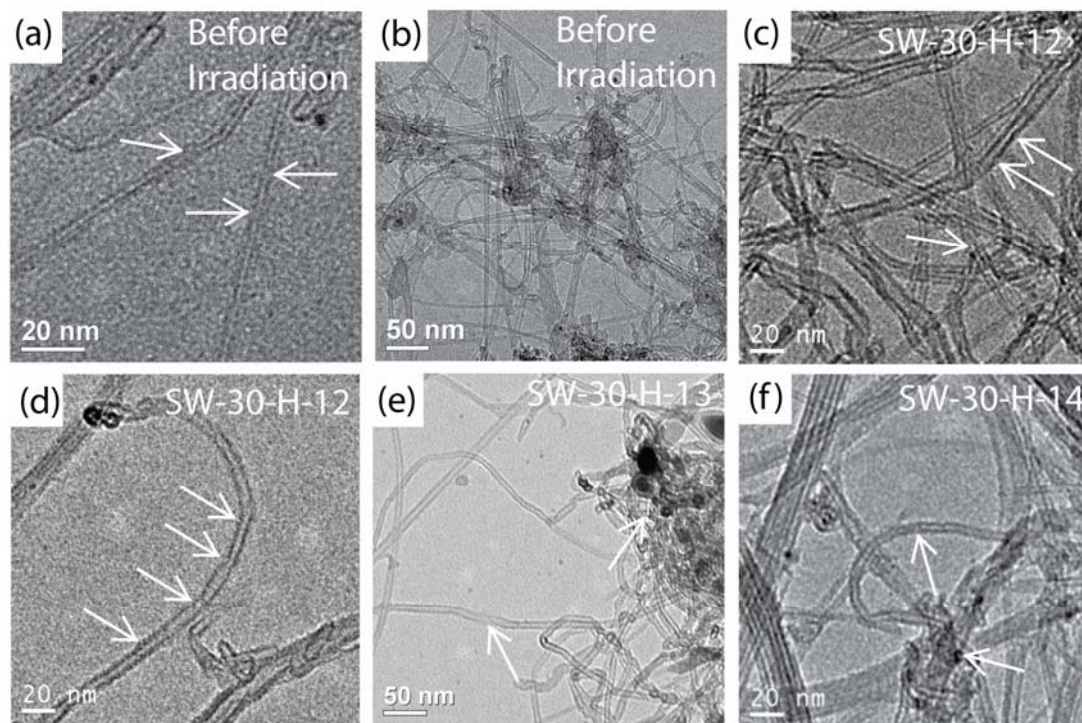


Figure 6-2: HRTEM studies of SWCNTs before and after H^+ irradiation. (a) and (b) HRTEM image of SWCNT-A before irradiation. Point defects are marked with arrows. (c) and (d) HRTEM image after 10^{12} ions/cm² H^+ irradiation, shows increase in the density of point defects. (e) Point defects and (e) a portion of amorphous carbon at 10^{13} dose. (e) A dose of 10^{13} ions/cm² leads to breaking of tube walls and formation of amorphous carbon. (f) At 10^{14} ions/cm² dose, shows formation of multiple vacancies and increase in the amount of amorphous carbon.

6.3.2 XRD Studies

The XRD spectra of SWCNT-A before and after H^+ irradiation at different doses are shown in Fig. 6-3(a). It also shows the typical voigt deconvoluted peaks of the SWCNT-A. Fitted parameters are summarized in Table 6-1. SWCNTs show too weak scattering intensity for the (100) and (101) in-plane peaks to be resolved. Apart from the characteristic features of CNTs, it also shows a broad peak near $\sim 12.88^\circ$ arising from the non-hexagonal carbon chains or amorphous carbon. Fig. 6-3(b) shows the variation in the Bragg angle for the (002) peak. At low dose, 2θ value increases from 25.72° to 26.09° and

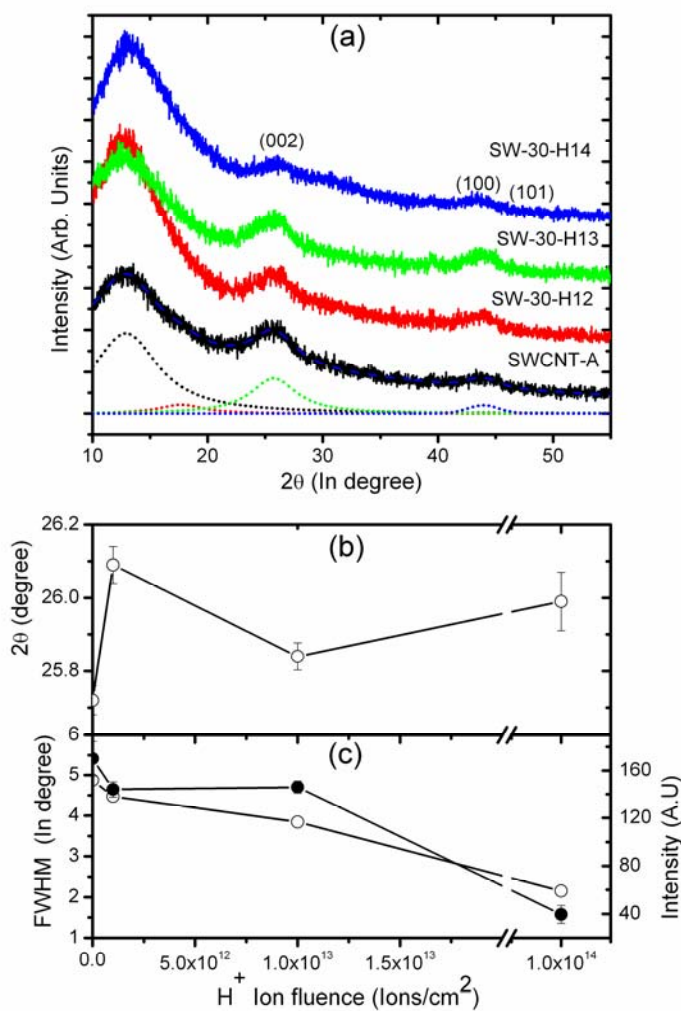


Figure 6-3: XRD spectra of SWCNT-A before and after irradiation of H^+ (10^{12} , 10^{13} and 10^{14} ions/cm² dose). Dotted lines shows the Voigt deconvoluted peaks for the pristine SWCNT-A. (b) Variation in the Bragg angle (2θ) of (002) peak with changing H^+ ion fluence range. (c) Variation in the FWHM and intensity of the (002) peak with increasing H^+ ion fluence range.

with intermediate dose, it down shifts to 25.84° , which is further down shifted to 25.99° at high dose. Similar to the peak position, FWHM of (002) peak is reduced at intermediate dose. This shows that the disorderness in the lattice is reduced upon 10^{13} ions/cm² irradiation dose. XRD peaks were too weak for accurate quantification, but provide information from the milligram volume of the sample, i.e a statistically correct result.

Table 6-1: Fitted parameters for XRD pattern of SWCNT-A before and after H⁺ irradiation.

Sample		Peak1	Peak 2	Peak3	Peak4	Peak5
SWCNT-A (Before Irrad.)	Centre	12.88	17.67	25.72		43.93
	FWHM	6.90	4.76	4.88		3.24
	Ampli	384	42	170		39
SW-30-H12	Centre	12.81		26.09		43.50
	FWHM	7.49		4.47		2.89
	Ampli	697		144		50
SW-30-H13	Centre	13.05		25.84		43.80
	FWHM	7.31		3.84		2.86
	Ampli	332		146		67
SW-30-H14	Centre	13.31		25.99	27.99	43.36
	FWHM	9.00		2.15	15.81	3.40
	Ampli	792		40	145	46
Assignments		Non-Hexagons	Defects	(002)	Defects?	(101) & (100)

6.3.3 Raman Scattering Studies of H⁺ Irradiated CNTs

Fig. 6-4(a) shows modification of RBM modes of 30 keV H⁺ irradiated SWCNTs. Intensity of RBM modes monotonically decreases with increasing irradiation dose. Pristine SWCNTs (SWCNT-A) shows RBM modes at 171.2, 224.7, 289.6 and 307.9 cm⁻¹. At low dose and intermediate dose, 289.6 and 307.9 cm⁻¹ peaks downshifts to 285.29 and 305.0 cm⁻¹. At high dose, it shows further reduction in the intensity of RBM modes. Fig. 6-4(b) shows modification of IFM modes of SWCNTs upon 30 keV Ar⁺ ion irradiation. With increasing irradiation dose, the intensity of the 666.8 cm⁻¹ peak monotonically decreases. Interestingly at intermediate dose, 666.8 and 928.0 cm⁻¹ peak reappears. With further increase of dose to 10¹⁴ H⁺ ions/cm², all the IFM modes disappear.

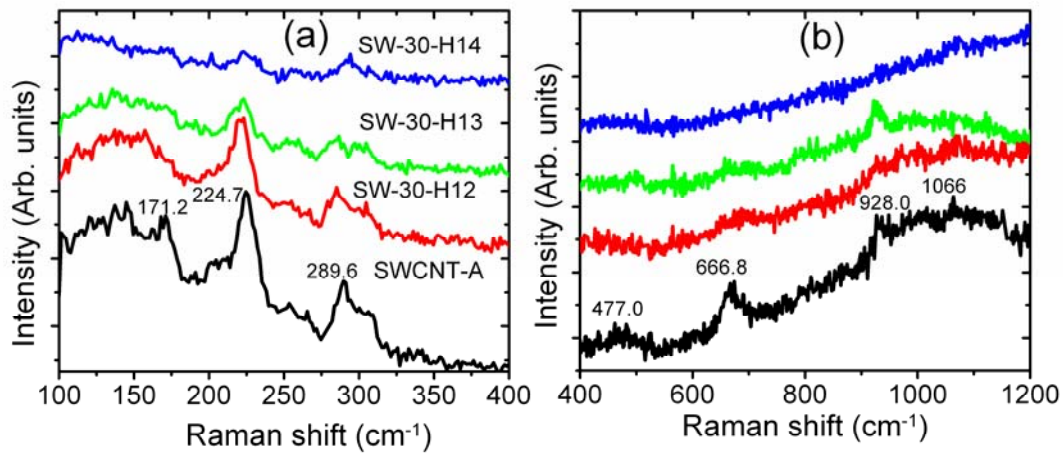


Figure 6-4: Raman spectra of SWCNTs before and after H^+ irradiation (a) RBM Modes shows decrease in the peak intensity of 224.7 and downshift of 289.6 cm^{-1} peak with increasing irradiation dose. (b) With increasing irradiation dose the intensity of the 666.8 cm^{-1} peak monotonically decreases. With intermediate dose of irradiation, 666.8 and 928.0 cm^{-1} peak reappears. At high irradiation dose all the IFM modes disappears.

Modification in D and G modes of SWCNTs after 30 keV H^+ ion irradiation is shown in Fig. 6-5(a). These spectra were deconvoluted using combination of Lorentzian and Fano line shape as shown in Fig. 6-5(b) for SWCNTs irradiated at low dose of 30 keV H^+ (SW-30-H12). The fitted parameters are summarized in Table 6-2. Variation in the Raman shift of D band, $G^-(M)$ band and $G^-(S)$ band is shown in Fig. 6-5(b), (c) and (d) respectively. D band and $G^-(M)$ band upshifts upon low dose and intermediate dose irradiation, while at high dose, these band downshift. Fig. 6-5(d) and (e) shows variation in the peak width and intensity of D, $G^-(M)$ and $G^-(S)$ band upon H^+ irradiation. Intensity of the characteristic $G^-(M)$ and $G^-(S)$ monotonically decreases with increasing irradiation dose. Fitted parameters are presented in Table 6-2.

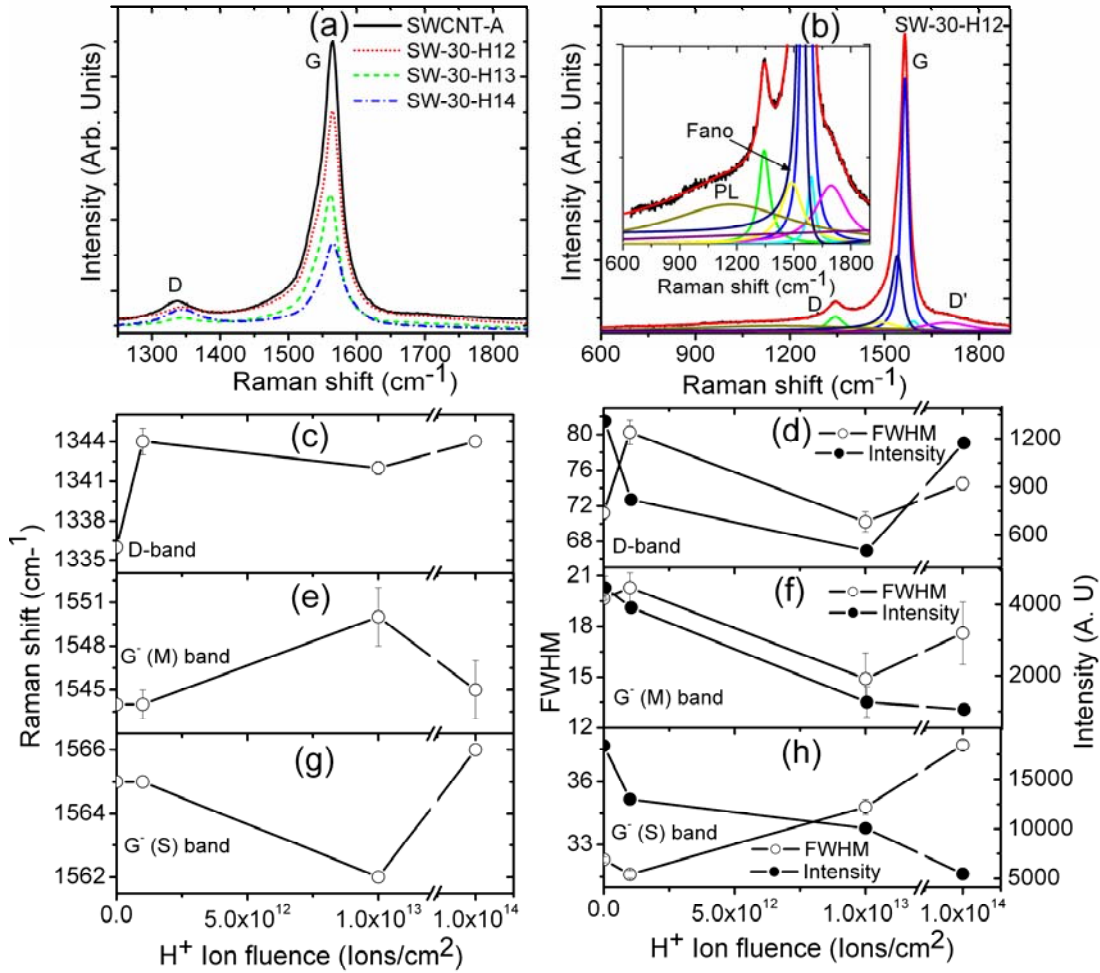


Figure 6-5: Raman spectra of SWCNT-A before and after irradiation of H⁺ (10¹², 10¹³ and 10¹⁴ ions/cm² doses). (b) Deconvoluted peaks using combination of Lorentzian and Fano lines typically for SWCNT-A irradiated at low dose. (c) and (d) shows variation in the peak centre, FWHM and intensity of SWCNT-A irradiated with various fluences of H⁺ ions. (e) Raman shift and (f) FWHM and intensity of G⁻(M) metallic component changing with irradiation dose. Variation in (g) Raman shift (h) FWHM and intensity of G⁻(S) band with irradiation dose.

Fig. 6-6(a) shows the second-order Raman modes of SWCNT-A irradiated with 30 keV H⁺ ions. These spectra were deconvoluted using combination of Lorentzian line shapes, as shown for SWCNT-A before irradiation in Fig. 6-6(b). These fitted parameters

are summarized in Table 6-3. Fig. 6-6(c) shows variation in the Raman frequency of G' band

Table 6-2 Fitted parameters for first order Raman spectra of SWCNT-A before and after 30 keV H⁺ irradiation.

Sl. No.	Profile	Peak1	Peak2	Peak3	Peak4	Peak5	Peak6	Peak7	I _G /I _D
SWCNT-A	Centre	1479	1336		1544	1565	1602	1700	15.17
	FWHM	92.2	71.2		19.65	32.3	39.8	223.3	
	Intensity	511.1	1309		4469	18360	472	533.1	
	Fano (1/q)				-0.186				
SW-30-H12	Centre	1168	1344	1489	1544	1565	1592	1696	18.47
	FWHM	941.9	80.25	157.3	20.3	31.6	50.6	235.5	
	Intensity	345.3	821	537.6	3914	13010	587	512	
	Fano (1/q)				-0.137				
SW-30-H13	Centre	1042	1342	1532	1550	1562	1589	1663	19.30
	FWHM	588.7	70.2	16.5	14.9	34.8	63.01	353.7	
	Intensity	141.5	500.7	286.6	1260	10070	511.3	622	
	Fano (1/q)				-1				
SW-30-H14	Centre	1280	1344	1487	1545	1566	1596	1710	5.41
	FWHM	819.9	74.5	211.2	17.6	37.7	48.4	236.7	
	Intensity	318.6	1174	298.8	1053	5467	516.6	176.7	
	Fano (1/q)				-0.161				
Assignments		LO/?	D- band	LO	Fano	G ⁻	G ⁺	Defects	

with irradiation dose. It downshifts upon irradiation at low and intermediate dose H⁺ irradiation. The FWHM of this peak increases with increasing irradiation dose, while the intensity of this peak monotonically decreases as shown in Fig. 6-6(d). The variation of the intensity ratios I_G/I_D and I_{G'}/I_D with increasing H⁺ irradiation dose is shown in Fig. 6-6(e). Both the ratios indicate a structural improvement upon irradiation dose of 10¹² and 10¹³ H⁺ ions/cm² and degradation upon 10¹⁴ H⁺ ions/cm² irradiation dose. Since intensity of G' is not affected by structural defects, I_G/I_D is taken as the measure of crystalline order.

The highest $I_{G'}/I_D$ ratio is achieved upon 10^{12} dose, indicating a better defect annihilation, probably by dynamic annealing process. Hydrogen is well known for passivation of defects in solids. Due to the passivation effect, defect density may be reduced, which could be better accessed by EPR studies.

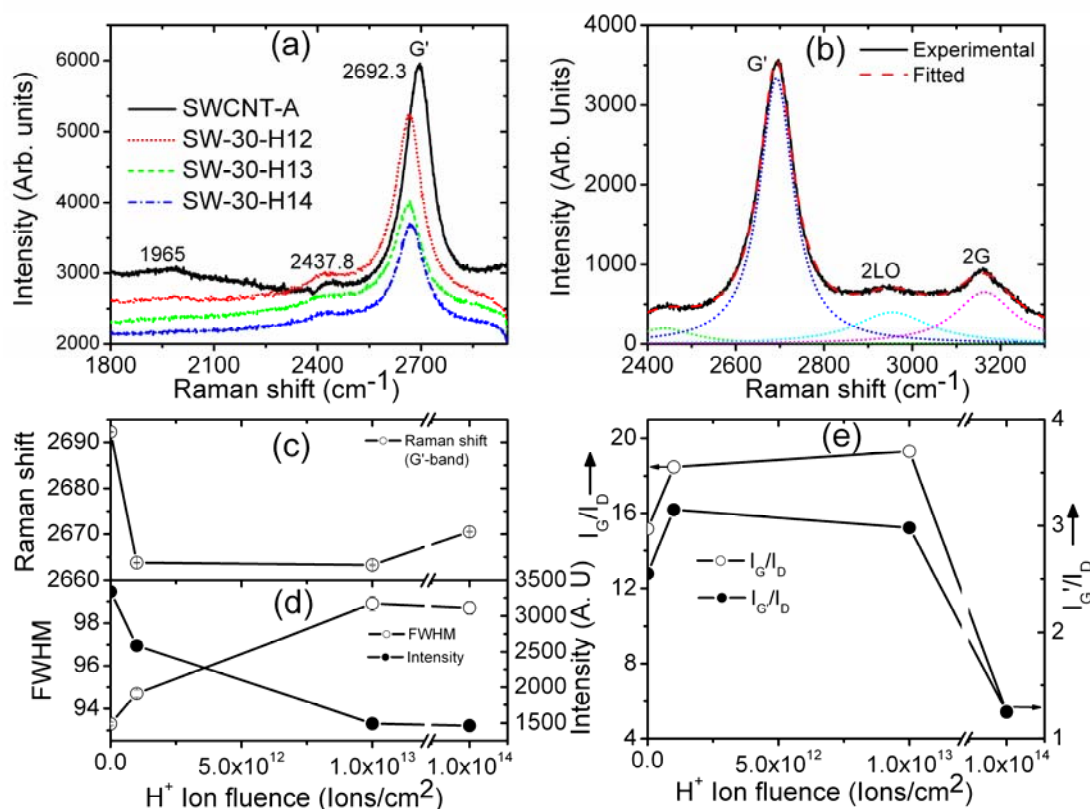


Figure 6-6: (a) Second-Order Raman modes of SWCNT-A before and after H^+ irradiation (b) Typical deconvolution of second-order Raman modes of SWCNT-A before irradiation. (c) Change in the peak position of G' band with increasing irradiation dose. (d) FWHM of G' band monotonically increases and the intensity of G' band decreases with increase of irradiation dose. (e) Variation in the intensity ratio of G band to D band and G' band to D-band with change in the H^+ ion fluence. Low and intermediate dose shows improvement in the structure upon irradiation.

Table 6-3 Fitted parameters for second-order Raman modes of SWCNT-A before and after H^+ irradiation.

Sl. No.	Profile	Peak1	Peak2	Peak3	Peak4	I_G/I_D
SWCNT-A	Centre	1965	2437.8	2692.3	2954.5	2.55
	FWHM	137.7	162.7	93.3	205.8	
	Intensity	334.9	197	3339	399	
SW-30-H12	Centre	1974.2	2439.0	2663.8		3.15
	FWHM	177.7	255.5	94.7		
	Intensity	65	325	2587		
SW-30-H13	Centre	1999.8	2460.3	2663.3	2840.8	2.98
	FWHM	117	416.5	98.9	147.3	
	Intensity	33	319	1493	115	
SW-30-H14	Centre	2067.3	2453.0	2670.5	2855	1.25
	FWHM	338.6	316.4	98.7	106.5	
	Intensity	24	247	1465	92	
Assignments		Defects	G' ($q = 0$)	G' ($q = 2k$)	$2LO$	

6.4 Effect of C^+ Ion Irradiation

The effect of C^+ ion (self) irradiation on SWCNT-A and MWCNT-A is presented in this section. We have investigated the structural modification due to 30 keV and 80 keV ions. Samples before irradiation and after irradiation were investigated with HRTEM, XRD and Raman spectroscopy for the possibility of controlled structural modification and spectroscopic properties of structural defects.

6.4.1 HRTEM Studies

HRTEM images of the SWCNTs irradiated with 30 keV C^+ ions is shown in Fig. 6-7. Fig. 6-7(a) shows the pristine SWCNT-A before irradiation. A dose of 10^{12} ions/cm² of 30 keV C^+ ions damages the tubular structure (Fig. 6-7(b)) and creates vacancies on the outer wall (Fig. 6-7(c)). Fig. 6-7(d) shows the welding of the two crossing tubes of

different diameter upon 10^{13} ions/cm² of 30 keV C⁺ irradiation. It also leads to fully collapsing of the tubular structure as shown in Fig. 6-7(e). Fig. 6-7(f) shows heavily damaged tubes and amorphous carbon deposits on the tube walls upon 10^{14} ions/cm² of 30 keV C⁺ irradiation dose.

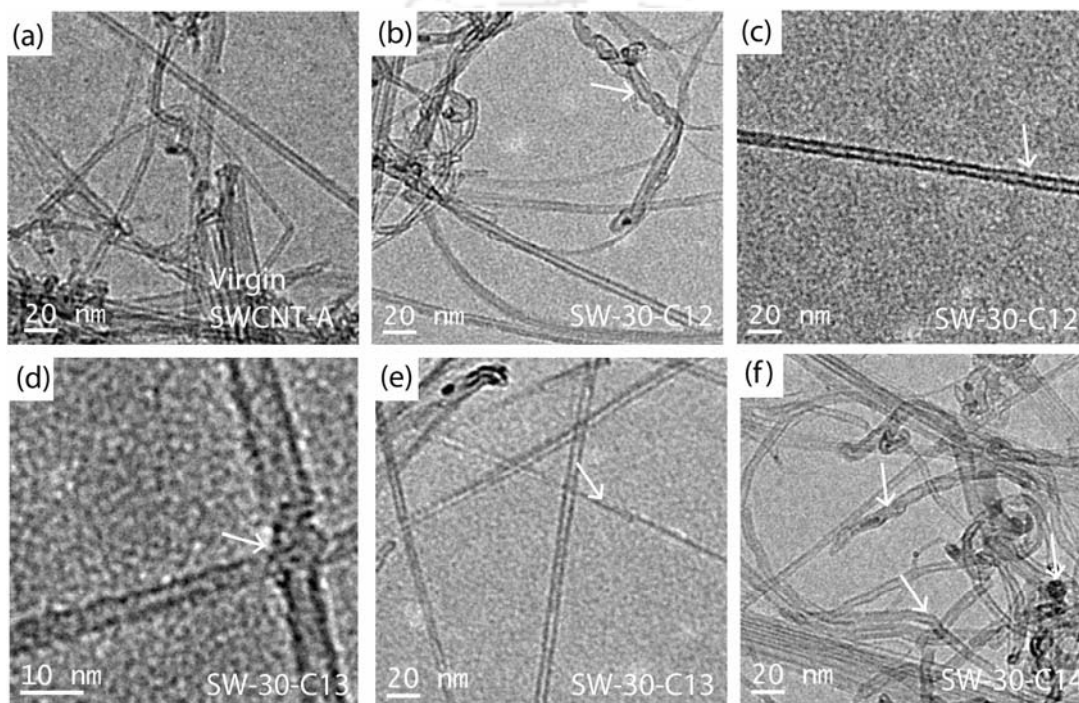


Figure 6-7: HRTEM images of SWCNT-A before and after 30 keV C⁺ irradiation. (a) Before irradiation. (b) Damaged wall structure at low dose. (c) Formation of surface void upon low dose. (d) Welding of two crossing CNTs with different diameter at low dose irradiation. (e) A fully collapsed SWCNTs upon intermediate dose irradiation. (f) High dose irradiation shows formation of a large number of surface defects and amorphous carbon deposits.

Fig. 6-8 shows the HRTEM image of MWCNTs irradiated with 30 keV C⁺ ions. Fig. 6-8(a) shows a portion of the pristine MWCNT-A. (b) MWCNT-A irradiated at low dose shows growth of bamboo like structure / wall linkages resulting into formation of compartments. Similar formation of compartments upon irradiation has been observed by Ramanath et. al. upon 30 keV Ga⁺ ion irradiation [221] and similar effect has been

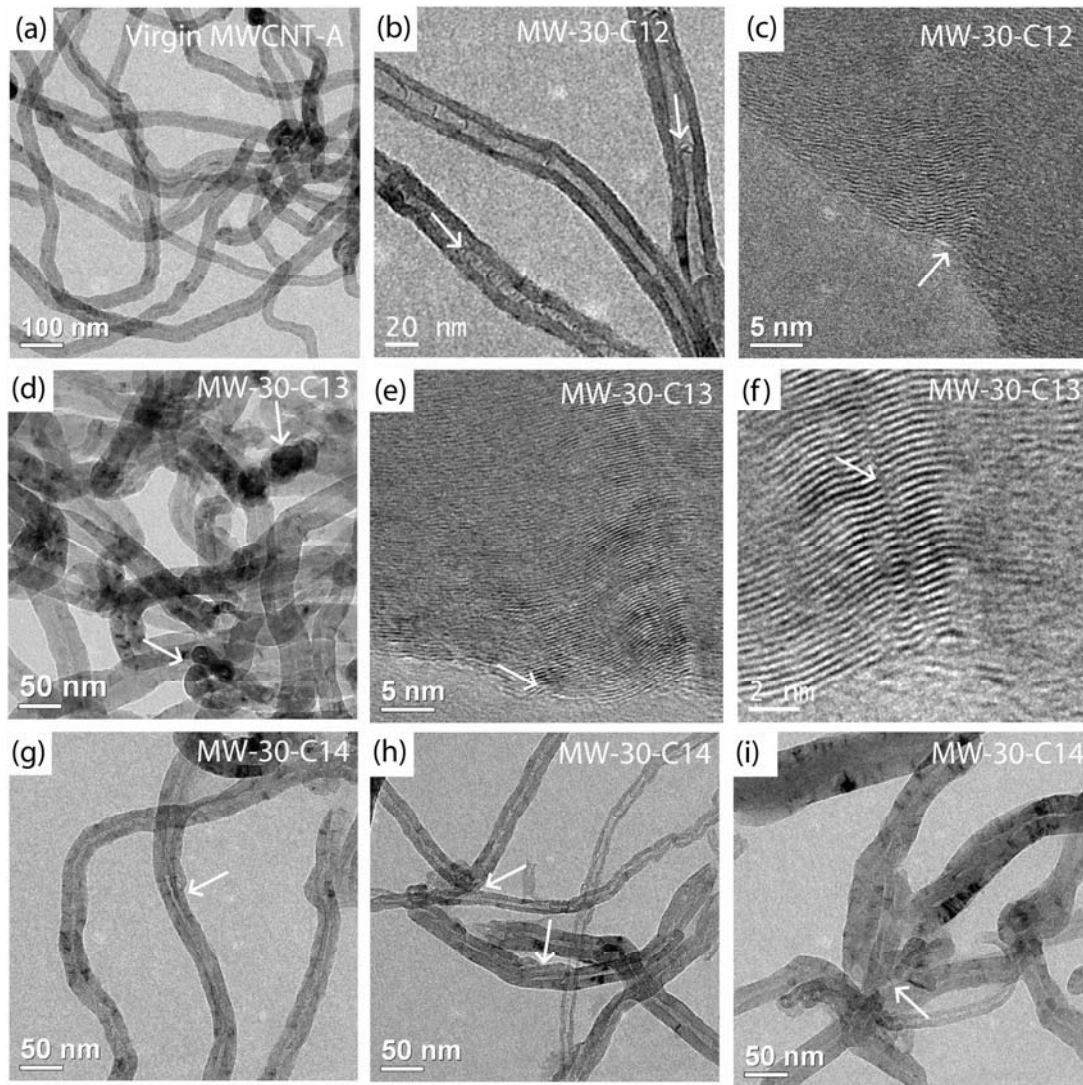


Figure 6-8: HRTEM image of 30 keV C^+ ion irradiated MWCNT-A. (a) Virgin MWCNT-A (b) Growth of bamboo like structure within MWCNT-A low dose irradiation. (c) A void formed on the outer wall upon low dose irradiation. (d) MWCNT-A after irradiation with 10^{13} ions/cm² showing formation of fullerene like structure and amorphous carbon deposits on the wall. (e) Damage to the outer walls and formation of curved graphitic structure. (f) Ion tracks formed in the MWCNTs wall leads to staking faults. This results into formation of curved graphitic structures. (g) 10^{14} ions/cm² shows comparatively much higher damage to the wall structures. A portion of the wall clipped off upon irradiation is shown. (h) Damage produced upon 10^{14} ions/cm² results into the formation of sharp bent like structures. (i) A portion of MWCNTs irradiated at high dose showing large amorphous carbon deposits from the broken walls of MWCNT-A.

observed in-situ under 300 keV electron exposure in TEM [239]. Low dose irradiation also creates voids on the outer walls of MWCNTs. Irradiation at intermediate dose leads to formation of fullerene like structure and amorphous carbon deposits on the wall as shown in Fig. 6-8(d). A HRTEM image of a portion of outer wall structure of a MWCNT is shown in Fig. 6-8(e). This shows defected outer wall structure and evolution of curved graphic forms upon intermediate dose irradiation. Fig. 6-8(f) shows formation of ion tracks in the outer walls of MWCNT-A leading to staking faults. As formed stacking faults in the outer walls introduces curvature in the graphitic structure leading to formation of fullerene like structures. MWCNT-A irradiated at high dose shows comparatively much higher damage on the outer walls. It leads to peeling of a portion of outer walls as shown in Fig. 6-8 (g). Damage produced upon high dose irradiation also results into the formation of sharp bent like structures and complete removal of a portion of walls as shown by arrows in Fig. 6-8(h). A portion of MWCNTs irradiated at high dose showing large amorphous carbon deposits from the broken walls of MWCNT-A is shown in Fig. 6-8(i). Interestingly, as compared to other ions (H^+ , Ar^+ and N^+) only C^+ ions shows formation of compartment like structure upon irradiation.

6.4.2 XRD Studies

XRD spectra of SWCNTs before and after irradiation with 30 keV C^+ ion irradiation are shown in Fig. 6-9(a). It also shows the typical deconvoluted peaks with fitted spectra for the pristine SWCNTs. These spectra were fitted with Voigt line shapes. The fitted parameters are summarized in Table 6-4. Fig. 6-9(b) shows shift in the Bragg angle (2θ) for (002) peak upon 30 keV C^+ irradiation, while changes in the FWHM and

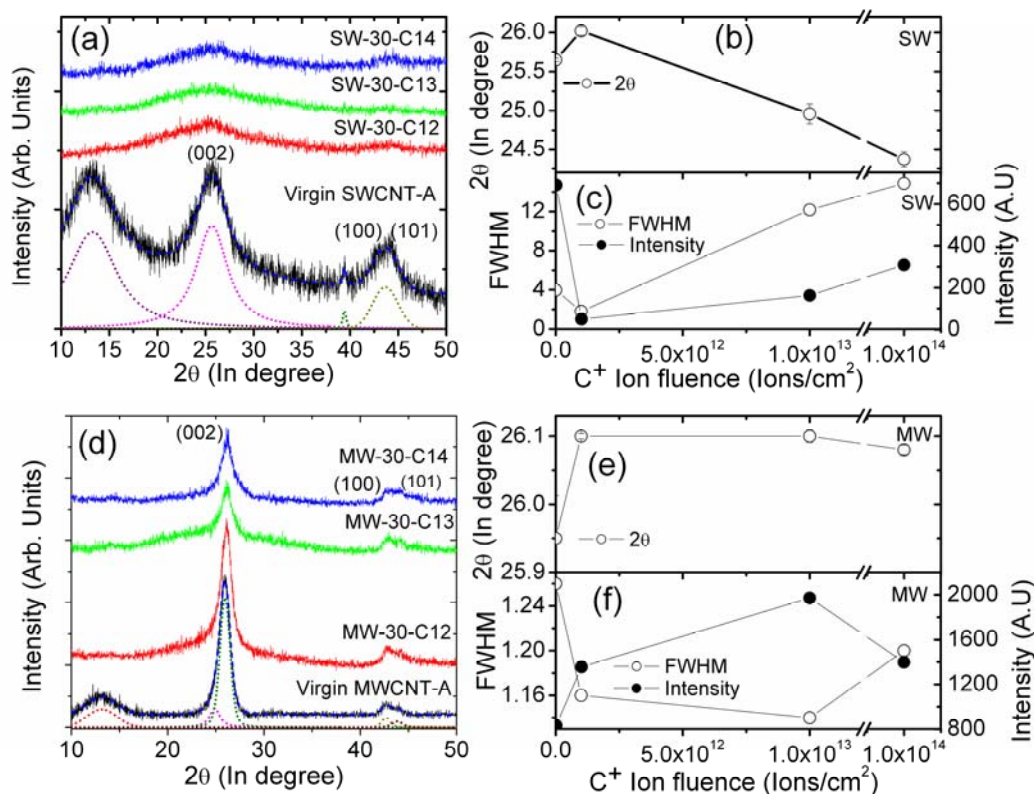


Figure 6-9: XRD spectra of 30 keV C^+ irradiated samples (a) XRD pattern of SWCNT-A before and after irradiation. Dotted lines shows deconvoluted peaks for pristine SWCNTs. Variation in (b) (2θ), (c) FWHM and intensity with C^+ irradiation at different doses. (d) XRD pattern of MWCNT-A before and after irradiation. Deconvoluted peaks are shown by dotted lines. (e) Change in 2θ and (b) FWHM and intensity with C^+ irradiation dose.

intensity is shown in Fig. 6-9(c). The 2θ value increases upon irradiation at low dose, while it decreases at intermediate dose and high dose. Whereas the intensity decreases at low dose and recovers upon intermediate and high doses. Recovered intensity is much lower than the pristine SWCNTs, indicating ion irradiation induced defects formation. Fig. 6-9(d) shows the XRD pattern of MWCNT-A before and after 30 keV C^+ irradiation. Deconvoluted peaks for the pristine MWCNT-A is shown by dotted lines and parameters

Table 6-4: Fitted parameters of XRD pattern of SWCNT-A and MWCNTs-A before and after 30 keV C⁺ irradiation at three different fluence levels.

Sample	Spectral profile	Peak1	Peak 2	Peak3	Peak4	Peak5
SW-Virgin (SWCNT-A)	Centre	13.26	----	25.65	39.42	43.67
	FWHM	5.94		3.97	0.44	3.11
	Ampli	649		691	121	280
SW-30-C12	Centre	----	----	24.89		43.85
	FWHM			12.09		3.35
	Ampli			201		33
SW-30-C13	Centre	----	----	25.07	33.33	43.91
	FWHM			10.64	7.13	8.07
	Ampli			148	37	20
SW-30-C14	Centre	----	----	24.96	32.17	44.11
	FWHM			8.95	3.81	2.12
	Ampli			136	19	37
MW-Virgin	Centre	13.15	24.88	25.95	42.66	43.85
	FWHM	3.69	1.26	1.26	1.07	1.29
	Ampli	115	121	833	60	38
MW-30-C12	Centre	----	24.63	26.09	42.79	43.91
	FWHM		7.27	1.24	0.90	2.67
	Ampli		145	731	61.88	74
MW-30-C13	Centre	14.23	24.51	26.13	42.84	44.08
	FWHM	1.63	12.59	1.26	0.86	2.09
	Ampli	16	133	278	56	53
MW-30-C14	Centre	13.74	25.50	26.18	43.09	44.65
	FWHM	2.88	8.95	1.43	1.79	3.11
	Ampli	14	55	334	57	45
Assignments		Defects	(002) Peak1	(002) Peak2	(100)	(101)

are summarized in Table 6-4 along with the parameters of SWCNTs. Fig. 6-9(c) show variation in the 2 θ and Fig. 6-9(d) shows changes in the FWHM and intensity of (002) peak with increasing dose. Peak position (2 θ) of (002) peak upon low and intermediate

dose irradiation, while corresponding FWHM decreases. Increase in 2θ indicates reduction in the interplanar spacing i.e higher lattice ordering achieved due to defect annihilation. A closer look at the (100) and (101) profile variation shows upshift of the Bragg angle peak with the increasing irradiation dose, indicating reduction in the lattice strain upon irradiation. However, the FWHM is considerably increased upon high dose irradiation, indicating increase in disorderness.

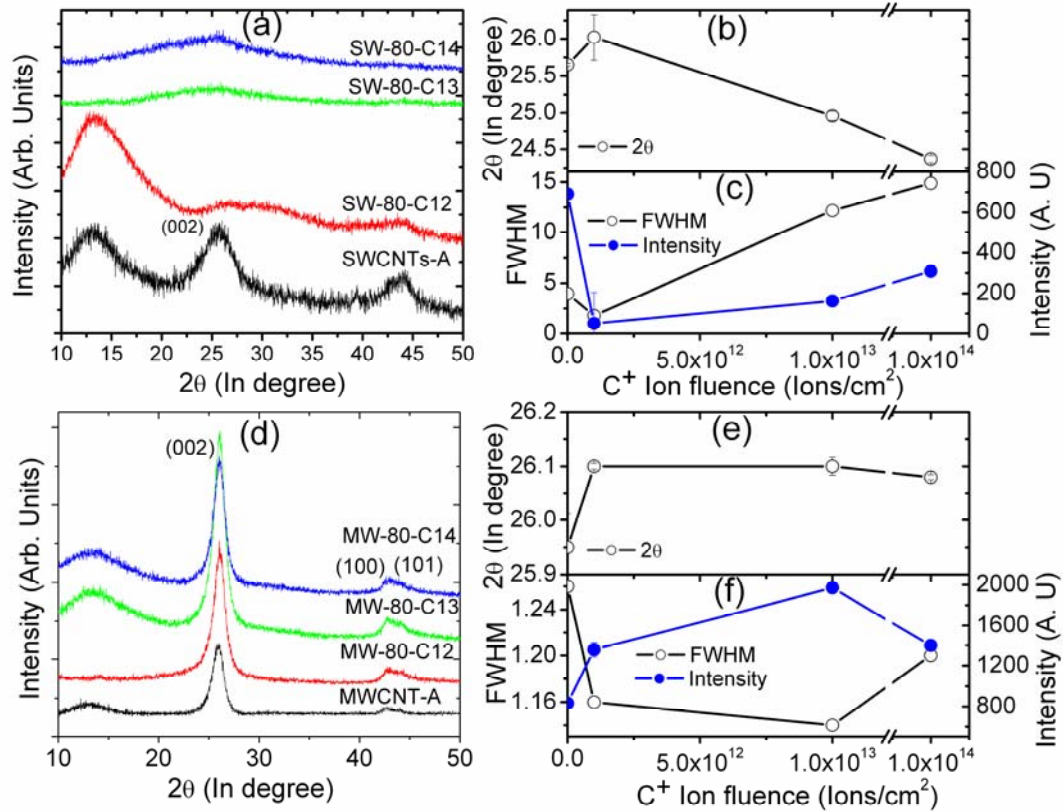


Figure 6-10: XRD pattern of CNTs before and after 80 keV carbon (C^+) irradiation. (a) XRD pattern of SWCNTs irradiated with various fluences. (b) Variation in the peak centre (2θ) and (c) FWHM and intensity of (002) peak of SWCNT-A with increasing C^+ irradiation fluence. (d) XRD pattern of MWCNTs irradiate with various fluences. (e) Variation in the peak centre (2θ) and (f) FWHM and intensity of (002) peak of MWCNT-A with increasing C^+ irradiation fluence.

Results of higher ion energy (80 keV) C^+ irradiation is shown in Fig. 6-10. Fig. 6-10 shows modification of XRD pattern of SWCNTs and MWCNTs with C^+ irradiation. These spectra were deconvoluted with the Voigt line profile and the parameters are summarized in Table 6-5. The 2θ value for the (002) peak slightly increases upon low dose irradiation, while at intermediate and high doses, it decreases, as shown in Fig. 6-10(b), showing strong modification of SWCNTs upon 80 keV ion irradiation. Even the width of this peak is reduced upon low dose irradiation and gets broadened after irradiation at intermediate and high dose. Reduction of peak width upon low dose occurs along with evolution of a new very broad feature at 29.55° . This shows that even at low dose, 80 keV C^+ ions damages SWCNT-A heavily. Drastic decrease in XRD intensity upon low dose indicates substantial modification of SWCNTs structure, as shown in Fig. 6-10(c). With higher doses, the structural damage becomes prominent.

Table 6-5: Fitted parameters of XRD pattern of SWCNT-A and MWCNTs-A before and after 80 keV C^+ irradiation at three different fluence levels.

Sample	Raman shift (cm^{-1})					
	Peak1	Peak 2	Peak3	Peak4	Peak5	Peak6
SW-Virgin	13.26		25.65		39.42	43.67
SW-80-C12	13.29	16.69	26.02	29.55		43.22
SW-80-C13	----	----	24.96	----	----	44.02
SW-80-C14	----	----	24.37	----	----	----
MW-Virgin	13.15	24.88	25.95	----	42.66	43.85
MW-80-C12	----	25.38	26.10	----	42.76	43.99
MW-80-C13	13.70	25.61	26.10	----	42.74	43.86
MW-80-C14	13.56	25.49	26.08	30.97	----	----
Assignments	Defects	(002) Peak1	(002) Peak2	Defect	(100)	(101)

Fig 6-10(d) show the XRD pattern of MWCNTs before and after 80 keV C^+ irradiation. The deconvoluted parameters of these spectra are summarized in Table 6-5

along with the SWCNTs. Fig 6-10(e) show variation in the 2θ and Fig. 6-10(f) shows modification of FWHM and intensity with irradiation dose. Bragg angle (2θ) increases with irradiation at low and intermediate doses, while it decreases at high dose. Correspondingly, the FWHM decreases and intensity increases at low and intermediate dose, while at high dose it shows opposite trend. This indicated structural improvement upon 10^{12} and 10^{13} ions/cm² dose of 80 keV C⁺ irradiation in case of MWCNTs.

6.4.3 Raman Scattering Studies

Raman spectra of SWCNTs before and after irradiation with 30 keV C⁺ ions are shown in Fig. 6-11. Fig. 6-11(a) shows the modification of RBM modes upon irradiation. New RBM feature evolves at low and intermediate dose, while at high dose intensity of RBM modes is drastically reduced. Changes in the RBM modes indicates modification of diameters upon low and intermediate doses, while destruction of SWCNTs upon high dose irradiation. Fig. 6-11(b) shows changes in IFM modes upon 30 keV C⁺ ion irradiation. The IFM modes shows reduction in the intensity of peaks observed in pristine samples at 684, 854, 975 and 1096 cm⁻¹. Fig. 6-11(c) shows modification of the characteristic D, G and G' modes. These spectra were deconvoluted using combination of a Fano line shape for G'(M) component and Lorentzian line for all other components /modes. The deconvoluted parameters are summarized in Table-6-6 for first order modes, while parameters of overtone modes is summarized in Table 6-7. Fig. 6-11(d) shows variation in the intensity ratio of G' to D band with increasing irradiation dose. It clearly shows structural improvement upon 10^{12} and 10^{13} ions/cm², while destruction upon 10^{14} ions/cm². This is in agreement with the XRD results.

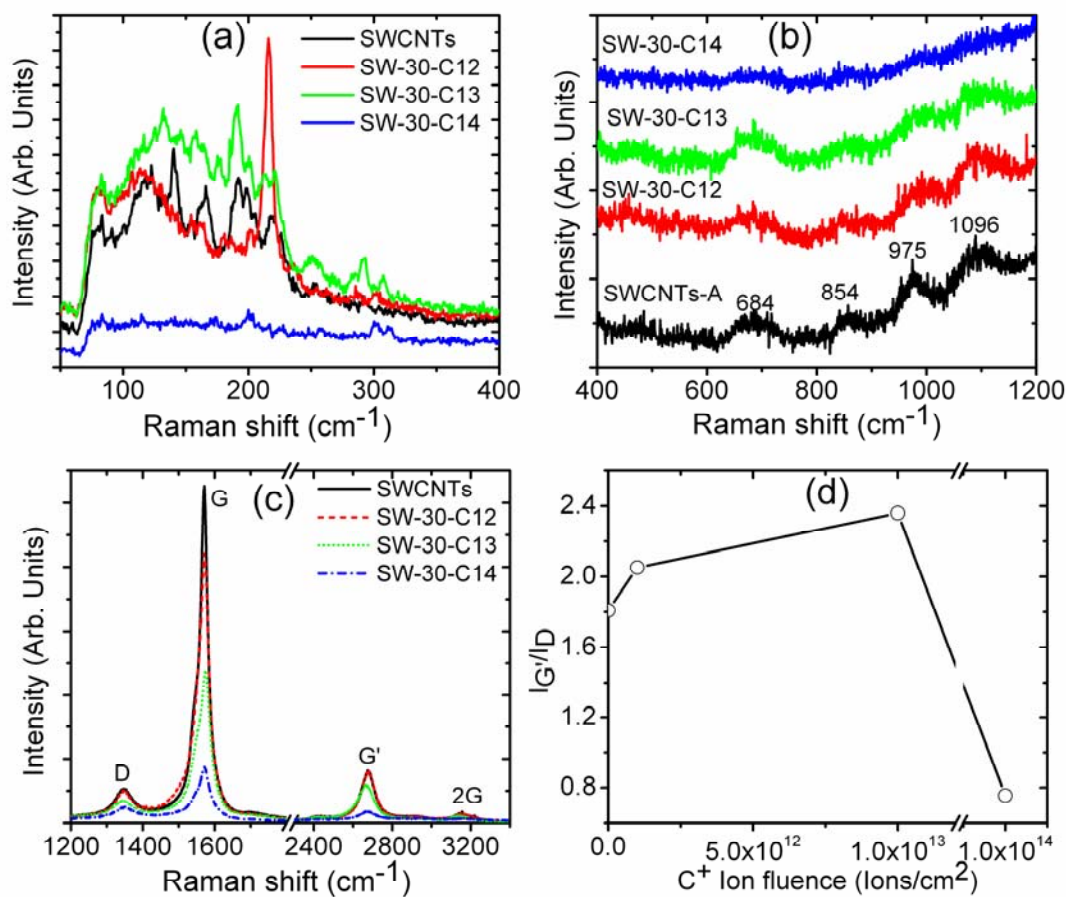


Figure 6-11: Raman studies of SWCNTs before and after 30 keV C^+ irradiation. (a) Modification of RBM mode indicating diameter modification upon 10^{12} and 10^{13} ions/cm^2 . (b) Decrease in the intensity of IFM modes upon irradiation. (c) Changes in the characteristic D, G and G' mode with increasing irradiation dose. (d) Variation in the intensity ratio of G' by D band ($I_{G'}/I_D$) ratio with increasing irradiation dose.

Table 6-6: Fitted parameters of first order Raman spectra of SWCNT-A before and after Carbon (C⁺) irradiation at 30 and 80 keV.

Sl. No.	Profile	Peak1	Peak2	Peak3	Peak4	Peak5	Peak6	Peak7	I _G /I _D
SWCNT-A	Centre	1546	1347	1489	1571	1596	1715	1985	12.4
	FWHM	15.9	71.7	100.7	27.1	54.1	87.0	104.1	
	Intensity	4269	1687	245	19160	864	235	38	
	Fano (1/q)	-0.05							
SW-30-C12	Centre	1555	1347	1499	1573	1606	1709	1959	11.3
	FWHM	20.6	61.6	61.9	33.0	49.7	171.2	217.4	
	Intensity	3821	1482	364	14920	628	321	67	
	Fano (1/q)	-0.23							
SW-30-C13	Centre	1552	1345	1486	1575	1600	1709	1959	10.0
	FWHM	18.2	73.9	31.2	35.7	55.0	129.9	122.8	
	Intensity	2781	943	31	8407	501	216	30	
	Fano (1/q)	-0.18							
SW-30-C14	Centre	1557	1348	1479	1571	1597	1708		5.0
	FWHM	14.7	84.5	73.9	37.5	80.85	101.85		
	Intensity	505	682	66	3429	555	70		
	Fano (1/q)	-1.00							
SW-80-C12	Centre	1550	1343	1321	1569	1604	1701		5.54
	FWHM	18.5	71.8	793.3	39.8	47.3	126.9		
	Intensity	1649	1781	244.3	9081	492.2	213		
	Fano (1/q)	-0.28							
SW-80-C13	Centre	1547	1346	1493	1571	1601	1706		10.22
	FWHM	15.5	78.4	172.2	32.8	60.2	104.3		
	Intensity	3198	1481	178.9	14110	794.5	245.9		
	Fano (1/q)	-0.25							
SW-80-C14	Centre	1554	1347	1484	1574	1598	1699		6.73
	FWHM	15.2	75.1	101.5	35.7	72.5	126.0		
	Intensity	2460	1333	160	82	1006	212		
	Fano (1/q)	-0.40							
Assignments		PL	D- band		Fano	G ⁻	G ⁺	Defects	Ratio

Table 6-7: Fitted parameters of second order Raman spectra of SWCNT-A before and after 30 and 80 keV Carbon (C^+) irradiation.

Sample	Raman shift (cm^{-1})					I_G/I_D
	Peak1	Peak 2	Peak3	Peak4	Peak5	
SWCNT pristine	2428.3	2676.1	2920.4	3156.4		1.8
SW-30-C12	2428.2	2677.5	2926.9	3153.9	3216.6	2.1
SW-30-C13	2421.7	2665.8	2922.3	3145.9		2.4
SW-30-C14	2430.5	2673.1	2921.3	3159.4		0.8
SW-80-C12	2422.3	2669.7	2916.2	3137.5	3178.2	1.8
SW-80-C13	2428.4	2672.1	2916.4	3146.8	3209.4	1.5
SW-80-C14	2430.8	2673.9	2933.8	3153.4	3210.1	1.4
Assignments	$C=O$	D band	PL	G^- band	G^+ band	

Fig. 6-12(a) shows the Raman spectra of SWCNTs modified with 80 keV C^+ ions. Fig. 6-12(a) shows the modification of RBM modes with increasing irradiation dose. Low dose irradiation shows reduced intensity of RBM modes, while with intermediate and high dose new peaks evolve implying modification of the diameters. IFM modes do not show evolution of any new peak after 80 keV of C^+ irradiation, as shown in Fig. 6-12(b). Fig. 6-12(c) shows characteristic D, G and G' modes for different doses. The deconvoluted parameters of these spectra are summarized in Table 6-6 along with results of 30 keV C^+ irradiation. Fig. 6-12(d) show the variation in the intensity ratio of G' and D band. I_G/I_D ratio marginally improves upon irradiation at low dose, while it is drastically reduced with intermediate and high dose. This shows that 80 keV C^+ ions have more damaging capability than to improve the structure of CNTs. Fig. 6-13 show the comparison of the Raman spectral features of MWCNT-A upon 30 keV and 80 keV C^+ ion irradiation. Fig. 6-13(a) show the modification of characteristic modes D, G and G' modes of MWCNTs with increasing ion irradiation dose of 30 keV C^+ ions. These spectra were fitted with combination of Lorentzian line shapes and the deconvoluted parameters are

summarized in Table-6-8 for first order modes and in Table 6-9 for the second order modes. Fig. 6-13(b) shows the variation in the I_G/I_D intensity for MWCNTs irradiated with 80 keV C^+ ions. A dose of 10^{12} ions/cm² show improvement in the I_G/I_D . Further intermediate dose irradiation shows reduction in the I_G/I_D ratio, while high dose irradiation shows slight improvement, but lower than that of the pristine samples. Thus, a dose of 10^{12} ions/cm² can be used for structural improvement of SWCNTs. Fig. 6-13(c) shows the

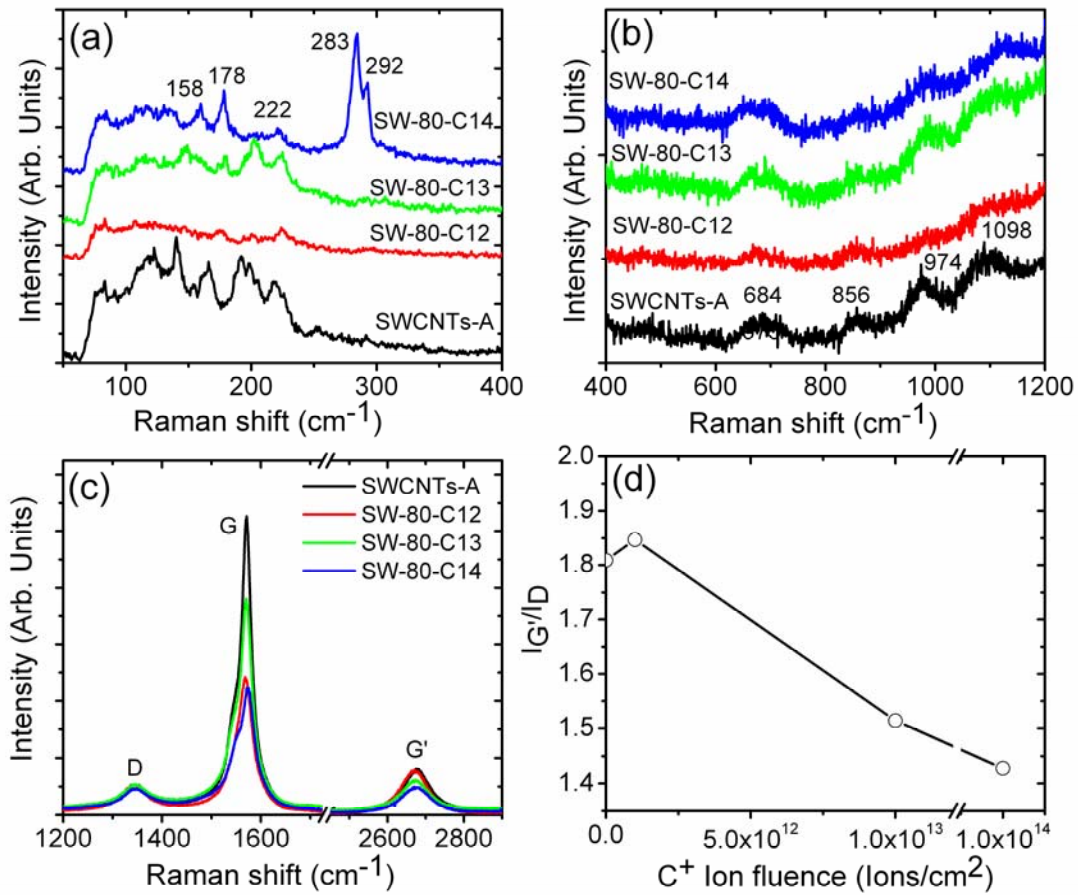


Figure 6-12: Raman studies of SWCNTs before and after 80 keV C^+ irradiation. (a) Modification of Raman shift of RBM modes (b) Variation in the intensity of IFM modes with increasing irradiation dose. (c) Relative changes in the characteristic D, G and G' modes with increasing irradiation dose. (d) Variation in the intensity ratio of I_G/I_D with varying C^+ ion fluence range.

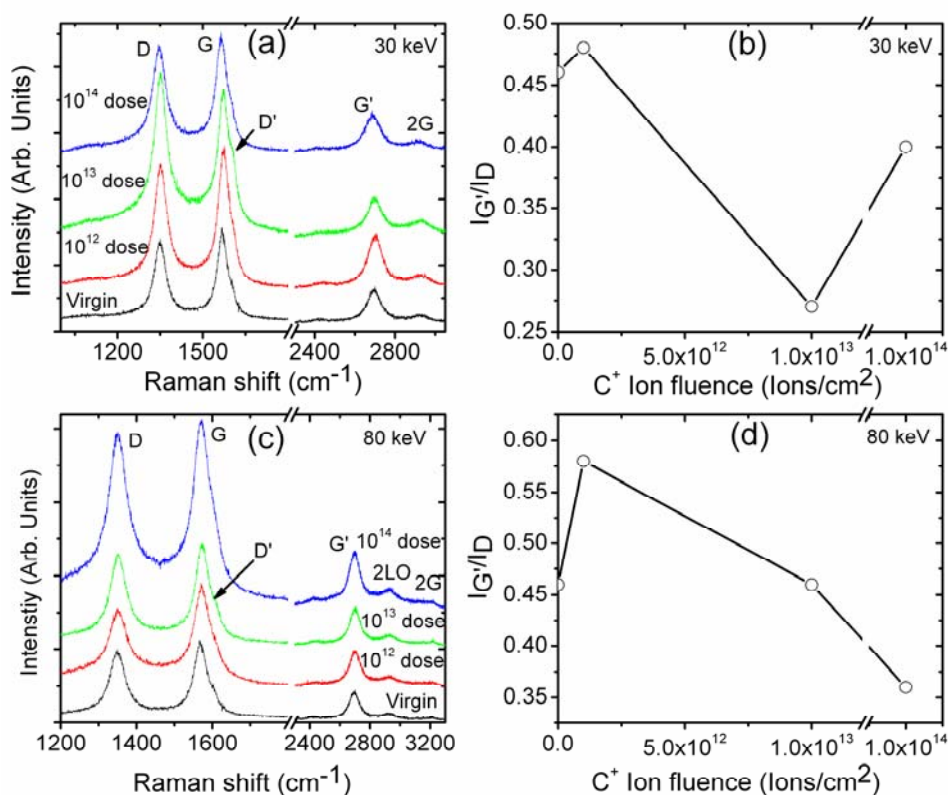


Figure 6-13: (a) Raman spectra of MWCNT-A irradiated with 30 keV C^+ ions. (b) Variation in the intensity ratio $I_{G'}/I_D$ with increasing ion irradiation dose at 30 keV. (c) Raman spectra of MWCNT-A irradiated with 80 keV C^+ ions. (d) Variation in the intensity ratio $I_{G'}/I_D$ ratio with increasing 80 keV C^+ ion irradiation dose.

modification of Raman spectra of MWCNT-A upon 80 keV C^+ ion irradiation with varying ion doses. These spectra were deconvoluted using combination of Lorentzian line shapes and parameters are summarized in Table 6-8 for first order Raman modes and Table 6-9 for the second order Raman modes. Fig. 6-13(d) show modification of $I_{G'}/I_D$ intensity ratio with increasing ion fluence. Low dose irradiation shows improvement in the ratio, while further increase of irradiation dose to intermediate and high level shows drastic reduction in the intensity ratio. This indicates that similar to 30 keV only a dose of 10^{12} ions/ cm^2 of 80 keV of C^+ ion leads to structural improvement.

Table 6-8: Fitted parameters of first order Raman spectra of MWCNT-A irradiated with 30 and 80 keV Carbon (C^+ ions).

Sample		Peak1	Peak 2	Peak3	Peak4	Peak5	I_G/I_D
MWCNT pristine	Centre	1083.5	1349.5	1367.7	1568.7	1604.2	1.3
	FWHM	179.9	48.7	316.9	42.9	24.37	
	Amplitude	27	633	62	767	97	
MW-30-C12	Centre	1088.2	1351.3	1379.9	1573.5	1610.0	0.7
	FWHM	218.0	50.7	327.0	47.4	23.7	
	Amplitude	48	953	130	1176	151	
MW-30-C13	Centre	1082.6	1351.0	1366.1	1572.2	1601.3	0.9
	FWHM	166.7	48.7	359.0	55.4	50.7	
	Amplitude	40	1158	275	1031	192	
MW-30-C14	Centre	1106.3	1346.5	1363.0	1564.2	1595.5	1.4
	FWHM	74.1	53.7	376	49.1	53.0	
	Amplitude	21	777	158	874	139	
MW-80-C12	Centre	1077.9	1351.2	1369.2	1571.9	1608.1	1.9
	FWHM	192.9	51.3	340.08	49.40	36.0	
	Amplitude	34	604	172	955	136	
MW-80-C13	Centre	1091.1	1351.7	1379.5	1573.3	1609.8	1.4
	FWHM	133.3	490.6	354.3	43.7	27.60	
	Amplitude	29	816	117	996	152	
MW-80-C14	Centre	1074.2	1350.7	1375.5	1570.8	1606.3	1.4
	FWHM	208.2	55.0	367.7	51.1	31.8	
	Amplitude	68	1465	317	1768	279	
Assignments		C=O	D band	PL	G ⁻ band	G ⁺ band	

Table 6-9: Fitted parameters of second order Raman spectra of MWCNT-A irradiated with 30 and 80 keV Carbon (C^+) ions.

Sample	Spectral profile	Peak1	Peak 2	Peak3	Peak4	I_G/I_D
MWCNT pristine	Centre	2426.7		2695.2	2922.5	0.46
	FWHM	92.5		83.5	109.0	
	Amplitude	20.2		292	49.3	
MW-30-C12	Centre	2437.8		2700.7	2925.4	0.48
	FWHM	99.8		89.6	115	
	Amplitude	29		462	84	
MW-30-C13	Centre	2466.5		2698.5	2922.8	0.27
	FWHM	202.0		91.7	91.7	
	Amplitude	21		315	315.4	
MW-30-C14	Centre	2419.4		2688.4	2911.1	0.40
	FWHM	110.8		96.7	122.1	
	Amplitude	22.9		308.4	61	
MW-80-C12	Centre	2432.5		2700.2	2924.7	0.58
	FWHM	106.8		88.6	123.6	
	Amplitude	25.9		351	65	
MW-80-C13	Centre	2439.9		2700.7	2926.8	0.46
	FWHM	105.8		85.5	120	
	Amplitude	27		378	72	
MW-80-C14	Centre	2430.3	2550.2	2696.9	2920.0	0.36
	FWHM	101	81.3	90.6	142.3	
	Amplitude	50	32	539	131	
<i>Assignments</i>		<i>G'</i>	<i>Defects</i>	<i>G'</i>	<i>2LO</i>	<i>Ratio</i>

6.5 Effect of N^+ Ion-irradiation

6.5.1 HRTEM Studies

Fig: 6-14 shows the HRTEM images of SWCNTs before and after irradiation. Perfect tubular structure of SWCNTs before irradiation is shown in Fig. 6-14(a).

Irradiation at low dose leads to the formation of small number of carbon vacancies in the structure but majority of the tubes remains intact as clearly shown in Fig: 6-14(b).

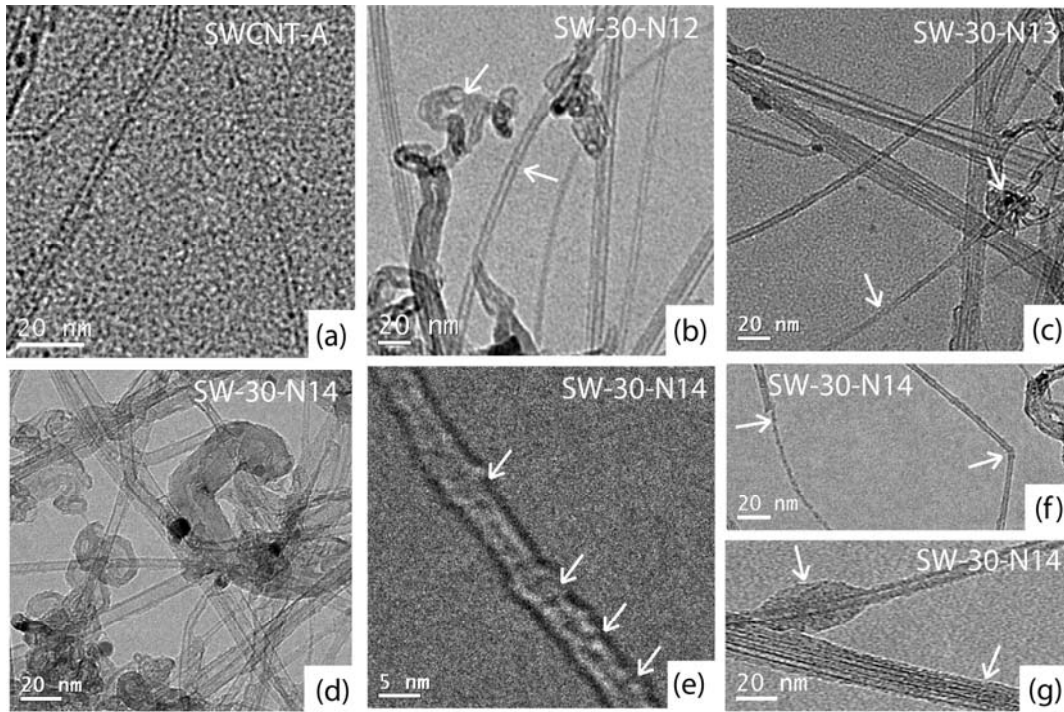


Figure 6-14: HRTEM image of SWCNTs irradiated with 30 keV N^+ ions (a) Virgin SWCNT-A (b) SWCNT-A irradiated with 10^{12} N^+ ions/cm² showing damaged wall structure. (c) SWCNT-A after 10^{13} N^+ ions/cm² irradiation. (d) Conversion to multiwalled structure and formation of large amount of amorphous carbon after 10^{14} N^+ ion irradiation dose. (e) A large vacancies formed on the surface of SWCNT-A after 10^{13} N^+ ions dose. (f) A bisected SWCNT and possibility to peel off a portion using 10^{14} N^+ ions/cm². (g) Coating of amorphous carbon on the tube wall and formation of a large number of surface vacancies.

At few locations low dose irradiation also showed damage to the wall structure as shown in Fig. 6-14(b). At intermediate dose, along with vacancies on the tube structure, presence of amorphous carbon was observed as shown in Fig: 6-14(c). The tubular carbon structure is heavily damaged after high dose irradiation, as shown in Fig. 6-14(d). It shows destruction of tubular structure and formation of amorphous carbon and conversion from

single walled structure to multiwalled tubular structure. High irradiation dose creates a large number of surface vacancies as shown in Fig. 6-14(e). Fig. 6-14 (f) shows complete

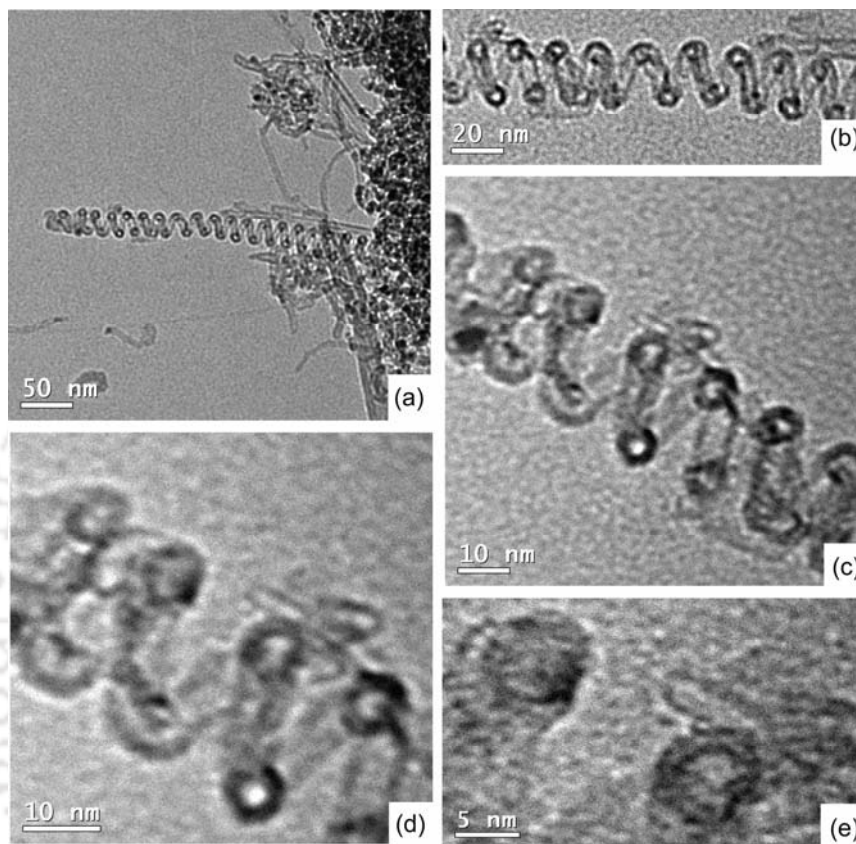


Figure 6-15: (a) Renucleation of amorphous carbon upon $30 \text{ keV } 10^{14} \text{ N}^+ \text{ ions/cm}^2$ irradiation results into formation of nano-springs like structure. (b) It is a perfect spiral structure of size $\sim 20 \text{ nm}$. (c) Image taken at comparatively higher magnification. (d) and (e) HRTEM images of the nanospring shows it consists of small linear chain of carbons of length typically $\sim 20 \text{ nm}$ and double layered fullerene structures at the ends.

bisection of CNTs as a result of ion irradiation and partial removal of tube wall, demonstrating the potential of ion irradiation as a tool for surface engineering of CNTs. It also shows formation of a number of vacancies and local structural defects upon ion irradiation. Coating of amorphous carbon on tube walls and a number of vacancies were formed (indicated by arrows) upon high irradiation dose as shown in Fig. 6-14(g).

As a result of high irradiation dose, re-nucleation of amorphous carbon takes in the shape of nano-springs like crystalline structure of carbon observed at few places as shown in Fig 6-15. Higher resolution HRTEM image of these nanosprings are shown in Fig. 6-15 (a-c). The HRTEM images show that these structures are made up of small linear chain of carbons of length ~ 20 nm (shown in Fig:6-15(d)) and double layered fullerene structures at the ends (shown in Fig. 6-15(e)) arranged in the order to form nano-springs.

Physical changes in the structural morphology of MWCNTs as a result of ion-irradiation are shown in Fig. 6-16. Fig. 6-16(a) shows the TEM image of MWCNTs before irradiation. Fig. 6-16(b) shows the creation of wall damages after low dose irradiation. A dose of 10^{12} ions/cm² results into disorders and wall defects, as shown in Fig. 6-16(c). Regions indicated by α and ε shows voids on the outer wall, regions- β and γ indicates disordered wall structure and region- δ surface damages. Even a dose of 10^{12} N⁺ ions/cm² initiates formation of curved outer wall structure, as shown in Fig. 6-16(d). In some portion of the sample, low dose irradiation shows formation of amorphous carbon as shown in Fig. 6-16(e). HRTEM image of a portion of the MWCNT-A irradiated at intermediate dose is shown in Fig. 6-16(f). In many portions of the sample irradiated at intermediate dose heavily damaged wall structure was observed as shown in 6-16(g). With 10^{13} N⁺ ions/cm² dose prominent curved outer wall structure is formed as evident from Fig. 6-16 (h). Curved graphitic structure formation initiates with the formation of line defects as shown in 6-16(i). Fig. 6-16(j) shows the MWCNTs irradiated at high dose. It shows that Fullerenes like structures were formed upon irradiation. Fig. 6-16(k) shows that a portion of the tube turned into amorphous carbon. At high dose, surface damages (vacancies) and curved graphitic structure formation is enhanced as shown in Fig. 6-16(l).

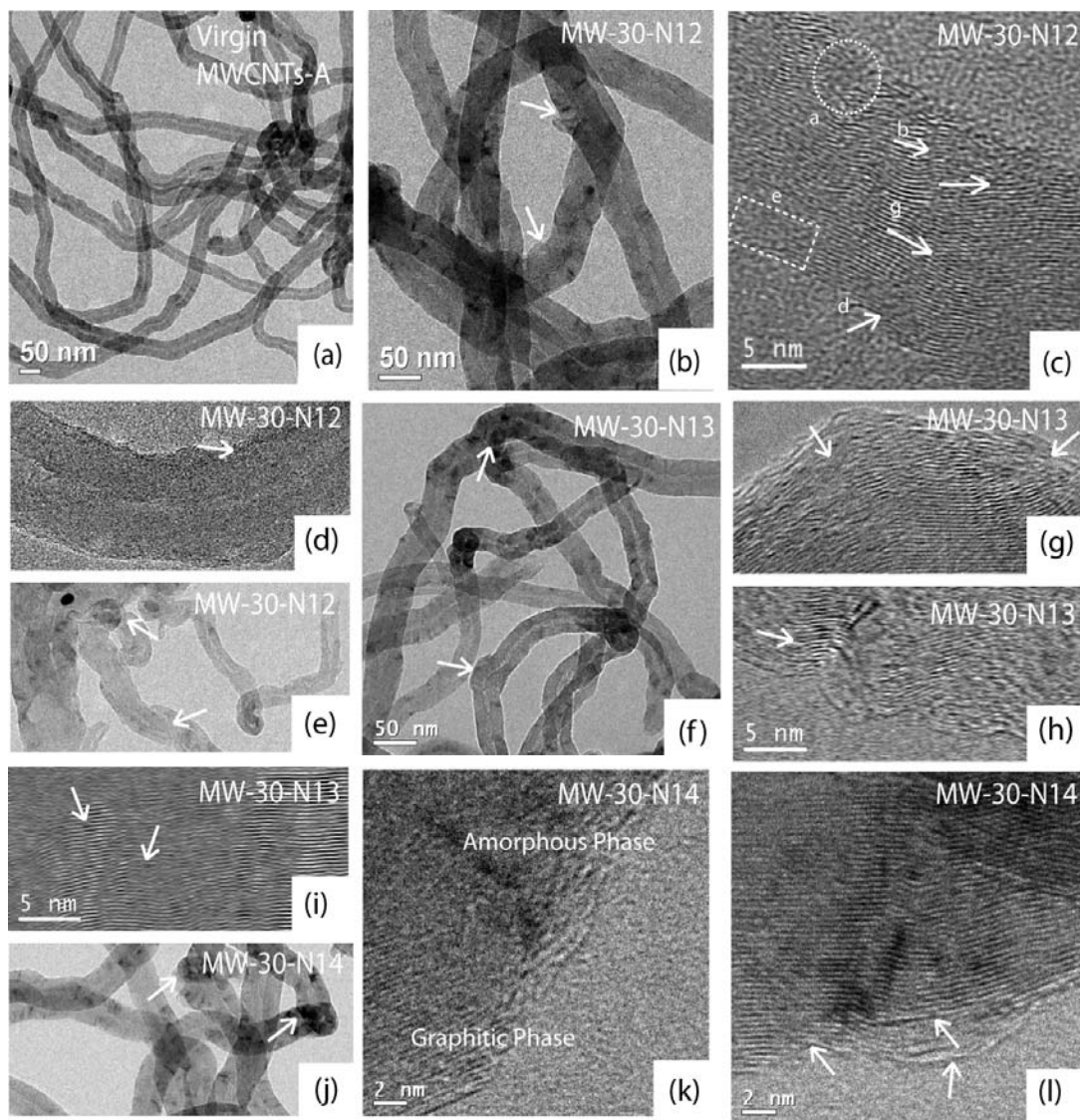


Figure 6-16: TEM images (a) Virgin MWCNT-A (b) MWCNT-A after 10^{12} N^+ ions/cm² (c) Low dose irradiation results into voids on the outer wall (region- α and ϵ), disordered wall structure (regions- β and γ) and surface damages (region- δ). (d) Damage on the one side of MWCNTs and initiation of formation of curved outer wall structure. (e) Damages leading to the formation of amorphous portions and cutting of the walls. (f) MWCNT-A after 10^{13} N^+ ions/cm² irradiation dose. (g) Heavily damaged outer walls after 10^{13} N^+ ions/cm² dose. (h) Formation of curved outer wall structure (hillock like surface) becomes prominent after 10^{13} N^+ ions/cm² dose. (i) Curved graphitic structure formation initiates after formation of line defects. (j) MWCNT-A after 10^{14} dose. Fullerene like structures are formed upon irradiation. (k) A portion of the tube turned amorphous. (l) Vacancies and curved graphitic structure after 10^{14} dose.

6.5.2 XRD Studies

XRD pattern of SWCNT-A before and after irradiation is shown in Fig 6-17(a) for 2θ range 5-30 degree and Fig. 6-17(b) for 35-55 degree for three irradiation doses. XRD spectra is shown in two parts because of weaker intensity of (100) and (101) peak compared to the most prominent (002) peak. In case of SWCNTs, due to very weak scattering intensity (100) and (101) peaks were not clearly distinguishable. These XRD spectra were analyzed by fitting Voigt spectral profile. All the deconvolution parameters are listed in Table 6-11. We assign the peak observed at $2\theta = 13.24^\circ$ to C_{60} and higher fullerenes containing non-hexagonal carbon rings. TEM observations show considerable amount of fullerene and cage like carbon structures in irradiated nanotube sample. At high dose, various kinds of new carbon structures evolve. A continuous increase in the amplitude of this peak is seen with increasing irradiation dose.

Fig: 6-17(c) shows that the peak centre of (002) peak increases from 25.75° to 25.84° and 25.88° at low and intermediate irradiation doses, respectively. However, at high dose it decreases to 25.63° . Increase in 2θ value for (002) graphite plane indicates reduction in the interplanar lattice spacing with increasing irradiation dose. Fig. 6-17(d) show modification of FWHM and intensity of (002) with variation in N^+ ion fluence. FWHM is reduced upon low dose irradiation from 3.63° to 3.01° , with intermediate dose it gets broadened to 3.745° and at high dose FWHM is reduced to 2.63° . On the other hand, intensity of the (002) peak shows monotonic decrease with increasing ion-irradiation dose from 131 counts before irradiation to 75 and 73 counts upon low and intermediate dose and further to 37 counts upon high dose irradiation. X-ray diffractometry shows that irradiation at low and intermediate doses relax the lattice, while high dose results in

increased lattice strain in the CNTs. The cumulative intensity of (100) and (101) peak decreases

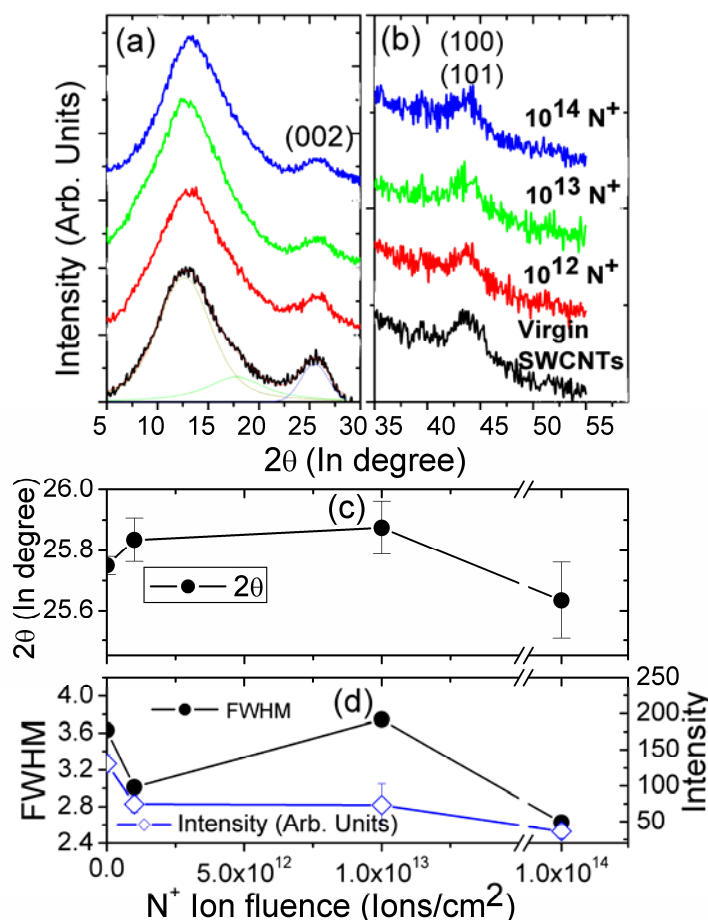


Figure 6-17: XRD spectra of SWCNT-A before and after irradiation with 30 keV N^+ ions (a) Modification of the (002) peak. (b) Changes in the (100) and (101) peaks are shown separately due to their weaker intensity. (c) Variation of the 2θ with changing irradiation dose. (d) Change in the FWHM and intensity after irradiation.

first decreases and again it increases at intermediate dose. This shows that a dose of $10^{13} \text{ Ions}/\text{cm}^2$ leads to structural improvement. In contrast to the intensity changes, the FWHM increases upon intermediate irradiation dose suggesting increases in disorderness. Such a contradictory result may arise due to very low intensity of XRD features of SWCNTs. For

a better understanding Raman spectroscopy and XPS studies were performed for SWCNTs, presented later.

Table 6-10: Fitted parameters of XRD pattern of MWCNT-A irradiated with 30 keV N⁺ ions.

Sample	Profile	Peak1	Peak 2	Peak3	Peak4
SWCNT-A	Centre	12.62	23.20	25.75	43.82
	FWHM	8.72	23.79	3.63	4.48
	Ampli	496	143	131	56
SW-30-N12	Centre	13.07	25.84	27.59	43.68
	FWHM	10.02	3.01	20.46	4.37
	Ampli	514	75	105	38
SW-30-N13	Centre	12.86	25.86	31.02	43.39
	FWHM	9.53	3.75	11.73	5.16
	Ampli	565	73	44	46
SW-30-N14	Centre	13.39	25.63	28.36	43.31
	FWHM	9.17	2.63	15.65	6.90
	Ampli	529	37	103	43
Assignments		Amorphous carbon	(002)	(002)	(101) & (100)

XRD spectra along with its diffraction profiles for MWCNTs before and after irradiation are shown in Fig: 6-18. Fig. 6-18(a) shows a broad peak along with the well known graphitic (002) peak and Fig. 6-18(b) shows the (100) and (101) peaks. Similar to the SWCNTs, these spectra were fitted with Voigt line profile as shown in Fig. 6-18(a) for Virgin MWCNTs. Fitted parameters are summarized in Table 6-11. It is visibly evident from Fig. 6-18(a), which show that upon low dose irradiation the intensity of the (002) peak falls, whereas it is highly enhanced upon intermediate dose indicating relative structural improvement in the graphitic ordering with intermediate dose due to dynamic

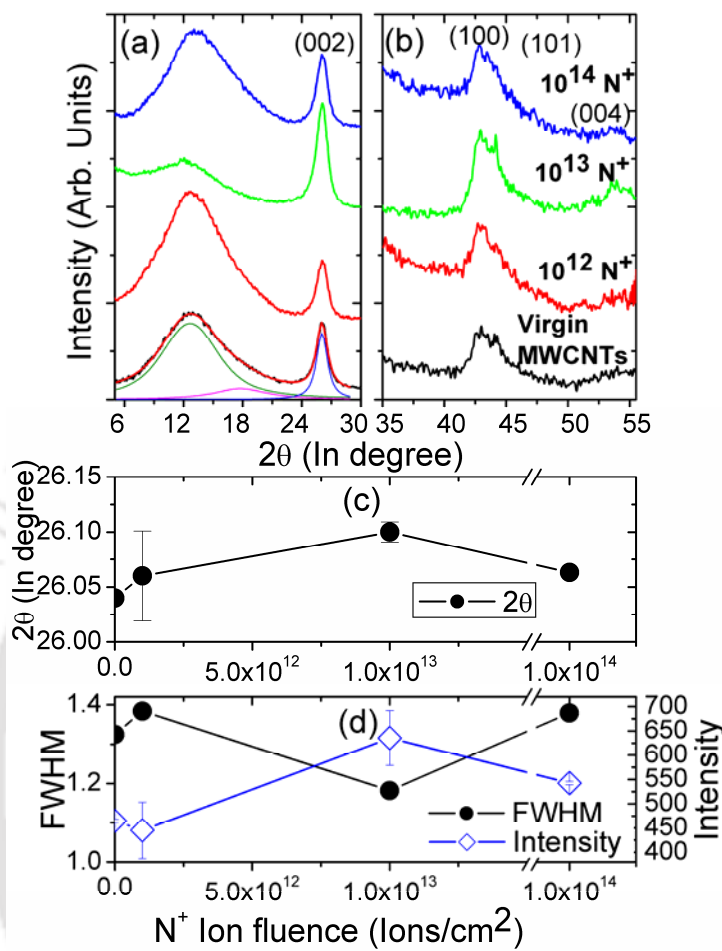


Figure 6-18: XRD spectra of MWCNT-A irradiated with 30 keV N^+ ions. (a) Changes in the (002) peak and (b) (100) and (101) peak. (c) Variation in the peak centre of (002) peak with increasing irradiation dose. (d) Variation in the FWHM and intensity of the MWCNT-A with irradiation dose.

annealing effect. Fig. 6-18(c) shows that 2θ value is higher for intermediate dose of irradiation indicating reduction of interlayer spacing corresponding to a more stable structure. Similarly, intensity of XRD peak increases and FWHM decreases for intermediate dose as shown in Fig. 6-18(d). Minimum FWHM and maximum intensity observed in case of MWCNTs irradiated with intermediate dose indicates structural improvement upon 10^{13} dose irradiation.

Table 6-11: Fitted parameters of XRD pattern of MWCNT-A irradiated with 30 keV Nitrogen (N^+) ions.

Sample	Profile	Peak1	Peak 2	Peak3	Peak4	Peak4	Peak4	Peak4
MWCNT-A	Centre	12.71	17.98	25.81	26.04	42.90	44.23	44.70
	FWHM	7.46	4.04	17.67	1.33	1.47	0.71	3.25
	Ampli	603	42	52	465	38	21	18
MW-30-N12	Centre	12.9	18.47	26.06	30.63	42.83		44.18
	FWHM	8.14	4.07	1.38	6.17	1.26		2.67
	Ampli	1004	47	445	64	40		37
MW-30-N13	Centre	12.32		25.46	26.10	42.90	44.12	44.59
	FWHM	8.11		2.19	1.18	1.32	0.73	4.43
	Ampli	295		158	636	63	48	20
MW-30-N14	Centre	12.84		16.36	26.06	30.73	42.73	43.55
	FWHM	7.33		8.80	1.38	8.95	0.66	3.52
	Ampli	686		248	543	93	24	63
Assignments		Amorp. carbon	Defect	(002)	(002)	(100)	(101)	(101)

6.5.3 Raman Scattering Studies

Modification in the low frequency Raman spectra of SWCNTs are shown in Fig. 6-19 (a).

With the change of irradiation dose, a systematic and prominent change is observed in Raman spectra of SWCNTs. The line profile of RBM modes before and after 30 keV N^+ ion irradiation is summarized in Table 6-12. Low frequency RBM modes slowly disappears with increasing irradiation dose. It is due to structural modification in the tubular structure of SWCNTs or conversion into MWCNT bundles. However, conversion to MWCNTs was not detected in HRTEM studies. Fig. 6-19(b) shows that new feature evolves in the intermediate frequency ranges (observed in the range $400-1200\text{ cm}^{-1}$) as a result of ion irradiation. The exact peak position and FWHM of these features obtained on deconvolution using Lorentzian lineshape is summarized in Table 6-13. Raman active

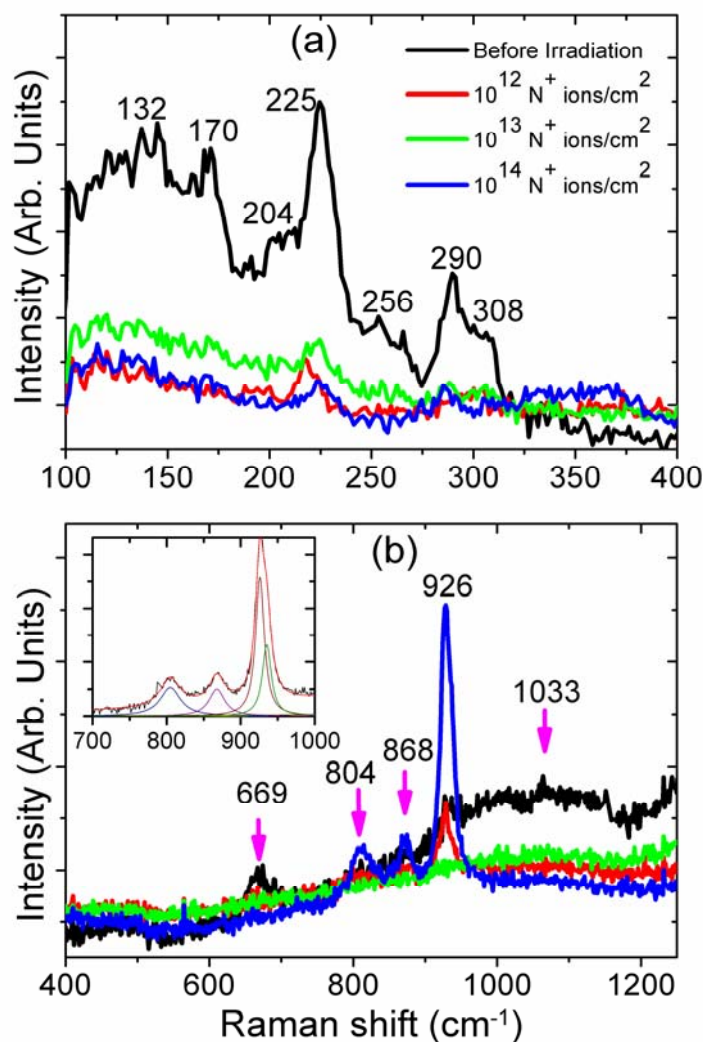


Figure 6-19: Raman spectra of SWCNT-A irradiated with 30 keV N^+ ions of various fluences (a) RBM Modes and (b) Modification of IFM Modes of SWCNTs upon 30 keV N^+ ion irradiation. Peak at 669 cm^{-1} disappears due to ion irradiation induced defects, while 804 , 868 and 926 cm^{-1} peak appeared upon irradiation.

peak at 668.9 cm^{-1} observed in case of pristine SWCNTs disappears and new features at 928.2 and 1189 cm^{-1} appear upon low dose irradiation. Apart from these, two small peaks at ~ 805 and 868 cm^{-1} can be clearly observed after enlarging the graph. After irradiation at intermediate dose, these defect related IFM modes disappear indicating reduction in the

Table 6-12: Deconvolution of Raman shifts of low frequency RBM modes of SWCNTs before and after 30 keV N⁺ ion-irradiation.

Sample	Peak1	Peak 2	Peak3	Peak4	Peak5	Peak6
SWCNT-A Virgin	143.4	170.9	204.7	225.3	256.8	289.6
SW-30-N12	194.6	218.5				
SW-30-N13		222.8	288.4	305.1		471.8
SW-30-N14	160.8	224.82	285.5	338.6	368.2	470.3

defect density. These features are significantly enhanced upon high irradiation dose. Lorentzian fits to these IFM modes shows their positions at 804.9, 867.8, 926 and 935.3 cm⁻¹. Among these, 926 cm⁻¹ mode is the most intense and sharpest having a FWHM of 14.2 cm⁻¹. Along with these, a clear hump is observed at 935.3 cm⁻¹ having almost equal FWHM 14.6 cm⁻¹. Other two features observed at 804.9 and 867.8 cm⁻¹ have FWHM of 33.1 and 25.5 cm⁻¹, respectively. The gradual change in the intensity of IFM modes can be correlated with the structural modification of nanotubes upon ion irradiation. The origin of these features is not understood clearly in the literature, as discussed in chapter-4. Correlation of these features with extent of modification and amount of structural defects observed from various techniques like HRTEM, Raman spectroscopy and XPS studies are presented later clearly.

Table 6-13: Deconvoluted parameters of intermediate frequency modes (IFM) of the Raman spectra of SWCNTs before and after 30 keV N⁺ ion-irradiation at different doses.

Sample	Profile	Peak1	Peak 2	Peak3	Peak4	Peak5
SWCNT-A Virgin	Centre	668.9				1029.0
SW-30-N12	Centre	928.2				1189
SW-30-N13	Centre					1138
SW-30-N14	Centre	804.9	867.8	926	935.3	1171
<i>Assignments</i>		<i>IFM</i>	<i>IFM</i>	<i>IFM</i>	<i>IFM</i>	<i>C=O</i>

establishes that these modes originate from structural defects. Our experiment clearly demonstrates that 926, 804 and 868 cm^{-1} Raman modes are primarily due to the local structural defects introduced upon ion irradiation, While the 668.9 cm^{-1} mode is characteristic of the nanotubes and its intensity scales with the structural perfectness. New peaks are observed due to defect induced breakdown of momentum conservation and activation of phonons at interior k points of the Brillouin zone. Increase in the intensity of intermediate frequency modes; in the Raman spectra originates from modification of phonon density of states due to creation of defects upon irradiation [145].

Fig. 6-20(a) shows the D and G modes of SWCNTs before and after 30 keV N^+ ion irradiation. These spectra were deconvoluted into its constituent components using combination of Lorentzian and Fano lines, typically as shown for SWCNTs before irradiation in Fig. 6-20(b). In Fig. 6-20(b) most intense peak is clipped off to show the small features and is shown separately in the inset. Except the line indicated as Fano, all other components are Lorentzian in shape. G-band is deconvoluted into usual 3 components, one asymmetric Breit-Wigner-Fano (BWF) lines ($\sim 1550 \text{ cm}^{-1}$) and two symmetric Lorentzian line shapes ($G^-(s)$ and G^+) features. The deconvoluted parameters are summarized in Table 6-14. Fig. 6-20(c) shows the change in Raman shift frequency and the FWHM for defect induced D-band for different doses of irradiation. D-band frequency upshifts from 1337 cm^{-1} to 1348 cm^{-1} after low dose irradiation. A slight downshift (1344 cm^{-1}) of D-band frequency is observed for intermediate dose and again increases to 1346 cm^{-1} with high dose. The FWHM of this peak increases from 30.9 cm^{-1} before irradiation to 34.1 cm^{-1} after low dose and at intermediate and high dose, it decreases to 33.4 cm^{-1} and 32.8 cm^{-1} , respectively. Fig. 6-20 (d) shows the change in of Raman frequency and FWHM of $G^-(M)$ band, where M stands for metallic nanotubes. G^-

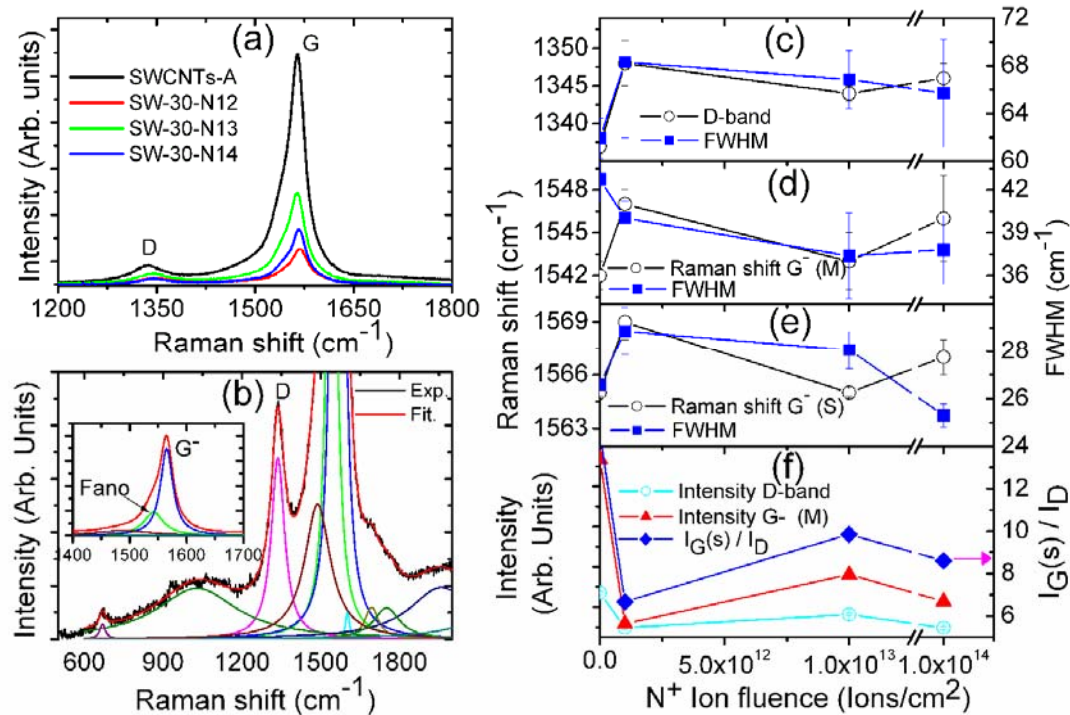


Figure 6-20: (a) First order Raman spectra SWCNTs before and after 30 keV N^+ ion-irradiation. (b) Typical deconvoluted spectra of SWCNT-A before irradiation. Variation of Raman shift and FWHM of (c) D-band of SWCNT-A (d) $G^-(M)$ metallic component and (e) $G^-(S)$, Semiconducting component before and after 30 keV N^+ ion-irradiation. (f) On the left axis shows the variation of the intensity of D band and $G^-(M)$ band, scaling with defects and metallic content in the sample. On the right axis it shows variation of intensity ratio of $I_{G(s)}/I_D$, a parameter of structural orderness in sp^2 carbon systems.

(M) band frequency up shifts from 1542 cm^{-1} before irradiation to 1547 cm^{-1} upon low dose irradiation. With intermediate dose, it shifts to lower frequency 1543 cm^{-1} and again increases to 1546 cm^{-1} . Peak width decreases from 21.3 cm^{-1} before irradiation to 20 cm^{-1} and 18.7 cm^{-1} upon low and intermediate dose, respectively. After further increase of irradiation dose of high fluence it remains same. Fig. 6-20 (e) shows the variation in the Raman shift of $G^-(S)$ band with increasing irradiation dose, Where S stands for semiconducting component. Raman shift decreases from 1565 cm^{-1} before irradiation to

1569 cm^{-1} and 1565 cm^{-1} after low and intermediate dose irradiation. With high dose irradiation, it up shifts to 1567 cm^{-1} . The G^+ band frequency is observed at 1602 cm^{-1} in the pristine sample. It down shifts to 1595 cm^{-1} at low dose and 1596 cm^{-1} upon intermediate dose, and again back to 1595 cm^{-1} at high irradiation dose. This peak gets broadened after irradiation from 17.4 cm^{-1} before irradiation to 65.8 cm^{-1} after low dose irradiation. At intermediate dose it sharply decreases to 28.2 cm^{-1} and with irradiation dose it gets slightly broadened to 36.9 cm^{-1} . Fig. 6-20 (f) shows the variation of intensity of D-band, $G^+(M)$ and ratio of $I_{G(S)}/I_{(D)}$ band ratio with changes in the radiation dose. The I_G/I_D ratio decreases sharply from 14.6 to 6.68 upon low dose. This ratio improves to 9.85 at intermediate dose and 10.32 upon high dose. An increase of intensity ratio I_G/I_D is expected with decrease of disorder in the hexagonal structure as suggested by Ferrari and Robertson [149]. Contrary the graphite where I_G/I_D ratio is taken as a measure of crystalline order, in CNTs it suffers from some drawbacks. In case of CNTs, $I_{G'}/I_D$ is taken as a better measure of crystalline order or defect estimation. A weak peak observed at 1488 cm^{-1} in pristine SWCNT, shows change in its spectral profiles (peak centre, peak width and amplitude) with change in irradiation dose. This peak appears due to distortion of the graphene network upon ion-irradiation [316].

Apart from these regular features, new bands has been observed at $\sim 1750 \text{ cm}^{-1}$ and 2186 cm^{-1} (not mentioned in table) between G-band and G' -band. The peak shows downshift from 1751 cm^{-1} to 1735 cm^{-1} and 1717 cm^{-1} upon low and intermediate dose respectively. It slightly up shifts to 1720 cm^{-1} upon high irradiation dose. Besides these, several other small features were observed in pristine SWCNTs at 1694 cm^{-1} , 1959 cm^{-1} , and 2186 cm^{-1} . After irradiation, these were too broadened to be distinguished properly for all the three doses of irradiation.

Table 6-14: Deconvoluted spectral line profiles of D and G modes of SWCNT-A before and after 30 keV N⁺ ion-irradiation.

Sample name	Spectral profile	Peak1	Peak2	Peak3	Peak4	Peak5	Peak12	Peak13	I _G /I _D
SWCNT-A	Centre	1337	1488	1542	1565	1602	1694	1751	14.6
	FWHM	61.9	119.3	42.7	26.6	17.4	64.1	121.6	
	Amplitude	1356	1009	4681	17390	205	240	235	
	Fano (1/q)			-0.03					
SW-30-N12	Centre	1348	1485	1547	1569	1595		1735	6.68
	FWHM	68.3	169.0	40.0	28.9	65.8		199.9	
	Amplitude	488	252	586	2642	240		177	
	Fano (1/q)			-0.05					
SW-30-N13	Centre	1344	1501	1543	1565	1596		1717	9.85
	FWHM	66.9	164.3	37.4	28.1	28.2		192.2	
	Amplitude	820	500	1810	6872	212		213	
	Fano (1/q)			-0.02					
SW-30-N14	Centre	1346	1495	1546	1567	1595		1720	10.32
	FWHM	65.7	179.4	37.8	25.3	36.96		193.74	
	Amplitude	483	305	1142	4152	201		178	
	Fano (1/q)			-0.02					
Assignments		D-band	LO ?	Fano	G ⁻ band	G ⁺ band	Defects?	Defects?	Ratio

Fig. 6-21(a) shows two phonon second-order Raman G' mode of SWCNTs before and after 30 keV N⁺ ion-irradiation. Inset of the Fig 6-21(a) shows the Lorentzian fitting for the pristine SWCNTs. Similar to the first order modes, these modes were deconvoluted using Lorentzian lineshapes and parameters are summarized in Table 6-15. Fig. 6-21 (b) shows the variation of the peak position and FWHM of 30 keV N⁺ ion irradiated SWCNTs, whereas change in the intensity of G' mode is shown in Fig. 6-21(c). G' mode down shifts from 2698.0 cm⁻¹ before irradiation to 2674.3 cm⁻¹ upon low dose and further decreases to 2667.5 cm⁻¹ and 2668.7 cm⁻¹ with intermediate and high dose, respectively. The FWHM of this peak slightly increases from 100.8 cm⁻¹ to 102.6 cm⁻¹ upon low dose

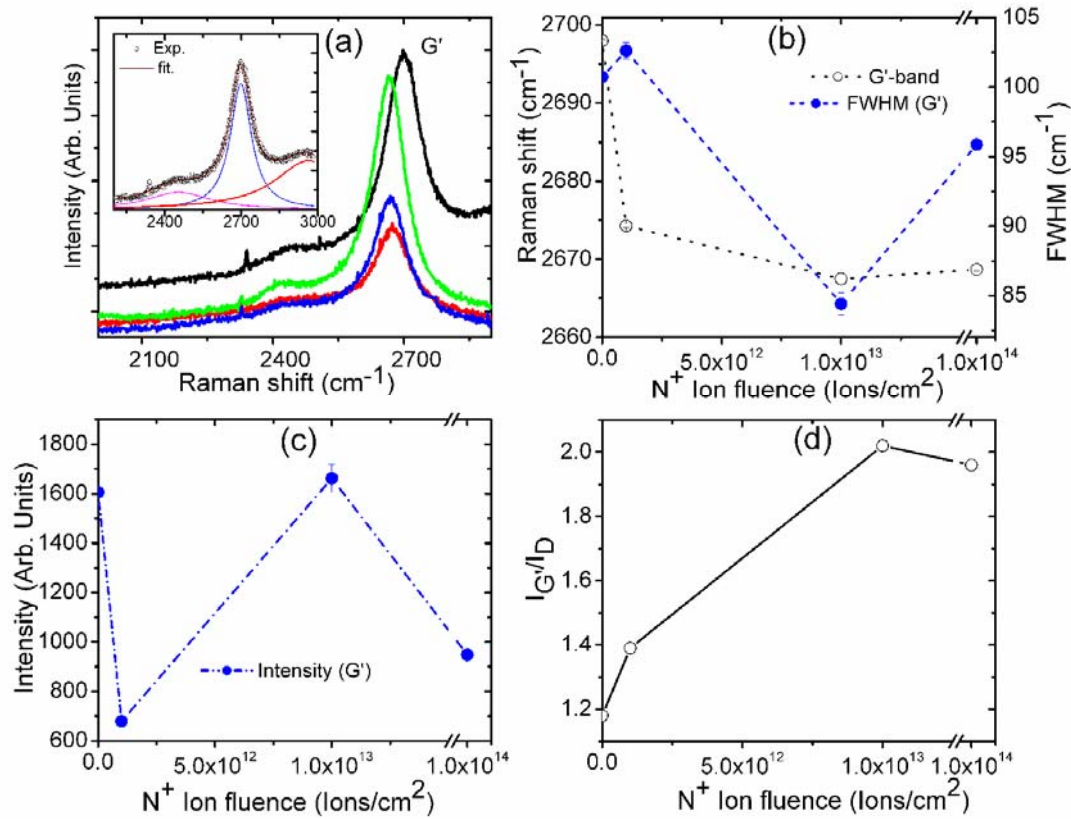


Figure 6-21: (a) Second order modes of SWCNT-A irradiated with 30 keV N^+ ions at different doses. (b) Variation in the Raman frequency and FWHM of G' mode with irradiation dose. (c) Change in the intensity of G' mode with irradiation dose. (d) Change in the I_G/I_D intensity ratio with irradiation dose.

irradiation. With intermediate dose the peaks width decreases to 84.42 cm^{-1} , whereas upon high irradiation dose it get broadened to 95.9 cm^{-1} . Peak intensity of this peak decreases sharply from 1606 counts to 680 counts upon low dose, whereas upon intermediate dose this again increases to 1663 counts, indicating a structural improvement upon 10^{13} ions/ cm^2 . Further, with increase in irradiation fluence to high dose, intensity sharply again falls to 948.2 counts, showing that this introduces a number of structural defects in the nanotubes. On the other hand, the I_G/I_D improves with low and intermediate irradiation dose as shown in Fig. 6-21(d). At high irradiation dose the ratio slightly drops. This

implies that a dose of 10^{13} ions/cm² is optimum for repairing of naturally occurring defect using ion irradiation. Similar effect has been observed with swift heavy ion irradiation (gold irradiation at 120 MeV), an intermediate dose leads to structural improvement of CNTs [317].

Table 6-15: Lorentzian deconvolution of Raman overtone modes of SWCNTs before and after irradiation.

Sample	Raman shift (cm ⁻¹)					
	Peak1	Peak 2	Peak3	Peak4	Peak5	I _G /I _D
SWCNT-A	----	----	2453.9	2698.0	2963.8	1.18
SW-30-N12	----	2150.9	2474.5	2674.3	2832.6	1.39
SW-30-N13	----	2618.7	2424.6	2667.5	----	2.02
SW-30-N14	2009.5	2221.1	2466.3	2668.7	2836.5	1.96
Assignments	Defects?	Defects?	G'	G'	2LO	Ratio

A very broad feature is observed at 2453.9 cm⁻¹ before irradiation in case of SWCNTs. The intensity of this peak shows the complimentary behavior with the G' band. Its intensity decreases upon 10^{12} and 10^{13} N⁺ ion irradiation dose, while increases upon 10^{14} dose. It is most likely to originate from structural defects in nanotubes, although a few literature claim its origin as $q = 0$ phonon G' band [183].

Centre of this peak shows large up shift from 2453.9 cm⁻¹ to 2474.5 cm⁻¹ upon 10^{12} ions/cm² and the FWHM increases from 298.6 to 384.2 cm⁻¹ upon 10^{12} ions/cm². With increasing dose of irradiation to 10^{13} ions/cm² this peak downshifts to 2424.6 cm⁻¹ and also the FWHM decreases to 142.6 cm⁻¹. Further increases of fluence to high dose, this peak upshift to 2466.3 cm⁻¹, and the FWHM increase to 401.8 cm⁻¹.

First order Raman spectra and deconvoluted spectral line parameters of MWCNT before and after 30 keV N⁺ irradiation are shown in Fig. 6-22. We do not observe any low

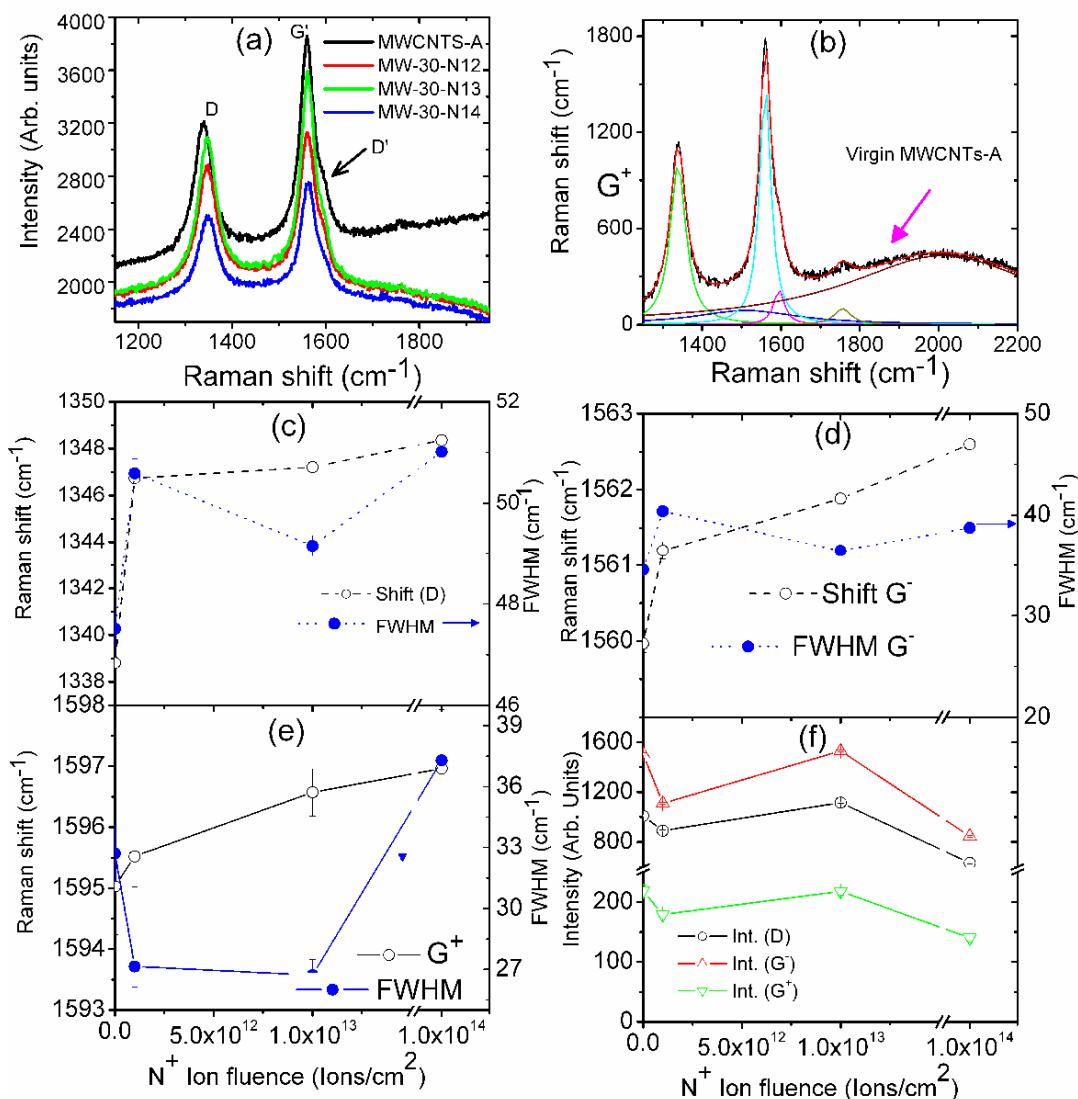


Figure 6-22: (a) Modification of the D and G modes of MWCNT-A after 30 KeV N^+ ion irradiation. (b) Deconvoluted spectra of pristine MWCNTs showing D band, G band and G' band. Change in Raman frequency and FWHM of D-band, G(M) and G+(M) is shown in (c), (d) and (e) respectively. (f) variation of intensity of these peak with irradiation dose.

frequency RBMs in our samples, indicating presence of a wide variety of inner diameters of MWCNTs in the sample. Unlike SWCNTs in MWCNTs, no significant modification of IFMs was observed upon irradiation. Fig. 6-22(a) shows the characteristic D and G modes of MWCNTs before and after irradiation. Arrow shows presence of D' band features

expected from structural defects. These spectra were deconvoluted using Lorentzian line shape, shown for pristine MWCNTs in Fig: 6-22(b) and summarized in Table 6-16. Fig: 6-22(c) shows the changes in the Raman shift and FWHM of D-band. With increasing dose, peak position monotonically upshifts from 1338.8 cm^{-1} (pristine). On the other hand width of D-band increase marginally after irradiation at different doses. The Raman shift of both G^- -band and G^+ -band upshifts with increasing irradiation dose. G^- -band gradually shifts from 1559.9 cm^{-1} before irradiation to 1562.5 cm^{-1} after N^+ irradiation dose respectively. Similarly, the G^+ -band upshifts from 1595 cm^{-1} to 1596.9 cm^{-1} after irradiation. The FWHM of this peak first decreases from 32.7 cm^{-1} before irradiation to 27.1 cm^{-1} and 26.7 cm^{-1} after irradiation dose, but after high dose it get broadened to 37.3 cm^{-1} .

Similar to the SWCNTs, a broad peak is observed between G^+ -band and the second order G' -band. At low dose, no appreciable change in peak position is observed. However, at high dose of irradiation, the peak shows large down shift (by 31 cm^{-1}). Intensity of this peak increases substantially with irradiation dose. Fig. 6-22(h) shows the variation of peak intensity of D-band, G^- -band and G^+ -band. The peak intensity D-band, G^- -band and G^+ -band drops after low dose, but at intermediate dose the intensity rises, while at high dose once again the intensity drops drastically.

The second order G' mode as a function of irradiation dose is shown in Fig. 6-23. The inset of the figure shows the deconvoluted second order modes for pristine MWCNTs. G' mode show large downshift after irradiation that marginally changes with irradiation dose. Similarly, the FWHM of this peak increases considerably, while the intensity drops to some extent upon irradiation. In case of pristine MWCNTs, Similar to the SWCNTs a small but distinct feature is observed at 2424.3 cm^{-1} on the lower frequency side of G' -band. The peak position of this peak upshifts by 68.2 cm^{-1} at low dose, and with further

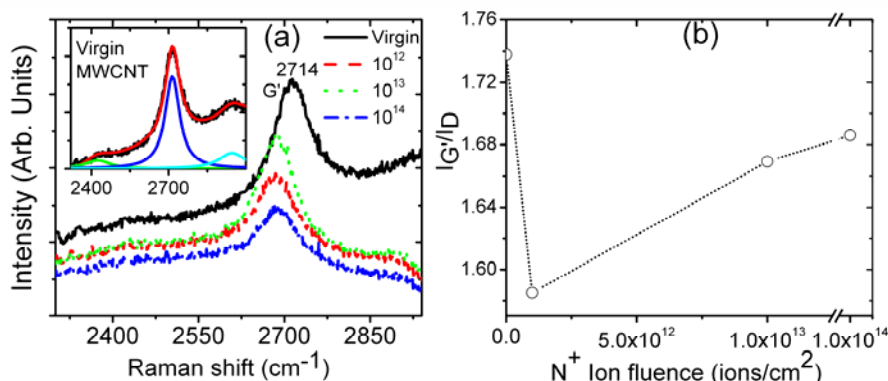


Figure 6-23: (a) Second order modes of MWCNTs under different doses of 30 keV N^+ ion irradiation. (b) Variation of I_G/I_D ratio with increasing N^+ ion fluence range.

Table 6-16: Lorentzian deconvolution first and second order Raman modes of MWCNTs before and after 30 keV Nitrogen (N^+) irradiation.

Sample		Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	I_G/I_D
MWCNT	Centre	1338.8	1511.4	1559.9	1595.0	1755.9	2424.3	2714.6	1.738
	FWHM	47.5	323.5	34.5	32.71	52.35	119.53	68.94	
	Amplitude	1009	88.0	1504	218.6	100	59.67	656	
MW-30-N12	Centre	1346.7	1482.1	1561.1	1595.5	1756	2492.5	2685.1	1.585
	FWHM	50.6	397.6	40.39	27.14	244.06	582.2	87.81	
	Amplitude	890	229.9	1109	179	106	178	419	
MW-30-N13	Centre	1347.2	1486.5	1561.8	1596.5	1746.8	2473.1	2686.1	1.669
	FWHM	49.15	297.5	36.47	26.71	293.6	509.0	81.91	
	Amplitude	1115	216.7	1530	217	129	184.9	639	
MW-30-N14	Centre	1348.3	1471.9	1562.5	1596.9	1724.9	2532.3	2688.8	1.686
	FWHM	51.0	180.6	38.74	37.28	328.8	792.4	83.1	
	Amplitude	630	135.6	845	139	153	248	307	
Assignments		D-band	LO	G ⁻	G ⁺	Defects	G'	G'	Ratio

increase of irradiation dose it downshifts. This peak is broadened significantly upon low dose irradiation, marginally narrows down upon intermediate dose and once again gets broadened upon high dose N^+ irradiation. Fig. 6-23(b) shows the variation of intensity ratio of G'-band to the D-band (I_G/I_D). The I_G/I_D ratio decreases from 1.738 for pristine MWCNT-A to 1.585 upon low dose irradiation. With increase of fluence to intermediate and high dose this ratio improves to 1.669 and 1.686 respectively. This shows structural

improvement upon intermediate dose and high dose N^+ ion irradiation. This can be used for defect annihilation in MWCNTs.

6.5.4 UV-VIS-NIR Studies

UV-VIS-NIR absorption spectra of SWCNTs irradiated with 30 keV N^+ ions is shown in Fig. 6-24. Virgin SWCNTs (Fig. 6-24(a)) shows a number of absorption peaks

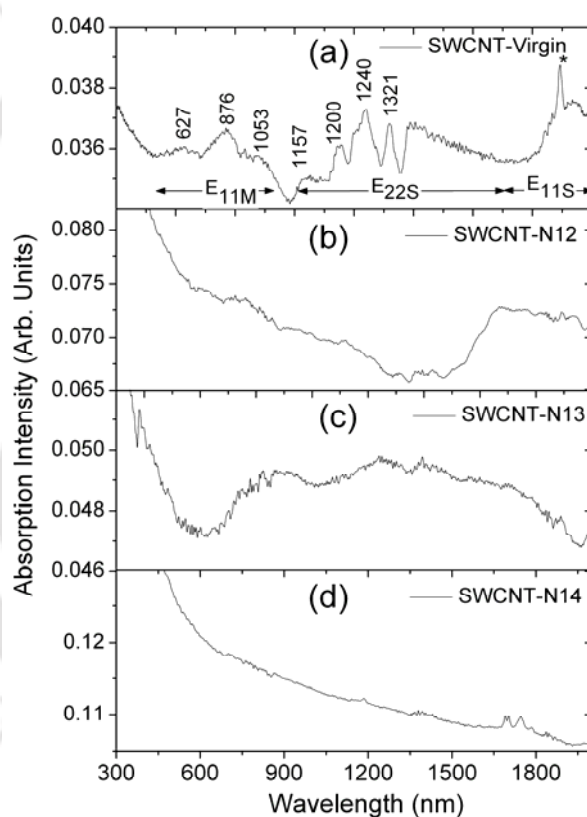


Figure 6-24: (a) Absorption spectra of SWCNTs before irradiation showing transition from E_{11S} , E_{22S} and E_{11M} energy levels. (b) Disappearance of sharp absorption peak, indicates destructive effect of 10^{12} dose of 30 keV N^+ ions. (c) A dose of 10^{13} ions shows broad features along with few sharp transition peaks, showing defect annihilation upon 10^{13} ions dose. Broad absorption feature are observed upon 10^{13} dose due to band gap modification in presence of defects. At 10^{14} ions/cm², no peaks were observed, indicating heavy damage of SWCNTs.

due to Van-Hove singularities in SWCNTs. The absorption spectrum is subdivided into three regions namely E_{11S} , E_{22S} and E_{11M} energy levels, S and M representing semiconductor / metallic components. In irradiated SWCNTs, a drastic reduction in the intensity of absorption peak is observed indicating destructive effect of low dose N^+ ions. At intermediate dose broad features along with few sharp transition peaks are observed. Band structure modification in various ways due to irradiation induced defects leads to broad absorption feature as shown in Fig. 6-24(a) and 6-24(b). At high dose no absorption peaks were observed, indicating heavy damage with 10^{14} ions/cm².

6.5.5 FT-IR Studies

FT-IR studies were performed to investigate the possibility of N^+ doping in the CNTs upon ion-irradiation. FT-IR spectra of SWCNTs and MWCNTs before and after 30 keV N^+ ion irradiation is shown in Fig. 6-25(a) and (b) respectively. In case of pristine SWCNT-A we observed peak at 799 cm⁻¹ (Close to first order A2 band of CNTs), 1030 cm⁻¹ (Second order 2E_g), 1389 cm⁻¹ (C-H deformation), 1568 cm⁻¹ (first order E1 band of CNTs), 1642 cm⁻¹ (C-C stretching) and 2921 (C-H stretching) cm⁻¹ from CNTs. We also observed bands at 2355 cm⁻¹ from CO₂ and 3440 cm⁻¹ moisture related band. Only mainly two IR active bands of CNTs A2 band (799 cm⁻¹) and E1 band (1562 cm⁻¹). These peaks were common to both SWCNTs and MWCNTs, although FT-IR peaks observed in case of MWCNTs are down shifted. These spectra do not show evolution of any new peak upon irradiation, eliminating the possibility of nitrogen doping in the CNT lattice as result of N^+ ion-irradiation.

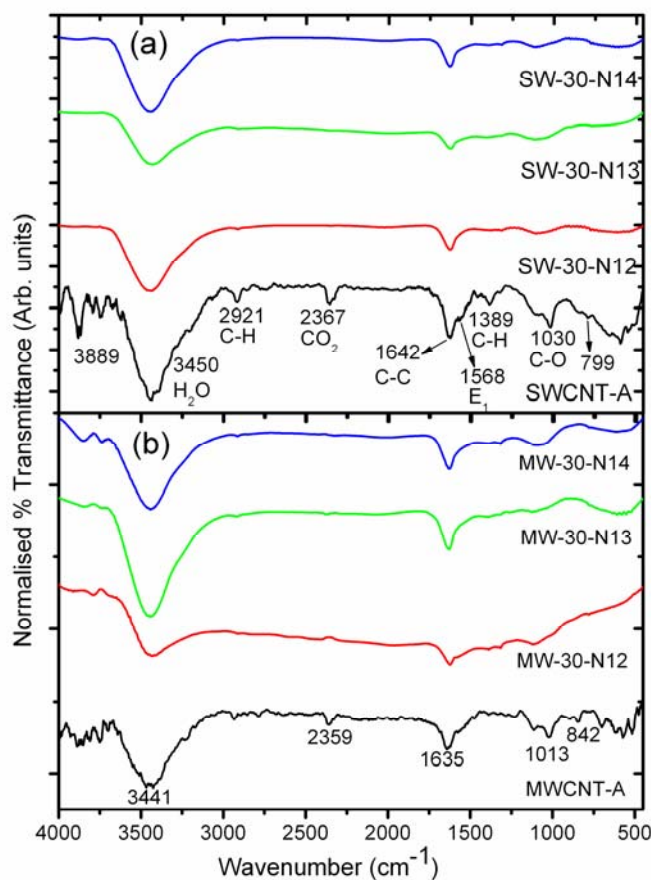


Figure 6-25: FTIR spectra before and after irradiation with 30 KeV N^+ ions (a) Single walled carbon nanotube (b) Multiwalled carbon nanotubes.

6.5.6 XPS Studies

XPS studies of N^+ irradiated SWCNTs were performed to probe the possibility of formation of C-N bonds in CNTs, as the result of irradiation. Fig. 6.26(a) shows the survey scan XPS spectra of SWCNTs in the range 0-1000 eV energy range. It shows presence of C1s core, O and Si peaks. Si appears from the substrate used for depositing CNTs. In the survey scan spectra shown in Fig 6-26(a) no peak was observed in the nitrogen core region 392-410 eV energy range. It clearly indicates that N is not incorporated in the lattice

during N^+ irradiation [225, 318]. This is in contrast to the experiments at 3 keV N^+ ion irradiation, where N^+ ion was found to bind at the defect sites of SWCNTs [225].

Fig: 6-26(b) shows the C_{1s} core spectra of SWCNTs before irradiation and its deconvoluted peaks. These spectra were deconvoluted using software XPSPEAK4.1. A

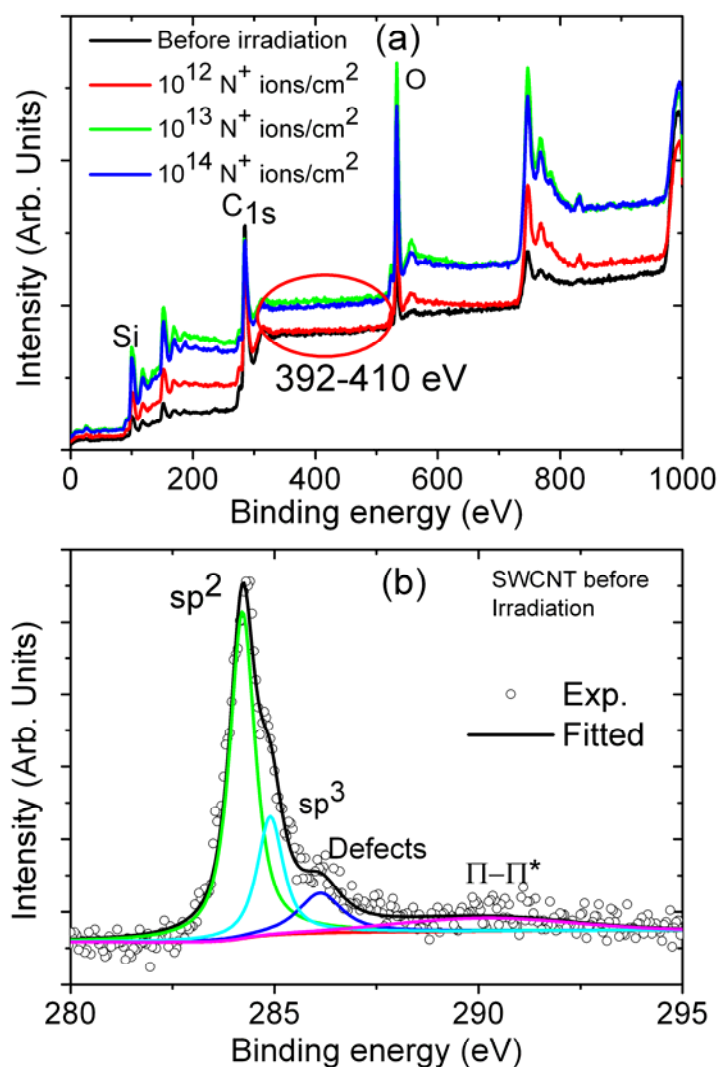


Figure 6-26: (a) XPS survey scan spectra shows absence of N-core (392-410 eV) (b) Typical deconvoluted C_{1s} core XPS spectra of SWCNTs before irradiation. It consists of sp^2 peak, sp^3 peak, defect induced peak and peak from $\pi-\pi^*$ transition.

closer look at the spectra shows the asymmetric lineshape arising from conducting carbon nanotubes. Such a lineshape is known to result from neutralization by conduction electrons of the holes created during photoionization. A Shirley type background was taken for spectral deconvolution. Typical fitting for the pristine SWCNT is shown in Fig 6-26(b). The deconvoluted peaks of SWCNTs irradiated with 30 keV N^+ ions at three fluence levels are summarized in Table 6-17. The deconvoluted spectra of SWCNT before irradiation shows three components of the C1s core peak at 284.21 eV, 284.89 eV and at 286.12 eV originating due to sp^2 carbon, sp^3 carbon and structural defects, respectively. Usually the peak of tetrahedral bonded sp^3 carbon is observed near 285.5 eV [98], However in pristine SWCNTs, it is shifted by 0.61 eV. Carbon in most of its usual compounds (with oxygen, fluorine, nitrogen) appears as less electronegative that is to say that it appears as donor of electrons and gives thus rise to C1s XPS peak shifted towards high binding energy relatively to the graphitic C-C one [319]. The shift observed in our

Table 6-17: Deconvoluted parameters of XPS Spectra of 30 KeV N^+ irradiated SWCNTs.

Sample		Peak1	Peak2	Peak3	Peak4	sp^2 %	sp^3 %
Virgin SWCNT	Centre	284.21	284.89	286.12	290.1	63.4	23.4
	FWHM	0.744	0.760	1.262	5.103		
	Area	4939	1826	1020	983		
10^{12} ions/cm ²	Centre	284.27	284.79	285.37	290.18	42.7	18.3
	FWHM	0.709	0.635	2.066	4.461		
	Area	2417	1036	2206	1026		
10^{13} ions/cm ²	Centre	284.23	284.8	285.7	290.17	53.7	13.9
	FWHM	0.935	0.658	3.33	3.52		
	Area	2894	749	1747	820		
10^{14} ions/cm ²	Centre	284.15	284.62	285.51	289.75	30.7	31.7
	FWHM	0.54	0.68	1.57	6.50		
	Area	1431	1479	1756	1985		
Assignment		sp^2	sp^3	Defects	II-II*		

sample arises due to oxidation i.e presence of C=O groups as evident from survey scan XPS spectra and presence of $\sim 1050\text{ cm}^{-1}$ peak in the Raman spectra. The C_{1s} spectrum has a tail at the higher energy side caused by defect or, disordering in the graphite [320]. This line appears is observed in graphitic systems with disorders and is known as defect peak [320]. Apart from these a broad feature is observed on the higher energy side at $\sim 290\text{ eV}$ arising due to $\Pi-\Pi^*$ plasmonic transition called as plasmon loss peak. The spectral lineshape of the XPS spectra depends on three factors, Lifetime of the core hole (Contributing Lorentzian lineshape), instrumental contribution (Gaussian shape) and the satellite features. The third contribution to the peak width can arise from the several sources such as vibrational broadening, multiplet splitting and shake-up satellites. These features typically have asymmetric lineshapes and depending on their E_B , may or, may not be resolvable from the main photoemission peak. The degree of the asymmetry depends on the density of states near E_F [321].

The lineshapes of the XPS peaks carries information about the chemical bonding environments in the sample. An estimate of the sp^2 hybridization, sp^3 hybridization and defects in each of these samples was found from the ratio of the corresponding peak area to the total C_{1s} peak area, as shown in Table 6-17. It shows drastic changes in the ratio of sp^2 and sp^3 contents with variation in irradiation dose. A dose of 10^{12} ions/cm^2 leads to decrease in the sp^2 content from 63.4 weight (wt) % to 42.7 (wt) %. With further increase of irradiation dose to 10^{13} ions/cm^2 sp^2 content is drastically enhanced (53.7 wt %), while the sp^3 content gets reduced (13.9 wt %). This shows structural improvement with a irradiation dose of 10^{13} ions/cm^2 in agreement with our Raman studies. A dose of 10^{14} ions/cm^2 once again leads to decrease in the sp^2 content 30.7 wt % and increase in the sp^3 content to 31.7 wt %. In consent with these results, the defect peak shows increase in the

area from 1020 before irradiation to 2206 after 10^{12} ions/cm². At 10^{13} ions/cm², it shows decrease in the area to 1747 and further increase in the irradiation dose to 10^{14} ions/cm² leads once again increase in the area of defect peak to 1756. Thus XPS studies, in agreement with Raman studies, show that a dose of 10^{13} ions/cm² 30 keV N⁺ leads to defect reduction and structural improvement of SWCNTs upon irradiation. It further confirms that new IFM features observed after irradiation arise from structural defects created by irradiation, not from C=N formation. Increased sp³ content at high dose is consistent with the increased amount of amorphous carbon observed under HRTEM. Similar effect has been observed with MeV ions, showing increased amount of amorphous carbon upon higher dose of Ag²⁺ ion irradiation [322].

6.5.7 EPR Studies

EPR spectra of SWCNTs and MWCNTs after N⁺ ion irradiation is shown in Fig. 6-27(a) and (b) respectively. We did not observe any significant modification of the ESR lineshape SWCNTs upon N⁺ ion irradiation. While MWCNTs shows modification in the EPR line shape in the range 100-400 mT. Intensity changes are not taken account in this sample because of different amount of samples used during experiment. A slower scan near the free electron g-value ($g_e=2.0013$) did not show any new sharp feature in case of SWCNTs. While in case of MWCNTs a number of sharp paramagnetic features appear upon N⁺ ion-irradiation as shown in Fig. 6-28. Virgin MWCNTs do not show any sharp feature corresponding to the paramagnetically active centre. At 10^{12} N⁺ ions/cm² shows paramagnetic active centres at $g = 1.913$ and 2.074 . A dose of 10^{13} N⁺ ions/cm² leads to the modification of paramagnetic active centres to $g = 1.9882$ and 2.074 . At 10^{14} ions/cm², these values shifts to $g = 1.986$ and 2.068 . Also a relatively strong new peak is observed at

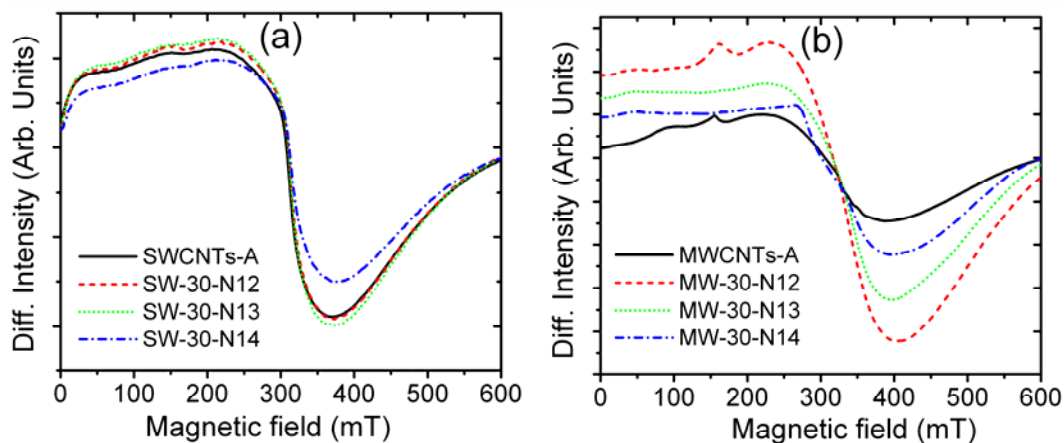


Figure 6-27: EPR spectra of (a) SWCNTs and (b) MWCNTs irradiated with various doses of 30 keV N^+ ions. It do not show any new peak expected to arise from the paramagnetic defects. A close look to the spectra of MWCNTs shows modification of the EPR absorption line in the 100-400 mT range upon ion-irradiation.

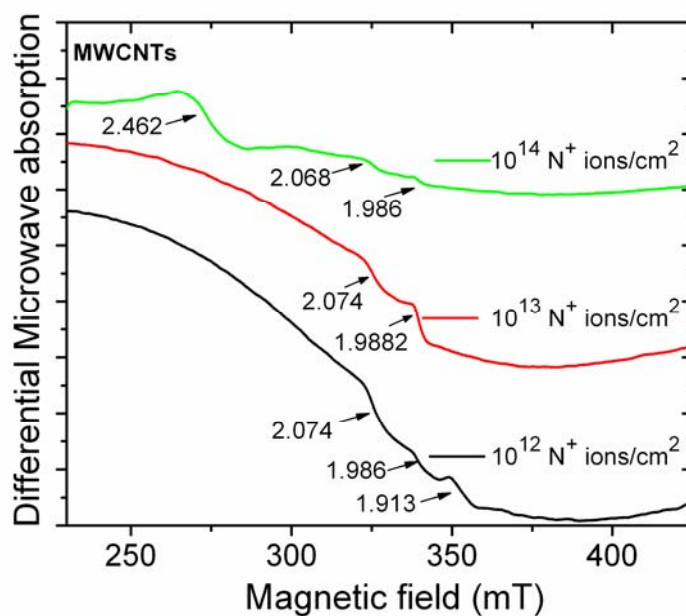


Figure 6-28: Higher Resolution EPR spectra shows a number of peaks in MWCNTs after irradiation.

$g = 2.462$. Absorption intensity of these paramagnetically active defect centres in case of 10^{14} ions/cm² irradiated MWCNTs is stronger due to the high damage after irradiation.

dose level of 10^{14} ions/cm² creates many surface damaged sites leading to observation of these peaks.

6.6 Effect of Argon (Ar⁺) Irradiation

6.6.1 HRTEM Studies of Argon (Ar⁺) irradiated CNTs

HRTEM Images of SWCNT-A before and after Ar⁺ irradiation is shown in Fig. 6-29. Virgin SWCNT-A contained very few defects as shown in Fig. 6-29(a). Effect of low dose irradiation on SWCNT-A is shown in Fig. 6-29(b) and (c). Low dose leads to formation of surface cavities as shown in Fig. 6-29(b). Low dose creates defects sufficient enough leading to perfect collapse of the tube and bisections as shown in Fig. 6-29(c). Effect of intermediate dose is shown in Fig. 6-29(d) to (e). Intermediate dose leads to formation of bent and damaged wall structure. Intermediate dose shows comparatively much higher damages than the low dose irradiation leading to the collapse of a large number of CNTs through formation of number of defects. It is also evident that a large number of tube fracture leads to finally increased amorphous carbon content as seen from Fig. 6-29(f). Effect of high dose irradiation is shown in Fig. 6-29(g) to (i). Many a times surface defects created upon irradiation results into bending of the tubes due to very high self healing property of CNTs as shown in Fig. 6-29(g). Fig 6-29(h) shows smooth sectioning of the SWCNTs as result of high dose irradiation. This shows the capability of the ion irradiation of structural engineering of CNTs. They can be seamlessly cut or, welded together using ion irradiation. A large number of surface damages created upon high dose irradiation leads to formation of curved wave like pattern of the outer walls of SWCNTs as shown in Fig. 6-29(i).

HRTEM images of MWCNT-A after 30 keV Ar^+ ion-irradiation is shown in Fig. 6-30. Fig 6-30(b) shows formation of surface cavities and presence of small amount of

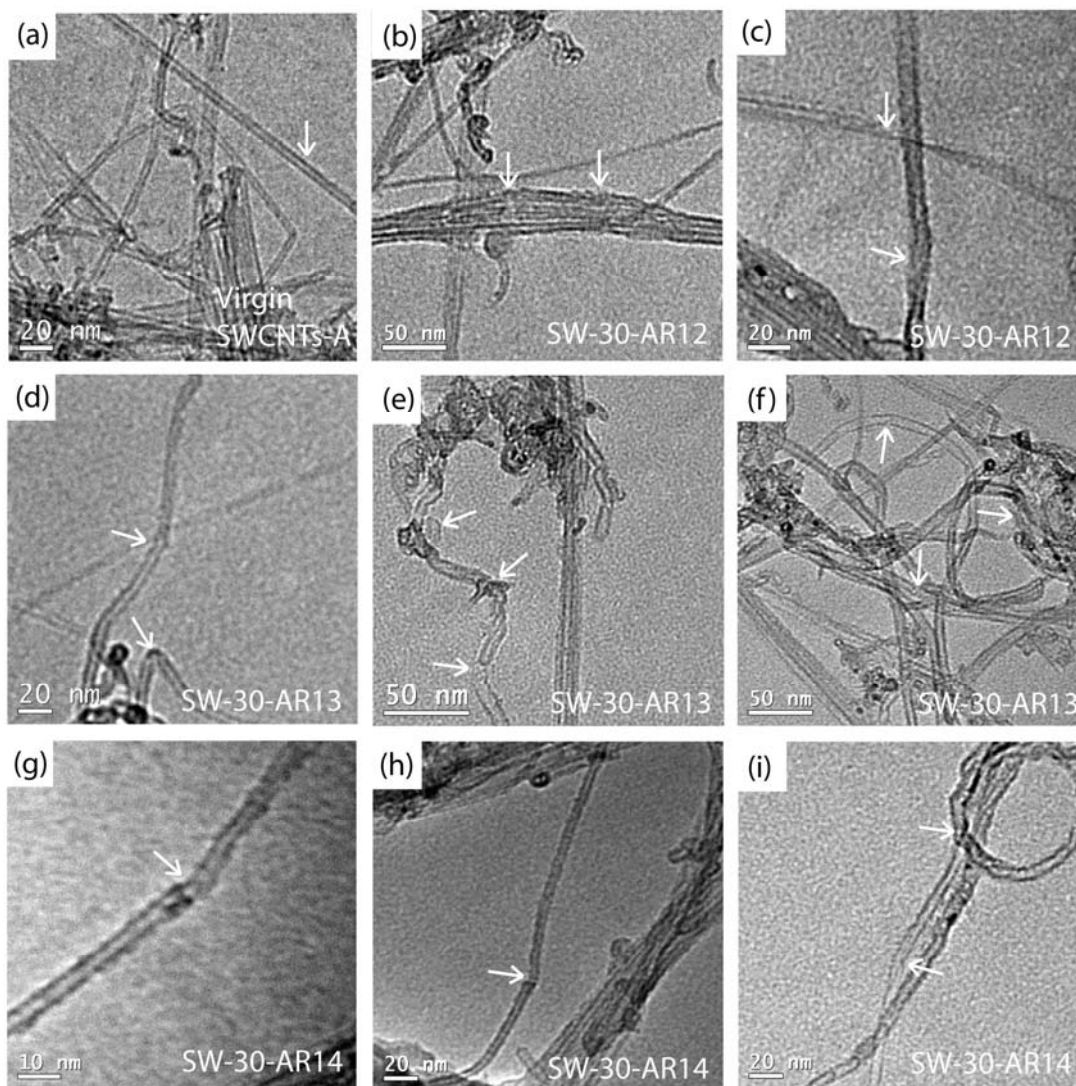


Figure 6-29: HRTEM Image (a) SWCNTs before irradiation, very few surface defects are visible. (b) Formation of surface cavities upon 10^{12} ions/ cm^2 Ar^+ irradiation. (c) A collapse tube and bisected portion upon 10^{12} ions/ cm^2 Ar^+ irradiation. (d) Formation of bent and damaged wall structure (e) Collapsing of the CNTs through formation of a large number of defects (f) A number of tube fracture leading to finally increased amorphous carbon content. A dose of 10^{14} ions/ cm^2 leads to (g) Bent tube through creation of defects (h) Smooth sectioning of the SWCNTs (i) A large number of surface damages leading to formation curved wave like pattern of the outer walls of SWCNTs.

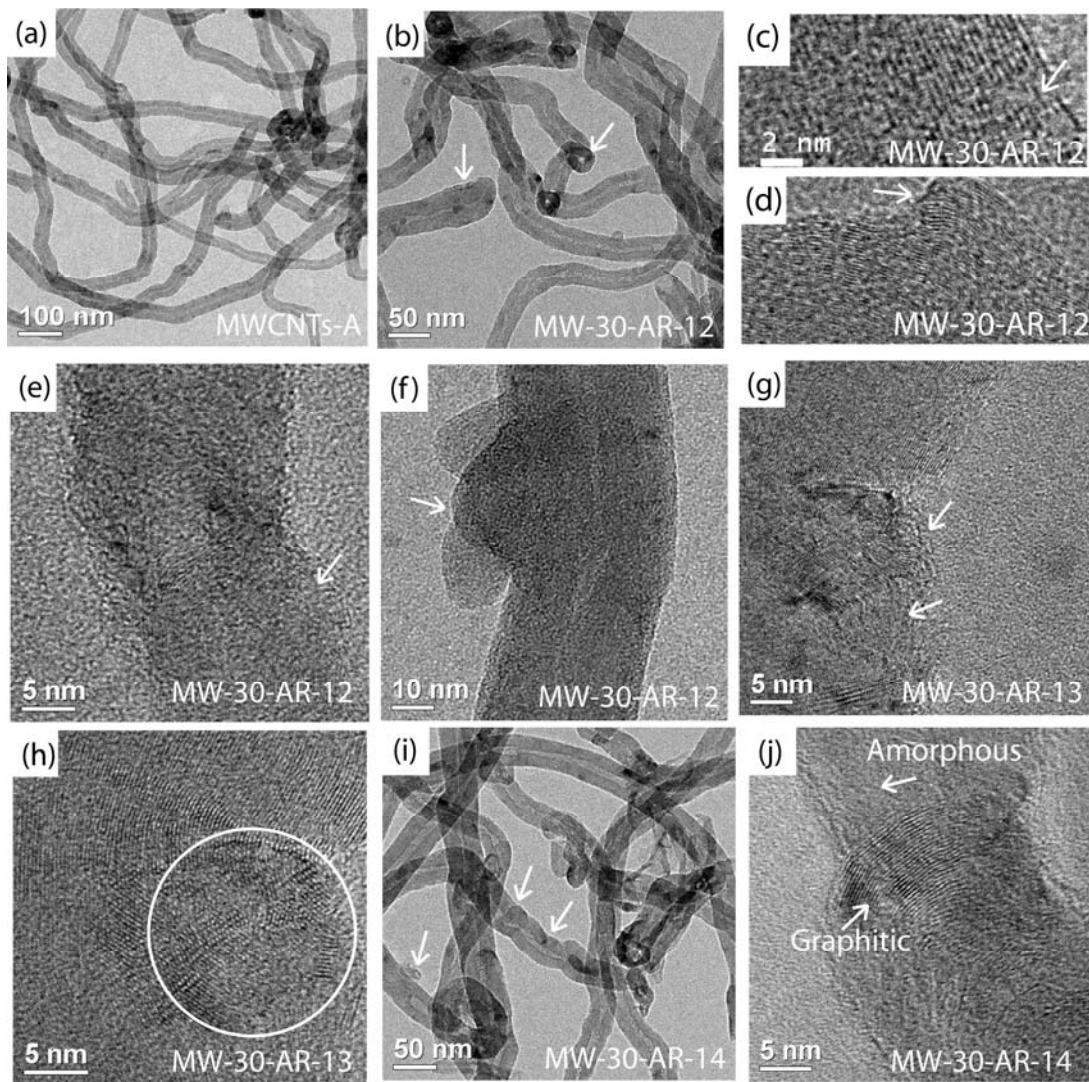


Figure 6-30: HRTEM image of (a) MWCNTs-A (b) Surface cavities and presence of small fullerene structure upon low dose irradiation. (c) Damaged outer wall. (d) A peeled off portion of outer wall introduction of curvature. (e) Narrowed diameter of a portion of MWCNTs and formation of curved graphitic structure. (f) Irradiation induced defects results into surface protrusions leading to the formation of curved graphitic structure even at low dose. (g) Surface damage leads to the formation of curved graphitic structure. (h) A portion of outer wall converted to diamond like structure at intermediate dose. (i) Increase in the density of surface voids and amount of fullerene and amorphous carbon at high dose. (j) Lattice images of damaged outer wall structure. Small portions of graphitic structure show heavy damage at 10^{14} ions/cm² dose.

fullerene like structures upon low irradiation dose. An irradiation dose of 30 keV Ar⁺ ion leads to outer wall damage as shown in Fig. 6-30(c). It also peeled off a portion from the outer wall of MWCNTs and introduces curved graphitic structure upon low dose Ar⁺ irradiation as shown in Fig. 6-30(d). Irradiation induced damages upon low dose leads to narrowing of diameter of a portion of MWCNTs shown in Fig. 6-30(e). Fig. 6-30(f) shows irradiation of low dose Ar⁺ ions on MWCNT-A results into surface protrusion leading to the formation of curved graphitic structure. Fig. 6-30(g) show irradiation induced defects in case of Irradiation at intermediate dose leads to comparatively large number of surface damages. Intermediate irradiation dose leads to conversion of a portion of MWCNTs to diamond like structure as shown in Fig. 6-30(h). An overview of MWCNTs irradiated at high dose is shown in Fig. 6-30(i). It shows many surface voids created upon irradiation along with increased amount of amorphous carbon. It also shows increase in the fullerene like structure upon high dose. Fig. 6-30(j) shows HRTEM image of creation of fullerene like structure upon high dose from MWCNTs. After high irradiation dose small portions of graphitic structure were observed in HRTEM, indicating heavy damage to graphitic structure upon high dose irradiation.

6.6.2 XRD Studies

XRD spectra of SWCNTs before and after 30 keV Ar⁺ irradiation show modification in the graphitic structure (Fig 6-31(a)). XRD spectra were fitted with Voigt spectral profile and summary of the spectral parameters is presented in Table 6-18. XRD spectra show increase in FWHM of (002) peak from 5.088 to 11.072 and 17.945 with low and intermediate doses and further slight decrease to 17.81 upon high dose. The peak area corresponding to (002) lattice plane continuously increases with increasing irradiation

dose. The FWHM and intensity of (001) plane also continuously increases with increasing irradiation dose. A drastic increase in the FWHM of (001) peak is observed from 28 to 83 as a result of increase in ion irradiation dose from low to intermediate dose. With ion

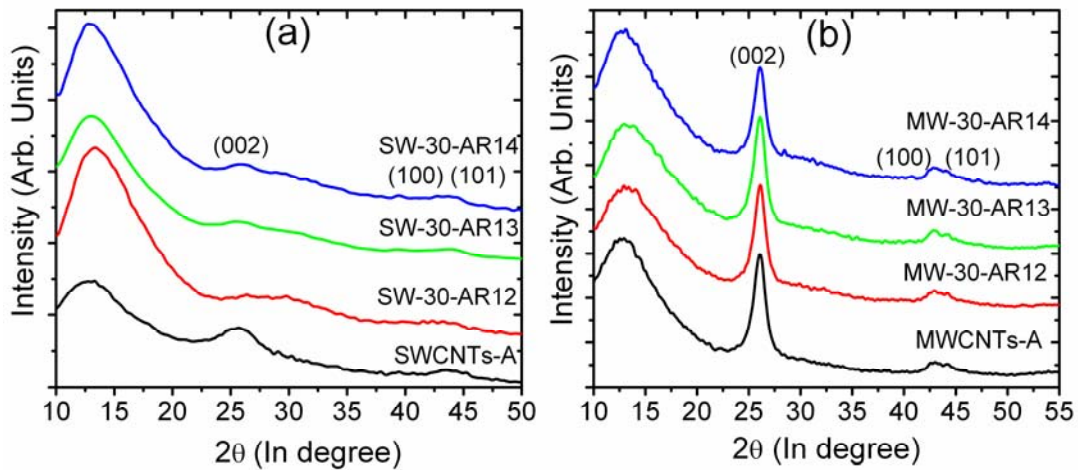


Figure 6-31: XRD spectra of Ar⁺ irradiated (a) SWCNT-A and (b) MWCNT-A, at different doses.

implantation (002) peak intensity continuously increases with increasing influences of irradiation. This indicates improvement in the graphitization upon ion-irradiation. The peak observed at $2\theta \sim 13^\circ$ is due to disordered carbon, more specifically indicates the formation of curved graphitic structures like higher order fullerenes. This peak increases with low dose and further decreases with intermediate dose and again increases with high dose. Low dose irradiation shows increase in Bragg angle for amorphous carbon peak observed at $2\theta \sim 13^\circ$ and (002) peak.

XRD spectra of MWCNTs are shown in Fig: 6-31(b). Voigt spectral profiles of these diffraction peaks are listed in Table 6-19. Modification in the X-ray diffraction profiles of MWCNTs is comparatively much less than the SWCNTs. Bragg peak

corresponding to (002) graphitic plane shows no appreciable change in peak centre and FWHM. The amplitude of this peak decrease with low dose, then again increases with intermediate dose and finally again decreases with high dose. Diffraction profiles of irradiation doses of intermediate and high dose shows peaks at 17.82 and 16.71 and

Table 6-18: Voigt deconvoluted XRD parameters of the 30 keV Ar⁺ Irradiated SWCNTs-A and MWCNT-A.

Sample	Profile	SWCNTs				MWCNTs				
0 Dose	Centre	13.24		25.76	43.60	12.93		26.03		45.60
	FWHM	7.07	----	5.09	2.66	7.27	---	1.33	----	3.00
	Ampl	220		110	27.40	337		314		29
10 ¹² Dose	Centre	13.37	18.42	28.99	42.92	13.57		26.06		43.45
	FWHM	7.03	5.72	11.07	4.69	6.79	---	1.33	----	2.72
	Ampl	647	113	117	28	242		294		31
10 ¹³ Dose	Centre	13.10		27.49	44.68	13.57	17.83	26.03		43.48
	FWHM	9.38	----	17.95	17.65	5.69	5.73	1.36	---	2.85
	Ampl	581		150	83.33	268	37	329		34
10 ¹⁴ Dose	Centre	13.23		27.87	44.28	12.86	16.71	26.04	30.32	43.51
	FWHM	9.26	---	17.81	17.60	4.98	5.07	1.34	5.38	3.23
	Ampl	747		181	106	306	86	279	27	39
Assignments		Defects	Defect	(002)	(100) (101)	Defect	Defect	(002)	Defect	(100) (101)

corresponding FWHM at 5.7346 and 5.07 respectively. The amplitude of this peak increases while going from intermediate dose to high dose level. A new broad hump like feature becomes prominent after high irradiation dose level. The peak intensity of (001) and (100) peaks appearing together increase monotonically with increasing irradiation doses. A slight modification of FWHM of this peak shows improvement in stacking order of graphitic planar structure with low and intermediate dose but again disordering with high irradiation dose. This behavior is different from SWCNTs where irradiation leads to

peak broadening with all the three doses. In case of MWCNTs, Bragg peak position of fullerene like carbon phase first shifts to higher 2θ for low and intermediate doses and then decreases to 12.856° with high dose. These new X-ray diffraction features are due to the formation of disordered carbon phases having curvature like higher order fullerenes. A new peak is observed at 18.42° in case of low dose irradiated MWCNTs is due to formation of damaged disordered structure of tubular Graphene structure.

6.6.3 Raman Studies

Fig. 6-32 shows the RBM modes of SWCNTs irradiated with Ar^+ ions. Peak position of RBM modes before and after irradiation is summarized in Table-6-19. Virgin SWCNTs shows RBM modes at 115, 141, 171, 207, 226, 259, 291 and 307 cm^{-1} , which disappears upon low dose Ar^+ irradiation. Modification of IFM modes is shown in Fig. 6-32. SWCNTs before irradiation shows a peak at 464 cm^{-1} is assigned to longitudinal acoustic mode (intravalley scattering, $q = 2k$) [33]. This peak completely disappears upon irradiation.

Modification of IFM modes are shown in Fig. 6-32(b) and are summarized in Table 6-20. The peak intensity of IFM mode observed at 669 cm^{-1} continuously decreases with increasing irradiation dose, where as FWHM of this peak changes in non-monotonic way. With low irradiation dose this peak becomes sharper than sample before irradiation, but with intermediate dose it broadens and then little reduction in peak width is observed with high dose. A new sharp peak is seen at 506 cm^{-1} in case of high dose irradiated sample. Broad hump like feature as observed in case of before irradiation and low dose irradiated sample, appears as prominent peaks at 814 cm^{-1} & 931 cm^{-1} after intermediate dose and at 812 cm^{-1} & 932 cm^{-1} upon high irradiation dose. These peaks originated from

structural defects of CNTs. Particularly these peaks arises from the non-hexagonal carbon rings formed after irradiation as evident from observed curved graphitic phases in HRTEM images and new diffraction peaks observed in XRD. The broad hump background centered around 1050 cm^{-1} slowly

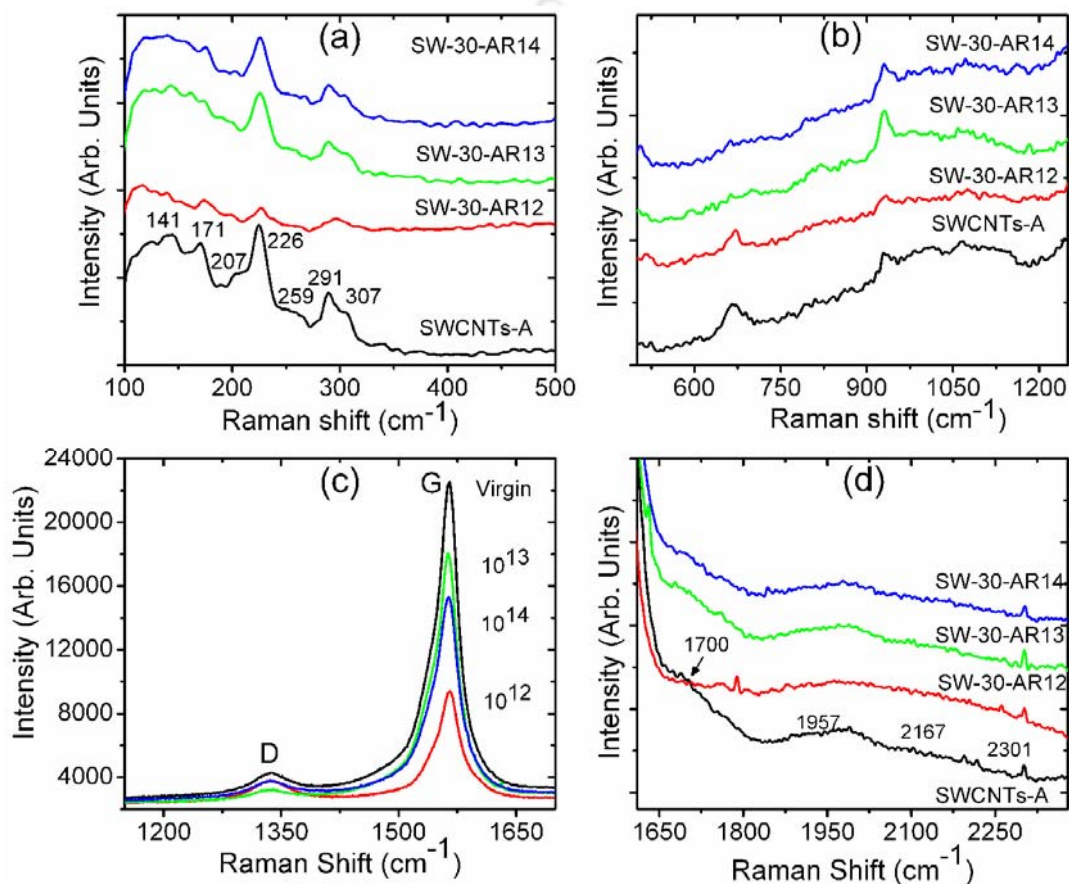


Figure 6-32: Effect of Ar^+ ion irradiation on (a) Low frequency RBM modes of SWCNTs, (b) Defect induced D-band, (c) First order Graphitic optical phonon mode G-band (d) Second-Order overtone G' mode, as a function of dose.

decreases in intensity with increasing irradiation dose. The peaks shifts towards higher Raman shift upon low irradiation dose and then peak centre decreases with increasing irradiation dose levels. In literature this is accounted to COOH group attached to the

carbon nanotubes during purification procedure. A small peak is seen at 1063 cm^{-1} in case of unimplanted sample.

Fig. 6-32(c) shows the modification of characteristic D and G modes of SWCNT-A before and after Ar^+ irradiation. The deconvoluted parameters of D and G modes are summarized in Table 6-22. Intensity and FWHM of G(M) modes decreases with low dose, then increases with intermediate dose and then again it decreases with high dose. This shows change in band structure due to creation of defects leading to transition from metallic to semiconducting SWCNTs at low dose and again to metallic tubes at intermediate dose. Such a modification upon ion irradiation can be used for controlled enrichment of a particular type of CNTs either metallic or semiconducting sample.

Table 6-19: Summary of RBM of 30 keV Ar^+ irradiated SWCNTs.

Sample	Raman shift (cm^{-1})								
	Peak1	Peak2	Peak 3	Peak4	Peak5	Peak6	Peak7	Peak8	Peak9
SWCNT	115.5	141	171	207	226	259	291	307	----
SW-30-AR12	118	----	177	200	227	----	297	----	485
SW-30-AR13	----	142	167	----	226	----	290	306	493
SW-30-AR14	----	142	----	----	226	251	293	----	498

Table 6-20: Spectral peak profiles of Raman shifts of IFM modes of 30 KeV Ar^+ -ions irradiated SWCNT-A.

Sample	Raman shift (cm^{-1})				
	Peak1	Peak2	Peak 3	Peak4	Peak5
SWCNT-A	464	669	----	----	1066
SW-30-AR12	----	669	----	----	1088
SW-30-AR13	----	679	814	931	1050
SW-30-AR14	----	678	812	932	1087
Assignments	IFM	IFM	Defects	Defects	C=O

The intensity of 1570 cm^{-1} peak $G^-(S)$ decreases upon low irradiation dose, while irradiation with intermediate dose again leads to increase in the intensity of this peak. Further, increase of irradiation dose to high fluence leads to slight fall of intensity. In case of SWCNTs before irradiation Longitudinal Optical (LO) phonon mode corresponding to the intravalley scattering ($q = 0$) is observed at 1480 cm^{-1} . The peak intensity of this mode follows similar pattern as that of $G^-(S)$ band. Disorder induced D-band does not show any appreciable change in Raman shift position. The FWHM of this peak increase from 57.8 cm^{-1} to 60.2 cm^{-1} upon low irradiation dose and again decreases to 57.8 cm^{-1} upon intermediate irradiation dose. At high irradiation dose it gets broadened to 61.8 cm^{-1} . SWCNTs show many other new modes in the region $1650\text{--}2350\text{ cm}^{-1}$ as shown in Fig. 6-

Table 6-21: Raman shifts of D and G-band of 30 KeV Ar^+ -ions irradiated SWCNTs.

Sl. No.	Profile	Peak1	Peak2	Peak3	Peak4	Peak5	Peak6	Peak7	Peak8	I_G/I_D
SWCNTs-A	Centre	1336	1480	1544	1565	1602	1700	1957	2167	15.49
	FWHM	57.8	70.6	20	27.4	32	129.6	274	252	
	Intensity	1281	487	4517	18180	418.9	337.5	333	162	
	Fano (1/q)			-0.16						
SW-30-AR12	Centre	1336	1481	1545	1565	1597	1740	1992	2189	5.44
	FWHM	60.2	68.8	15.2	29	39	201.4	253.0	195.0	
	Intensity	1296	122.1	1236	6545	561.9	119.6	286	160	
	Fano (1/q)			-0.24						
SW-30-AR13	Centre	1335	1484	1542	1564	1586	1705	1973	2172	27.47
	FWHM	57.8	80.8	19.5	26.2	44.6	165	229	234	
	Intensity	571.9	440.4	4062	13690	580	308.2	280	155	
	Fano (1/q)			-0.11						
SW-30-AR14	Centre	1336	1477	1545	1564	1596	1697	1984	2304	13.10
	FWHM	61.8	69.6	20.2	29.8	44.4	141.8	387.0	128.0	
	Intensity	975.3	203.2	2941	11610	554.6	261.9	400	317	
	Fano (1/q)			-0.23						
Assignments		D	LO	$G^-(M)$	$G^-(S)$	G^+	G^-	Defect	Defect	Ratio

32 (d); theoretically predicted to originate from pentagon-heptagon pair defects [108]. Before irradiation, these peaks are seen at 1704, 1778, 1957 and 2167 cm^{-1} . Relative changes in the peak frequency, FWHM and intensity of these peaks show modification in nature and density of defects due to variation of irradiation dose.

Fig. 6-33 shows modification of overtone modes of SWCNTs upon 30 keV Ar^+ ion-irradiation. The deconvoluted parameters are summarized in Table 6-22. In pristine samples, it was observed at 2692 cm^{-1} . This mode is believed not to depend on the excitation or defects. Therefore the intensity of $I_{G'}/I_D$ is used for estimation of the defect concentration. A broad peak centered around 2444 cm^{-1} is experimentally observed in the

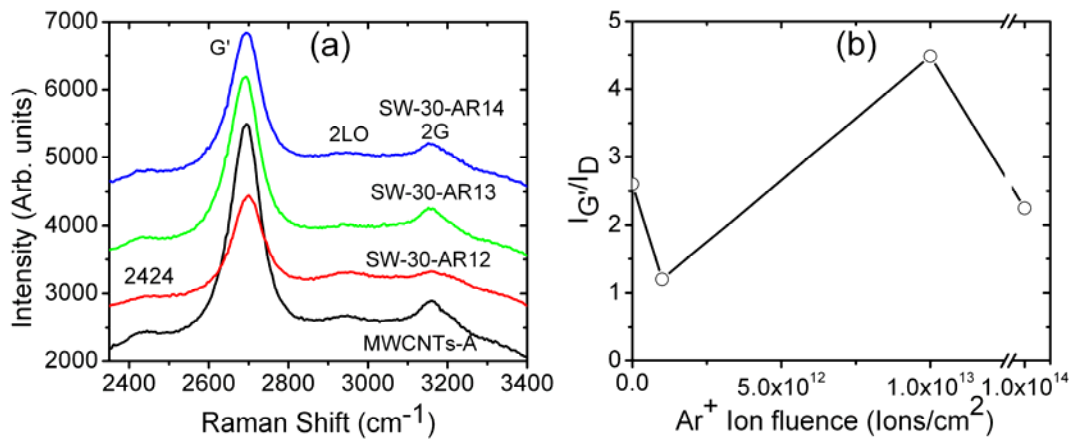


Figure 6-33: (a) Change in the G' mode as a function of ion dose (Ar^+). (b) Intensity ratio of G' band to D band as a function of ion dose.

pristine sample. This peak shift to higher frequency (2454 cm^{-1}) in case of low dose Ar^+ ion implanted samples. But it recovers back towards its original position after intermediate and high irradiation doses. Second order LO mode is seen at 2958 cm^{-1} . The peak intensity of this 2LO mode decreases monotonically with increasing Ar^+ ion irradiation dose, whereas its FWHM gets broadened by 43 cm^{-1} upon Ar^+ ion irradiation. With increasing dose a slight decrease in its FWHM is observed as compared to $10^{12} \text{ ions}/\text{cm}^2$ dose and

again with 10^{14} ions/cm² it gets broadened. Second order overtone of G- mode is seen at 3159.4 cm^{-1} before irradiation. Its intensity falls upon low and high irradiation dose, Whereas, intermediate dose shows improvement in the peak intensity. Maximum decrease

Table 6-22: Overtone modes of 30 KeV Ar⁺ irradiated SWCNTs for different doses.

Sample	Raman shift (cm ⁻¹)				
	Peak1	Peak2	Peak 3	Peak4	I _G /I _D
SWCNT-A	2444	2692	2958	3163	2.60
SW-30-AR12	2454	2698	2949	3175	1.20
SW-30-AR13	2443	2689	2962	3162	4.48
SW-30-AR14	2447	2692	2952	3165	2.25
Assignments	G'	G'	2LO	2G	

in intensity is seen for low dose and again gradually builds on intermediate and high irradiation dose. Similar modification is shown by FWHM of this peak. It gets broadened upon low and high fluences whereas much improvement is observed in terms of the decrease of the peak width upon intermediate irradiation dose. The variation of intensity ratio of G' by D band is shown in Fig. 6-33(b). I_G/I_D ratio decreases from 2.60 before irradiation to 1.20 after low irradiation dose. With intermediate irradiation dose it shows dramatic enhancement in the ratio to 4.48. Further with high irradiation dose it shows reduction in the ratio to 2.25. This shows that similar to the N⁺ ions, a dose of Ar⁺ ions leads to structural improvement through ion-irradiation induced annealing effect.

Fig. 6-34 shows the Raman spectra of MWCNTs before and after 30 keV Ar⁺ ion irradiation. Fig. 6-34(a) shows modification of low frequency RBM and IFM modes of MWCNTs upon 30 keV Ar⁺ irradiation. Summary of the peak position is presented in Table 6-23. MWCNTs do not show any sharp RBM modes before and after irradiation in all the conditions, shown in Fig. 6-34(b). Only a broad feature is observed in the RBM

mode at $\sim 116 \text{ cm}^{-1}$. Its FWHM decreases with increasing the irradiation to intermediate and high doses it decreases. A very weak and broad feature is seen in case of MWCNTs at

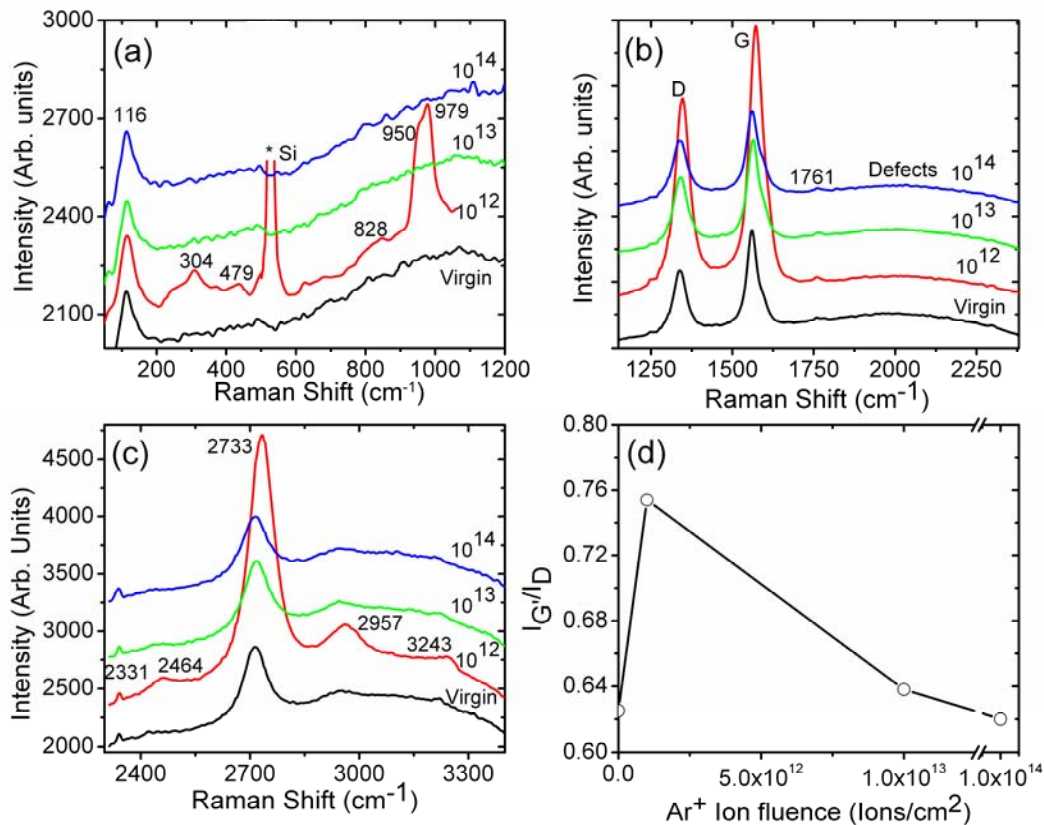


Figure 6-34: Raman spectra of MWCNTs before and after 30 KeV Ar^+ ion irradiation (a) Modification of RBM and IFM Modes (b) Disorder induced D-band and Graphitic G modes of MWCNTs along with defect induced modes (c) changes in second order overtone modes.

276 and 442 cm^{-1} which becomes prominent upon low irradiation dose. Raman shift at 442 cm^{-1} is similar to the LA mode observed in case of SWCNTs due to intravalley scattering at ($q = 2k$). These spectral features of MWCNTs disappear with increasing irradiation to intermediate and high doses. Intense Raman shifts observed near 521 cm^{-1} , 949 cm^{-1} and 979 cm^{-1} arises from the silicon wafer used as substrate. Apart from these many small features at Raman shifts 662 , 828 cm^{-1} gains observable intensity upon low irradiation

dose. The intensity of the broad IFM mode observed at 828 cm^{-1} continuously increases with increasing the irradiation dose. The peak centre of this peak downshifts and FWHM

Table 6-23: Peak profiles of RBM and IFM modes of Ar^+ irradiated MWCNTs at different doses.

Sample	Raman shift (cm^{-1})								
	Peak1	Peak 2	Peak3	Peak4	Peak5	Peak6	Peak7	Peak8	Peak9
MWCNT	116	276	442	----	----	----	----	----	1070
MW-30-AR12	116	304	479	527	662	828	949.7	979	1168
MW-30-AR13	117	----	452	----	----	820	----	----	1102
MW-30-AR14	115	----	447	----	----	794	----	----	1078
Assignments	RBM	RBM	LA	IFM	IFM	IFM	IFM	IFM	C=O

of this peak continuously increases with increasing the irradiation dose levels. It clearly shows that this peak originates due to defects in graphitic tubular structure created upon irradiation.

Fig. 6-34(b) shows modification of characteristic D and G modes of MWCNT-A upon Ar^+ irradiation. These spectra were deconvoluted using Lorentzian line profiles, as summarized in Table 6-24. Similar to the SWCNTs, the intensity of the D-band increases upon low dose, while it is decreased upon intermediate irradiation dose. The G⁻ band shows increase in the intensity upon low dose, while it is decreased upon intermediate dose. Before irradiation G⁺ feature is observed at 1596 cm^{-1} and it up shifts with low and intermediate irradiation doses and finally comes back to 1594 cm^{-1} with high dose. The peak intensity and FWHM of this peak increases with low dose and further decreases with intermediate dose and then again increases with high dose. All the bands show similar behavior for low dose irradiated samples. The improvement in the Raman spectral feature upon 10^{13} ions/cm^2 is possible through two ways (a) reduction in the point defect as result

of vacuum annealing. (b) Destruction of outer walls of the MWCNTs nanotubes leaving behind few walled MWCNTs. Few wall tubular graphitic structure will show more

Table 6-24: Peak profiles of D and G Raman modes of Ar⁺ ion irradiated MWCNTs for different doses.

Sample		Peak1	Peak2	Peak 3	Peak4	Peak5	Peak6	Peak7	Peak8
MWCNT-A	Centre	1338.9	1465.5	1559.9	1595.7	1675.3	1761.8	1981.8	2236
	FWHM	47.69	134.6	36	33.67	117.2	72.78	435	207.6
	Ampl	1024	102	1554	247	74.5	74.63	359	100.8
MW-30-AR12	Centre	1346.6	1468.2	1570.4	1598.6	-----	-----	-----	-----
	FWHM	51.59	66.5	46.08	49.77	-----	-----	-----	-----
	Ampl	3042.8	107	3865.6	655.91	-----	-----	-----	-----
MW-30-AR13	Centre	1340.9	1462.9	1563	1598	-----	1748	1995.1	2229.8
	FWHM	51.41	98.72	41.09	32.55	-----	140.1	452.4	181
	Ampl	1101	83.52	1607	253.7	-----	70.50	281.67	56.25
MW-30-AR14	Centre	1338.9	1462	1560	1594	-----	-----	1990	-----
	FWHM	54.2	165.6	39	44.58	-----	-----	565	-----
	Ampl	950	113.5	1261	269	-----	-----	283	-----
Assignments		D band	LO	G	G ⁺	Defect	Defect	Defect	Defect

scattered intensity in the Raman spectra than the thick MWCNTs. Second hypothesis is supported also from the X-ray diffraction studies. The intensity of (002) peak falls from 314 counts to 293 counts upon low irradiation dose, indicating reduction in the number of outer layers of MWCNTs. Even in case of MWCNTs some new Raman modes are observed in between Graphitic mode and second order overtone modes. Modifications in their peak profiles are listed in Table 6-25.

Fig. 6-34(c) shows the second order Raman modes of MWCNTs before and after 30 keV Ar⁺ ion irradiation. The deconvoluted parameters of these Raman modes before and after irradiation are summarized in Table 6-25. G' band shows up shift from 2713 cm⁻¹ before irradiation to 2732 cm⁻¹ upon low irradiation dose. Further with intermediate and

high irradiation dose it shows downshift in the peak position to 2718 and 2712 cm^{-1} respectively. The FWHM of this peak broadens with increasing ion-irradiation dose. Fig. 6-34(d) shows variation in the intensity ratio of G' band and D band, a measure of ordered

Table 6-25: Deconvoluted parameters of overtone modes of 30 KeV Ar^+ ion irradiated MWCNTs for different doses.

Sample		Peak1	Peak2	Peak 3	Peak4	Peak5	Peak6	Peak7	Peak8	Peak9
MWCNT	Centre		2443.7		2713	2759	2945	3084	3229	
	FWHM		82.5		75	382	186	237	259	
	Ampl		37.5		641	162	235	201	238	
MW-30-AR12	Centre	2340.7	2474.7		2731.9		2959	3125	3241	3335
	FWHM	2.19	147.5		87.13		168.6	225.5	119	66
	Ampl	145.8	162.75		2297.3		535	260	242	60
MW-30-AR13	Centre	2340	2446	2569	2718		2945	3111	3239	
	FWHM	3	72	155	94		285	225	259	
	Ampl	133	54	45	703		362	151	221	
MW-30-AR14	Centre	2331	2449		2712		2946	3088	3205	
	FWHM	0.52	58		97		281	102	306	
	Ampl	513	21		589		323	64	256	
Assignments					G'		2LO	2G	2G	

structure of CNTs. I_G/I_D ratio increases from 0.625 before irradiation to 0.754 upon low dose, While, with further increase of irradiation dose to intermediate and high fluence it varies to 0.638 and 0.620. It shows slight structural improvement upon 10^{12} and 10^{13} ions/ cm^2 irradiation dose. The improvement observed in I_G/I_D case of MWCNTs is negligible in comparison to the changes observed in case of SWCNTs. This is basically due to the different response of SWCNTs and MWCNTs towards ion irradiation created structural defects. SWCNTs show very high self healing capacity leading to relaxation of strain and defect annihilation with optimum dose of irradiation $\sim 10^{13}$ ions/ cm^2 .

6.7 In Situ modification of CNTs Under HRTEM

We have also observed in situ modification of structure defects in SWCNTs under 200 keV HRTEM. An accelerated electron imparts energy to the nanotube lattice, resulting in the release of strain through rearrangement of defects. Fig. 6-35 shows modification of typical

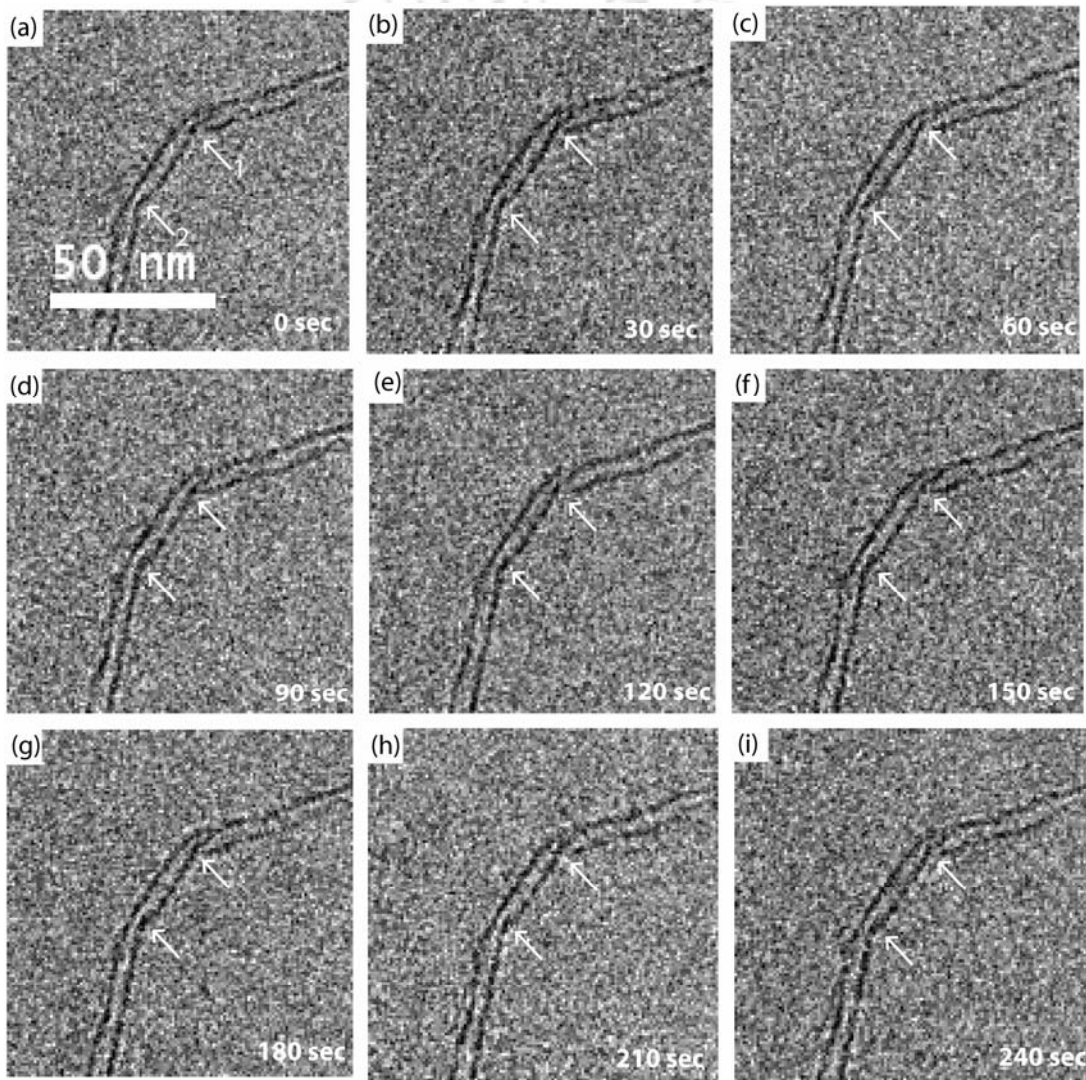


Figure 6-35: Time evolution of a portion of SWCNT taken under exposure of 200 keV electrons under HRTEM (a) Arrow in region-1 shows break in the tube wall and region-2 shows narrow section of the SWCNTs. Subsequent images (b) to (i) were taken with an gap of exposure time of 30 sec and normalised detector gain.

SWCNTs under 200 keV HRTEM. A series of images were acquired with a time gap of 30 seconds. These images were acquired with minimum electron current ($\sim$ pico-ampere/cm²) and normalized gain (CCD detector). Even such low energy electrons are capable of modifying the structural properties of CNTs. Fig. 6-35(a) shows two defective regions of a typical SWCNT observed under HRTEM. Region-1 shows void on the wall and region-2 shows a narrowed diameter portion of the SWCNT. Subsequent images show in situ defect evolution and annihilation with exposure time of accelerated electrons. After 30 seconds of exposure, region-1 shows clear re-construction around the defects and distances between the lower broken walls is narrowed. With further exposure i.e., after 60 seconds Fig. 6-35(c) broken wall are well connected to each other. Further exposure results into bisection of the tube as shown in Fig. 6-35(e). Region-2 shows increased disordered range with recovery of diameter after 30 seconds (Fig. 6-35(b)). With further increase of the exposure time, network of defects in the region-2 are healed out to minimize the lattice strain, resulting in the recovered diameter with a sharp bend, as shown in Fig. 6-35(f). An exposure of 240 seconds results into lowering of inclination angle showing reduction in the non-hexagonal rings. Such reconstruction after electron irradiation arises from the migration of vacancies in the CNTs [91] and high self healing capacity of CNTs [84]. Consistent to our results, C. Colliex et. al. have experimentally demonstrated the capability of in-situ electron irradiation under STEM for structural shaping of SWCNTs [240]. In addition to their work we have demonstrated the capability of in-situ electron irradiation for structural defect annihilation. These results show that similar to the ion beam, electron beam can be used for controlled structural modification and defect engineering of carbon nanotubes locally.

6.8 Summary and Conclusions

Through systematic studies of the effect of ion irradiation on CNTs, we have found the optimum dose of irradiation for structural improvement in SWCNTs and MWCNTs using H^+ , C^+ , N^+ and Ar^+ ions. In case of H^+ irradiation, structure of SWCNTs improves with 10^{12} ions/cm² and this is found to be optimum dose. H^+ irradiation at 30 keV creates mainly point defects as evident from voids found in the HRTEM studies. On the other hand, in case of other ions C^+ , N^+ and Ar^+ ions at 30 keV with a dose of 10^{13} ions/cm² show reduction in the defect density as reflected from improvement of I_G/I_D ratio. Improvement in the structure occurs due to the dynamic annealing (in case of C^+ , N^+ ions) and re-organization of lattice (in case of Ar^+ ions) of defects caused by accelerated ions. Increase of irradiation energy to 80 keV shows creation of higher density of defects at 10^{13} ions/cm². In case of H^+ , C^+ and N^+ , a dose of 10^{12} and 10^{13} both shows constructive effects in CNTs, while Ar^+ ions show increase in the defect density upon 10^{13} dose. This is due to higher contribution of electronic energy loss by H^+ , C^+ and N^+ ions (compared to the Ar^+ ions) at 30 keV which shows constructive effect by deposition of energy at the lattice sites leading to healing of defects. Nuclear energy loss increases with the mass of irradiated ions. Increasing nuclear energy loss (elastic collisions) knocks out atoms from the lattice, leading to reorganization of lattice. Such reorganization of lattice may lead to a defect free nanotube with different chirality (different atomic arrangement). Such structural modifications appears as defect free structure as observed at intermediate dose of 10^{13} ions/cm² of Ar^+ ion although lower dose shows destructive effect. In case of Ar^+ ions destructive effect observed at 10^{12} ions/cm² is due to higher nuclear energy loss. Thus in case of Ar^+ ions, structural improvement observed at intermediate dose is due to re-organization of lattice, not due to annealing effect. Irrespective of ion species / mass, an

irradiation dose of 10^{14} ions/cm² shows structural degradation as evident from the HRTEM and Raman studies. In case of 10^{14} ions/cm² N⁺ irradiation at 30 keV, renucleation of amorphous carbon shows formation of novel nano-spring like structures. This demonstrates the capability of ion-irradiation as a potential tool for fabrication of carbon based novel nanostructures for nano-electromechanical systems in future.

Another important observation is about origin of strong IFM modes observed in case of SWCNTs irradiated with 30 keV N⁺ and Ar⁺ ions. The intensity of Raman modes at 804, 868, 926 and 935 cm⁻¹ (IFM modes) was found to increase with ion dose and in turn with the structural defects created upon irradiation. This confirms that most of the IFM modes are finger print of defects in SWCNTs. In contrast, the intensity of IFM mode at 669 cm⁻¹ reduces with increasing defect concentration, showing their origin as combination modes in perfect CNTs. Similar to the N⁺ ions, Ar⁺ ions also shows monotonic decrease of the intensity of 669 cm⁻¹ peak with increasing irradiation dose, while new peaks from structural defects are observed at 814 and 931 cm⁻¹ upon 10^{13} and 10^{14} ions/cm² irradiation dose of 30 keV Ar⁺ ions. The intensity of these peaks increases with increasing dose. EPR studies on N⁺ ion irradiated MWCNTs showed new defect related EPR active centers with g = 2.462, 2.068, 2.074, 1.986, 1.9882 and 1.913. No such EPR active sharp peaks could be observed in SWCNTs, perhaps due to high metallic impurity content in SWCNTs as compared to the MWCNTs.

As compared to SWCNTs, MWCNTs show different response towards ion irradiation due to multilayered structure and lower self healing capacity. Similar to SWCNTs a dose of 10^{12} ions/cm² of 30 keV C⁺ leads to the structural improvement while at 10^{13} ions/cm² structural degradation is observed. Even a dose of 10^{12} ions/cm² shows formation of bamboo like structure in 30 keV C⁺ irradiated MWCNTs. At 10^{13} ions/cm²,

formation of ion-tracks resulting in the stacking faults in the layer of MWCNTs is observed. These staking faults introduce curvature in the walls of MWCNTs, which with further increase of irradiation dose leads to formation of fullerene like structures. With increasing nuclear energy loss from C^+ ions to N^+ ions and Ar^+ , these show increasing damaging capability, as expected. Ar^+ ions at intermediate dose shows conversion to the diamond like structure. A dose of 10^{14} ions/cm² of C^+ results into formation of curved fullerene like structure, while N^+ and Ar^+ results into amorphization of portions of the wall of MWCNTs. Ion irradiation in SWCNTs leads to formation of vacancies and stone-wales defects, while in case of MWCNTs, it leads to formation of curved graphitic structure. These curved carbon structures get converted to fullerenes at higher doses. In-situ HRTEM study of structural modification of CNTs under electron beam shows possibility of defect engineering locally.

Chapter -7

Defect Mediated Efficient Photoluminescence Quenching of Fluorophores

7.1 Introduction

Fluorescence/ photoluminescence (PL) quenching is an important tool for studying biochemical systems due to intrinsic role of molecular interactions responsible for it. A variety of molecular interactions like molecular rearrangements, excited-state reactions, energy transfer, ground-state complex formation and collisional quenching are responsible for it. PL quenching studies can reveal the diffusion of quencher over moderately large distances which are comparable to the sizes of proteins and membranes. Interaction of carbon nanotubes (CNTs) with numerous biomolecules is under extensive research such as biosensor [323], multifunctional biological transporter for selective cancer cell destruction [324] and interaction of DNA with single walled carbon nanotubes (SWCNTs) [325]. Even in case of polymer carbon nanotube composites the PL quenching of conducting polymer has been experimentally observed [326]. Reverse contrast in PL intensity around the nanotube after labeling with dyes has been used for imaging it [327]. PL quenching effect of carbon nanotubes has been used for visualization for nanomanipulation [328]. SWCNTs can act collectively as quenchers for their covalently tethered and /or π -stacked pyrenes, porphyrins [329] and chromophores [330-332] as well as the nearby quantum dots [333, 334], through energy-transfer or electron-transfer process [333]. W. Tan et. al. have reviewed role of CNTs as an efficient quencher [335]. It is thought that either energy transfer or electron transfer might contribute to such high quenching efficiency. PL biosensors can be developed integrating the quenching property of SWCNTs and the recognition property of functional nucleic acids.

The absorption spectrum of a typical SWCNTs sample spans over a wide range of wavelengths (approximately 500-900 nm), significantly overlapping the PL spectra of various fluorophores allowing Förster resonance energy transfer (FRET). Since CNTs contain highly delocalized π -electrons, the surface of CNTs can be easily functionalized through π - π interactions with compounds that possess a π -electron rich structure. Energy transfer has been found from Nile blue A to CNTs through FRET and dynamic quenching process was accounted to play role in the process. In this process, neither a chemical alteration nor complex formation takes place. The energy transfer is through long-range dipole-dipole interactions between the fluorophore and the quenchers [336]. In contrast, Rhodamine B was found to be quenched by static quenching process using CNTs [337]. Quenching by energy transfer was observed in case of squarylium dye to SWCNTs [338]. Polyanionic water soluble zinc-tetraaryl porphyrin was found to form long-lived electron transfer products with MWCNTs, resulting into quenching of photoluminescence zinc-tetraaryl porphyrin [339]. There is no explanation available for observed two different mechanisms, static [337] and dynamics quenching [340] process proposed for two different fluorophores Rhodamine B and Nile blue A, respectively. There have been very few serious attempts to study the nature of interaction between fluorophores and carbon nanotubes. Various mechanisms have been proposed to explain the observed PL quenching effect of CNTs. But none of the reports had analyzed the influence of various possible factors like amorphous carbon, nature of nanotubes SWCNTs or MWCNTs, metallic impurities, structural defects etc. contributing towards observed photoluminescence quenching effect.

Adsorptivity of nanotubes has also attracted a great deal of attention recently. Adsorption of dyes on the fluorophores surface leads to decrease in their concentration in

solution misleading the interpretation of observed PL quenching. Adsorption related applications of CNTs, depends on their internal pore volume. A wide range of adsorption surface areas (15-3000 m²/g) have been reported for nanotubes [341, 342]. Adsorption equilibrium of organic compounds toluene, methyl ethyl ketone (MEK), hexane and cyclohexane has been studied recently [343]. Ultrafast optoelectronic and numerous biological applications of CNTs require proper understanding of PL quenching effect of carbon nanotubes. Adsorption mechanism of organic chemicals on carbon nanotubes has been critically reviewed by B. Pan and B. Xing [344].

Surface adsorption of fluorophore on CNTs has been analyzed using Langmuir and Freundlich models. Surface adsorption studies shows adsorption to be a minor component contributing towards quenching. Structural defects enhance the photoluminescence quenching. A detailed study of surface adsorption and PL quenching effect of CNTs on three fluorophores is reported here. We present a systematic study of PL quenching effect of CNTs on three most common fluorophores Fluorescein, Rhodamine 6G and Quinine sulphate. This work establishes efficient PL quenching effect of CNTs and discusses the possible mechanism of quenching. Comparative study of different possible players of PL quenching like metal nanoparticles used as catalyst during synthesis and carbon nanoparticles through surface energy transfer (SET) from fluorescence dyes to CNTs has been studied.

7.2 Materials and Method

Details of the CNTs sample used in present study is given in chapter-2 and are well characterized using XRD, Raman spectroscopy, TGA and HRTEM studies as presented in preceeding chapters (Chap. 3-5). SWCNTs had diameter < 2 nm and length 5-15 nm. The

Table 7-1: Details of the CNTs used for quenching experiments.

Sample	Diameter	Length	Purity	Amorphous carbon	Surface area (m ² /gm)	Metal impurities
SWCNTs	< 2 nm	5-15 μ m	SW $\geq$ 50 %	< 5 %	> 400	9.3 %
MWCNTs-A	10-20 nm	5-15 μ m	MW $\geq$ 95 %	< 3 %	> 40-300	1.1 %
MWCNTs-B	20-40 nm	5-15 μ m	MW $\geq$ 95 %	< 3 %	> 40-300	0.12 %

purity of carbon nanotube was $\geq 90\%$ and purity of SWCNTs was $> 50\%$. The ash content in the sample was ≤ 2 weight % and amorphous carbon content was < 5 weight %. Specific surface area > 400 m²/g. MWCNTs-A had diameter in the range 10-20 nm and length in the range 5-15 μ m with purity ≥ 95 %, surface area 40-300 m²/gm and amorphous carbon < 3 %. MWCNTs-B had diameter in the range 20-40 nm and length in the range 5-15 μ m with purity ≥ 95 %, surface area 40-300 m²/gm and amorphous carbon < 3 %. MWCNTs-B contains very low amount of metallic impurities as estimated from TGA studies, presented in Chapter-4 [345]. Graphite powder and activated charcoal as obtained from Sigma-Aldrich were studied for comparison. SWCNTs vacuum annealed at 700°C for two hours to remove structural defects and these are named as SWCNT-700°C [346]. Fluorophores Fluorescein, Rhodamine 6G and Quinine sulphate were procured from Sigma-Aldrich and used for the quenching studies. In order to introduce structural defects in graphite, graphite powder was milled for 140 hours at 350 rpm using PM100 Retsch, Germany ball mill machine using Zirconium ball and vial in the 1: 10 power to ball weight ratio.

Standard fluorophores solution of 2 μ -molar concentration was prepared to avoid high optical density and turbidity which can result in decrease of PL intensity. Fluorophores Fluorescein, Rhodamine 6G and Quinine sulphate were prepared in 0.1M

NaOH, Water and 0.1M H₂SO₄ respectively. Concentration of fluorophores was estimated using their extinction coefficient (α) at absorption wavelengths (λ_{abs}) from Beer-Lamberts law. In the case of Fluorescein extinction coefficient was taken as 68908 cm⁻¹/m (at λ_{abs} = 496nm), for Rhodamine 6G α = 27033 cm⁻¹/m (at λ_{abs} = 488 nm) and for Quinine Sulphate α = 5607 cm⁻¹/m (at λ_{abs} = 350nm) [347]. For experiments, to prepare μ -molar solutions of fluorophores we added very small amount of fluorophores to the respective solvents and their absorbance was adjusted to ensure the concentration equals to 2 μ -molar. The absorbance value for making 1 μ -molar solution of the fluorophores studied was calculated using Beer-Lamberts law, $A = \alpha lc$ and is summarized in Table 7-2. Fig. 7-1 shows the schematic of the PL quenching experiment using CNTs.

Steady state PL measurements were performed at room temperature using a commercial fluorimeter (Thermo Electron, FA-357). CNTs were dispersed in

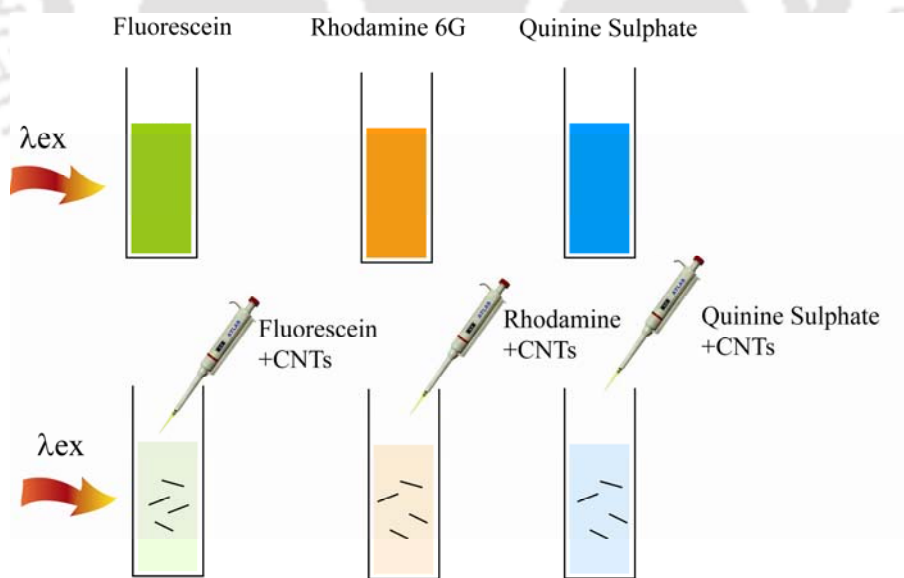


Figure 7-1: Shows the schematic of the experiment for Fluorescein, Rhodamine 6G and Quinine sulphate.

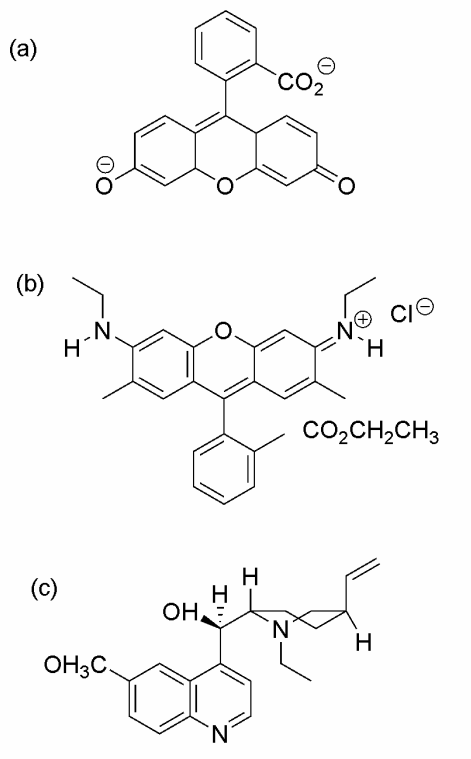


Figure 7-2: Molecular structure of fluorophores used (a) Fluorescein (b) Rhodamine 6G and (c) Quinine sulphate.

fluorophores solution in the concentration of 1mg/ml. In each step, 40 μl of the standard fluorophore solution was taken out and 40 μl of the nanotube solution was added continuously using micropipette to a 3 ml of the standard fluorophore solution taken in 10 mm quartz cuvette. CNTs, graphite and activated charcoal solution was made by dispersing these in 1 μM fluorophores solution to ensure that during addition the concentration of fluorophore remains constant. Table-7-2 summarizes the details of absorption, emission and other spectral parameters used /obtained during experiment. Time resolved photoluminescence measurements (TRPL) were performed using Life Spec-II Edinburgh Instruments. For time resolved measurements Pico-second pulsed diode lasers were used. Fluorescein and Rhodamine 6G both were excited with 475 nm

Table 7-2: Absorption and emission characteristics of fluorophores studied.

Fluorophore	Absorption (nm)	Extinction coefficient (cm ⁻¹ /M)	Solvent	Absorbance for 1μM conc.	Excitation (nm)	Emission (nm)
Fluorescein	472, 492*	68908	0.1 M NaOH	0.068	496	513
Rhodamine 6G	497, 527*	27033	Water	0.027033	488	550
Quinine Sulphate	316, 346*	5607	0.1 M H ₂ SO ₄	0.005607	350	445

*Strong peak.

laser and emission was monitored at 513 nm and 550 nm respectively. Quinine sulphate was excited with 375 nm laser and emission was observed at 445 nm. Fig. 7-2 shows the molecular structure of fluorophore (a) Fluorescein (b) Rhodamine 6G and (c) Quinine sulphate used for present study.

7.3 Results and Discussion

Fig. 7-3 shows the CLSM images of CNTs in Fluorescein. Solution was dropped on the curvature glass slide and was covered with very thin micro-slide for imaging. Fig. 7-3 (a) shows the fluorescence image of a drop of 2 μM Fluorescein solution. Fig. 7-3 (b) shows CLSM images after addition of SWCNTs. Dark contrast was observed near the nanotubes indicating PL quenching. Fig. 7-3 (c) shows CLSM image taken at higher magnification. Although major portion of the nanotubes, do not show any fluorescence from adsorbed fluorescein on SWCNTs surface. Few places shows green emission, probably these are the regions of MWCNTs present as impurity in the SWCNTs sample. Fig. 7-3 (d) shows a fluorescent carbon nanotube. Since majority of the SWCNTs are non-fluorescent, it indicates active role of SWCNTs towards PL quenching. It is predicted that hydrophobic aromatic fluorescein group binds to the sidewall of SWCNTs (likely via π -stacking) [192]. It is predicted that non-covalent interaction of dye to the CNTs occurs

through hydrophobic interaction. Low PL was observed from dye labeled CNTs in CLSM [327].

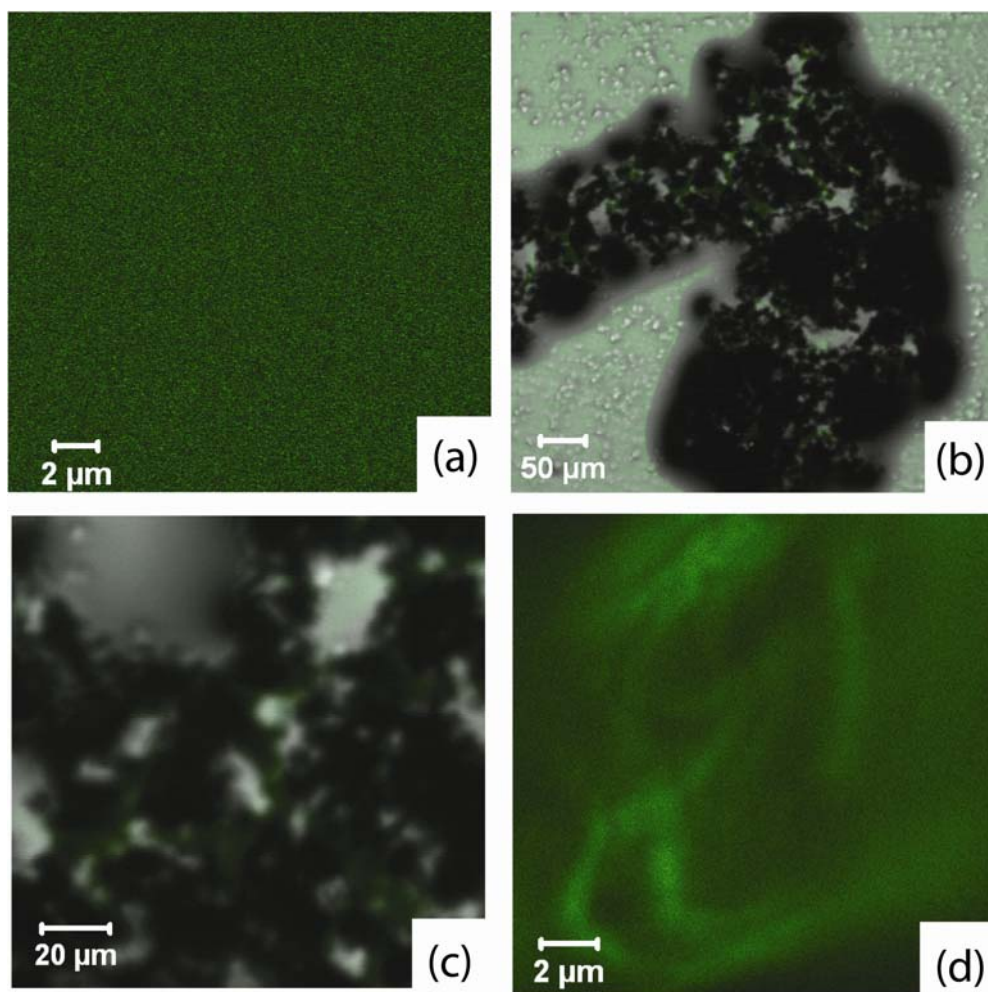


Figure 7-3: CLSM images of (a) Fluorescein before addition of carbon nanotubes, (b) after addition of SWCNTs at lower magnification shows dark contrast of nanotube bundles. It also shows an area around the SWCNTs where fluorescence is quenched. (c) Image taken at higher magnification shows fluorescence is quenched near the carbon nanotubes. Some portions of the bundles are fluorescent (d) shows green fluorescence from nanotubes (probably MWCNTs) due to adsorbed fluorescein. Majority of the nanotubes were non-fluorescent.

7.3.1 UV-VIS Absorption Spectroscopy

Perfect CNTs usually show poor solubility. Concentration of fluorophores was estimated using absorption spectra. Fig. 7-4(a) shows the typical absorption spectra of Fluorescein. It was further diluted for PL experiments to obtain 2 μ M solution of fluorophores. Absorption of fluorescein shows prominent peak at 492 nm along with a shoulder at 472 nm. Fig. 7-4 (b) shows the decrease in 492 nm absorption peak with

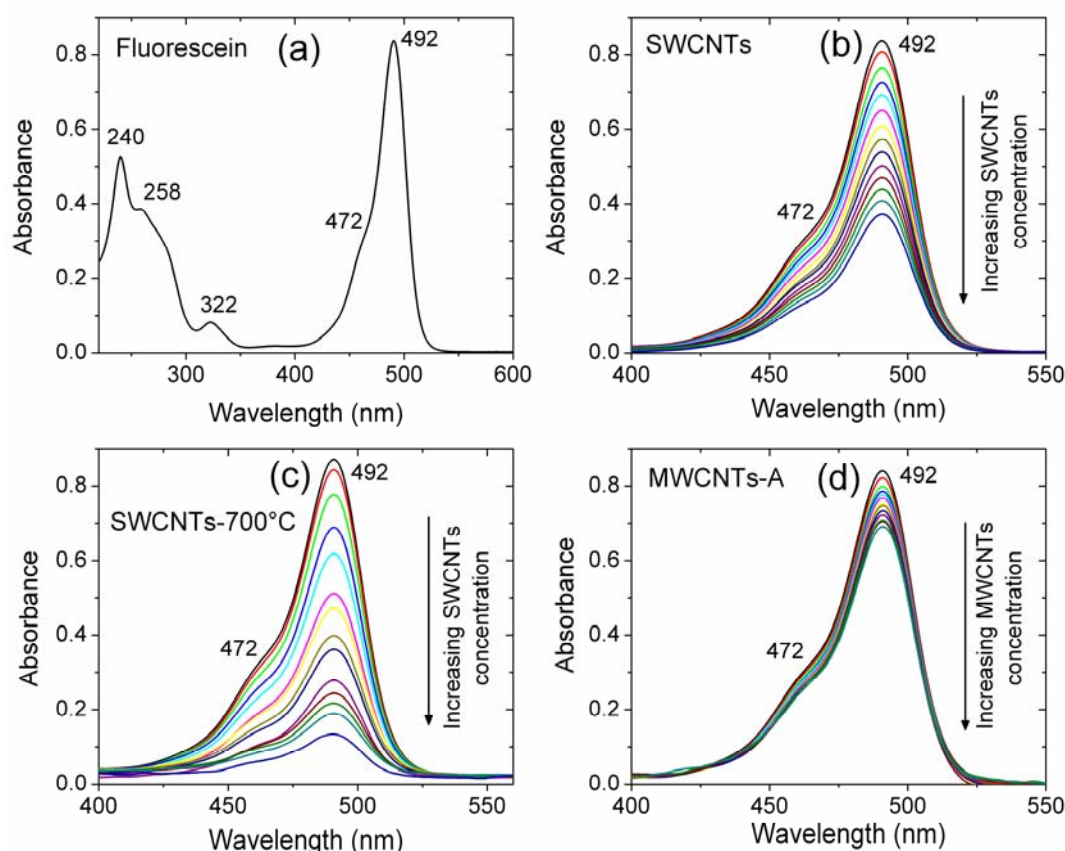


Figure 7-4: (a) Typical absorption spectra of Fluorescein, peak at 492 nm along with a shoulder at 472 nm (b) Decrease in the absorbance of Fluorescein with concentration of SWCNTs. (c) Change in absorbance with concentration of SWCNT-700°C (defect free CNTs) and (d) shows change in the absorbance peak intensity with addition of MWCNTs-A.

increasing concentration of dispersed SWCNTs in the fluorescein solution. Similarly absorption spectra were recorded after addition of SWCNTs-700°C and MWCNTs-A shown in Fig. 7-4(c) and 7-4(d) respectively. These spectra were fitted using two Gaussian peaks.

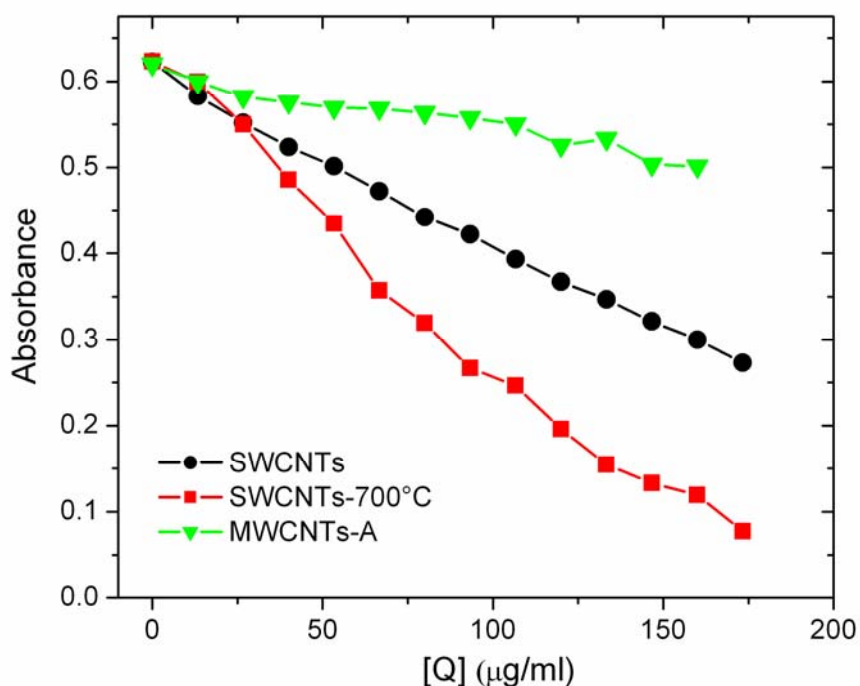


Figure 7-5: Comparison of variation in absorbance with increasing concentration of SWCNTs, SWCNTs-700°C and MWCNTs-A.

Variation in the absorption value is shown in Fig. 7-5. Absorption spectroscopy measurements were performed to quantify the quenching efficiency of nanotubes and surface adsorption separately. Fig. 7-6 (a) shows the typical absorption spectra of Rhodamine 6G. Fig. 7-6 (b) shows the variation in the absorption intensity of 527 nm peak of Rhodamine 6G with addition of SWCNTs-A. Similarly Fig. 7-6 (c) shows the variation in the absorption intensity of 527 nm peak of Rhodamine 6G with addition of

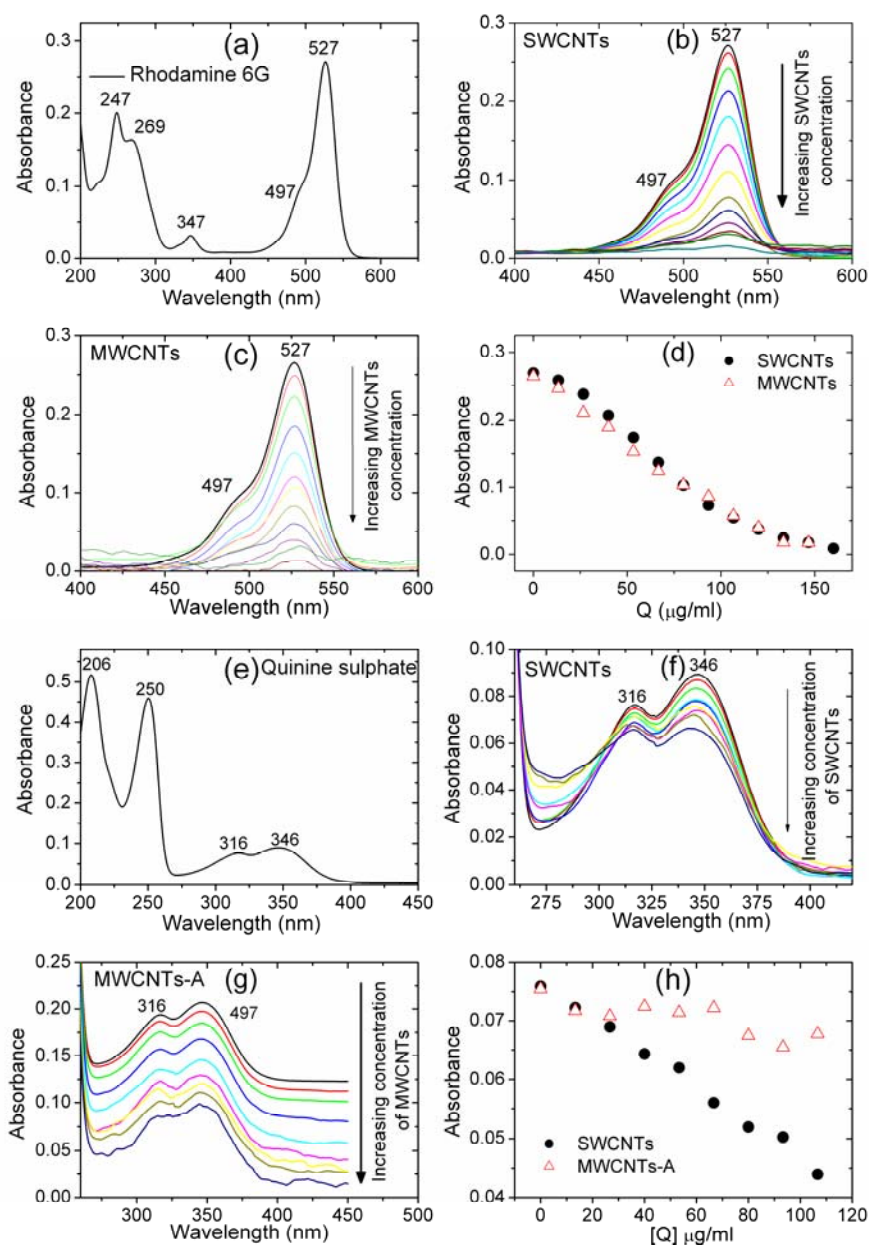


Figure 7-6: (a) Typical absorption spectra of Rhodamine 6G, peaks at 527 nm along with a shoulder at 497 nm (b) Decrease in intensity of absorbance peaks with increasing concentration of SWCNTs. (c) Change in absorbance with concentration of MWCNTs-A (d) Variation in absorbance of Rhodamine 6G with concentration of SWCNTs and MWCNTs-A. (e) Typical absorption spectra of Quinine sulphate. (f) Decrease in the absorbance of Quinine sulphate with increasing SWCNTs concentration (g) Decrease in the absorbance peak intensity with increasing concentration of MWCNTs-A (h) Comparison of change in absorbance of Quinine sulphate with increasing concentration of SWCNTs and MWCNTs-A.

MWCNTs-A. Fig. 7-6 (d) shows the comparative change in the absorbance of Rhodamine 6G after addition of SWCNTs-A and MWCNTs-A. Fig. 7-6 (e) shows the typical absorption spectra of Quinine sulphate. Fig. 7-6 (f) shows the variation of the absorption peak intensity of 316 and 346 nm peaks of Quinine sulphate after addition of SWCNTs. Fig. 7-6 (g) shows the change in the absorption intensity peak after addition of MWCNTs-A. Fig. 7-6 (h) shows the comparative study of effect of addition of SWCNTs and MWCNTs-A on the absorption peak intensity of 346 nm absorption peak of Quinine sulphate. Quantitative capability of surface adsorption of fluorophores on SWCNTs surface is shown in Fig. 7-7, after normalizing the absorption intensity.

Absorption monotonically decreases with increasing concentration of CNTs by addition of 40 μl of CNTs solution in each step. In case of fluorescein, vacuum annealed

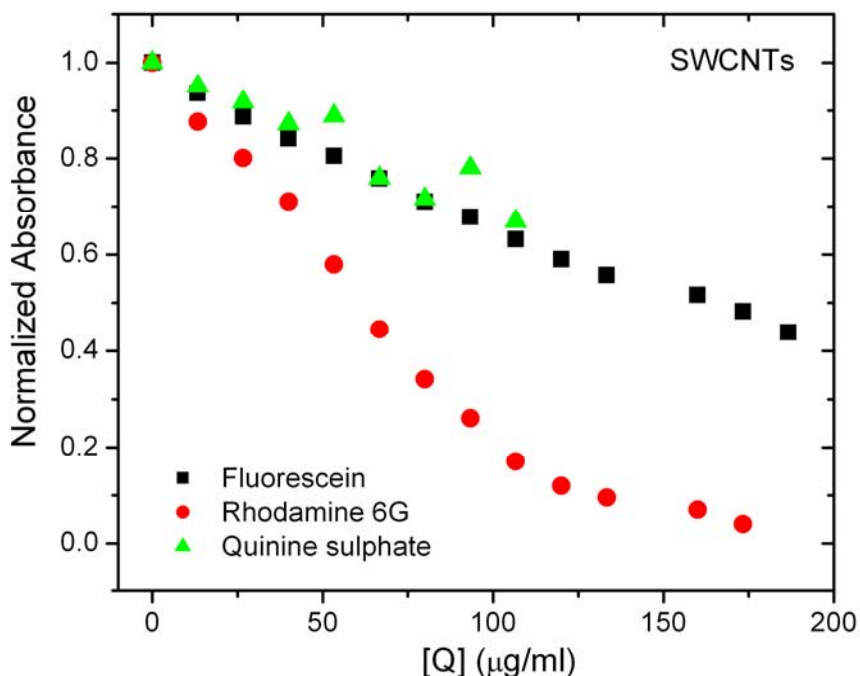


Figure 7-7: Comparison of change in normalized absorbance of Fluorescein, Rhodamine 6G and Quinine sulphate with increasing concentration of SWCNTs-A.

carbon nanotubes shows highest change in absorbance indicating comparatively higher surface adsorption of fluorescein on less defective SWCNTs. While, MWCNTs-A shows the least change in adsorption among the three, as shown in Fig. 7-5. Rhodamine 6G shows equal changes in absorbance for SWCNTs and MWCNTs-A. Quinine sulphate on the other hand shows mixed behavior. At low concentration of CNTs, identical changes in absorbance was observed in case of SWCNTs and MWCNTs. With increase of concentration of CNTs no change in absorbance was observed for MWCNTs-A, whereas SWCNTs continues to show monotonic decrease in absorbance with increasing concentration. It is interesting to note from Fig. 7-7 that Rhodamine 6G shows higher adsorption on SWCNTs surface as compared to Fluorescein and Quinine sulphate. Small fluctuations observed in the data points are due to nanotube-nanotube interaction leading to bundling.

7.3.2 Steady State Photoluminescence (PL)

A strong decrease in the PL intensity of fluorophores was observed after addition of CNTs. Fig. 7-8 (a) shows decrease in the PL intensity of Fluorescein after addition of SWCNTs. 3 ml of 2 μ M Fluorescein solution was taken in the Quartz cuvette and it was excited with 496 nm. Emission spectra was recorded before and after addition of 40 μ l of well dispersed solution of SWCNTs in fluorescein solution, after taking out 40 μ l of fluorescein solution from cuvette. PL intensity was found to decrease monotonically with increasing concentration of SWCNTs. Similarly Fig. 7-8 (b) shows decrease in the PL intensity of 550 nm emission peak of Rhodamine 6G after excitation with 488 nm and Fig. 7-8 (c) shows decrease in PL intensity of 445 nm emission peak of Quinine sulphate after excitation at 350 nm. Fig. 7-8 (d) shows the Stern-Volmer plot for all the three

fluorophores. Here, F_0 is the fluorescence intensity without addition of CNTs, F is the fluorescence intensity after addition of CNTs. $[Q]$ indicates the concentration of CNT. We can not express $[Q]$ for CNTs in terms of moles/cm³ as like other molecules, because molecular weight of CNTs depends on number of factors like chirality, length and number

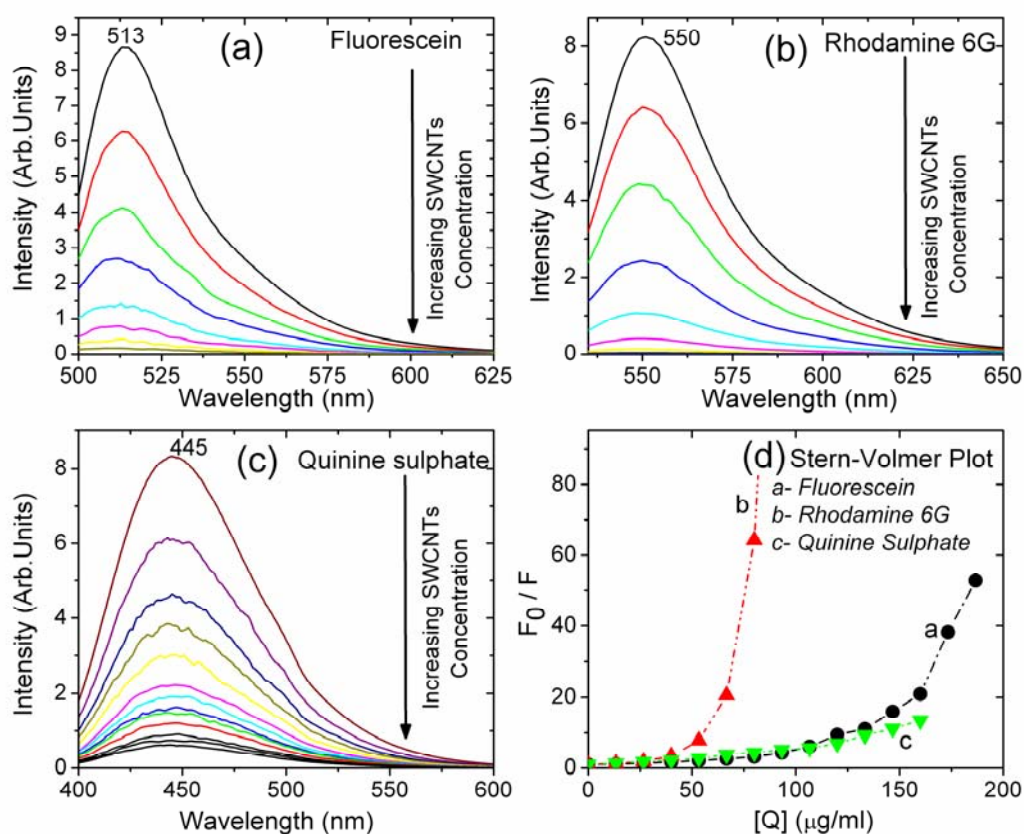


Figure 7-8: PL spectra showing monotonic decrease of PL intensity with increasing concentration of SWCNTs for (a) Fluorescein (b) Rhodamine 6G (c) Quinine Sulphate. (d) Stern-Volmer plot for Fluorescein, Rhodamine 6G and Quinine sulphate.

of walls. Here $[Q]$ is expressed in terms of volume of the nanotube in μl added from the dispersed solution of CNTs having concentration 1 mg/ml to 3 ml of fluorophore solution. Since nanotubes solution was initially prepared with concentration 1mg/ml in fluorophore

solution, addition of 40 $\mu\text{g/ml}$ represents addition of 40 μg of nanotubes to 3 ml of fluorophore in each step. Thus, $[Q]$ represents the mass of nanotubes in micro-gram added assuming uniform dispersion of nanotubes in the solution. The non-linear nature of Stern-Volmer plot indicates the possibility of combined dynamic and static quenching [348]. From Fig. 7-8 (d) it is clear that SWCNTs are the most efficient quencher for Rhodamine 6G. Next is the Fluorescein and Quinine sulphate is poorly quenched as compared to other two. Although the change in the absorption is same for both Fluorescein and Quinine sulphate upon addition of SWCNTs, they are quenched upto different extents. Quenching of fluorophores emission intensity can take place via two mechanisms (a) Static quenching and (b) Dynamic quenching. When a nonfluorescent complex is formed between the fluorophore and the quencher, it is called static quenching. When this complex absorbs light, it immediately returns to the ground state without emission of a photon. In the case of dynamic quenching (also called collisional quenching) the quencher diffuses to the fluorophore during the lifetime of the excited state. The fluorophore returns to the ground state upon contact, without emission of a photon.

The dependence of the PL intensity upon quencher concentration for static quenching is derived by consideration of association for complex formation resulting into equation

$$\frac{F_0}{F} = 1 + K_s[Q] \quad (7-1)$$

In this case F_0 / F depends linearly on $[Q]$.

Dynamic quenching (Collisional quenching) results from diffusive encounters between the fluorophore and the quencher during the lifetime of the excited state, which is a time dependent process. It can be described by the Stern-Volmer equation,

$$\frac{F_0}{F} = 1 + k_q \tau_0 [Q] = 1 + K_D [Q] \quad (7-2)$$

Where, k_q is the bimolecular quenching constant, τ_0 is the lifetime of the fluorophore in the absence of quencher, K_S and K_D are Stern Volmer constants. F_0 is the PL intensity in the absence of quencher and F represents PL intensity in the presence of quencher. Static and Dynamic quenching are distinguished by lifetime measurements. Since collisional quenching (dynamic quenching) is a rate process which depopulates the excited state, results into equivalent decrease in PL intensity and in the lifetime.

$$\frac{F_0}{F} = \frac{\tau_0}{\tau} \quad (7-3)$$

Where, τ_0 is the lifetime in the absence and τ in the presence of quencher. In contrast to dynamic quenching PL lifetime remains unchanged in the case of static quenching [348].

When fluorophore is quenched by collisions and by complex formation both, it is represented by equation

$$\begin{aligned} \frac{F_0}{F} &= (1 + K_D [Q])(1 + K_S [Q]) = 1 + (K_D + K_S)[Q] + K_D K_S [Q]^2 \\ &= 1 + K_{app}[Q] \end{aligned} \quad (7-4)$$

$$\text{Where, } K_{app} = \left(\frac{F_0}{F} - 1 \right) \frac{1}{[Q]} = (K_D + K_S) + K_D K_S [Q] \quad (7-5)$$

and F_0 / F represents the fractional PL remaining if given by the product of fraction not

complexed and fraction not quenched by collisional encounters. Deviations from the standard Stern-Volmer equation represented by eq. (4) could be due to limited accessibility of quenchers to the nanotubes due to bundling effect. But such effects would lead to negative deviation, contrary to the observed positive deviation. The plot of $\left(\frac{F_0}{F} - 1\right) \frac{1}{[Q]}$ versus $[Q]$ was not linear Fig. 7-9 (a), similar to that found by Ahmad et. al.

[337] Interestingly, the present data follows a compressed-exponential (faster than exponential growth) behavior (Fig. 7-9 (b)) given by:

$$\frac{F_0}{F} = \exp(b[Q])^\alpha \quad (7-6)$$

Where, $b=0.0149$ and $\alpha=1.307$. This is in contrast to that reported for Rhodamine B [337]. It may be noted that our quenching studies on Rhodamine 6G and Quinine sulphate shows qualitatively similar behavior. However, the efficiency of quenching is much higher (99.87%) in case of Rhodamine 6G. Note that when the extent of quenching is large, the usual Stern-Volmer equation is not obeyed. In the literature, large quenching behavior has been explained in terms of ‘sphere of action’ model when the fluorophore and quencher are closely spaced.¹⁸ The ‘sphere of action’ is expressed by modified form of Stern-Volmer equation given by

$$F_0 / F = (1 + K_D[Q])\exp([Q]VN/1000) \quad (7-7)$$

Where V is the volume of the sphere. This equation modifies to purely exponential growth when contribution of dynamic quenching is negligible, i.e., $K_D \approx 0$. Such positive deviation from Stern-Volmer equation has been observed when extent of quenching is large. This is expressed in terms of “sphere of action” within which the probability of quenching is unity [336]. Sphere of action is expressed by modified form of Stern-Volmer given by eqn. (7-7). In fact our time resolved PL studies indeed show that dynamic

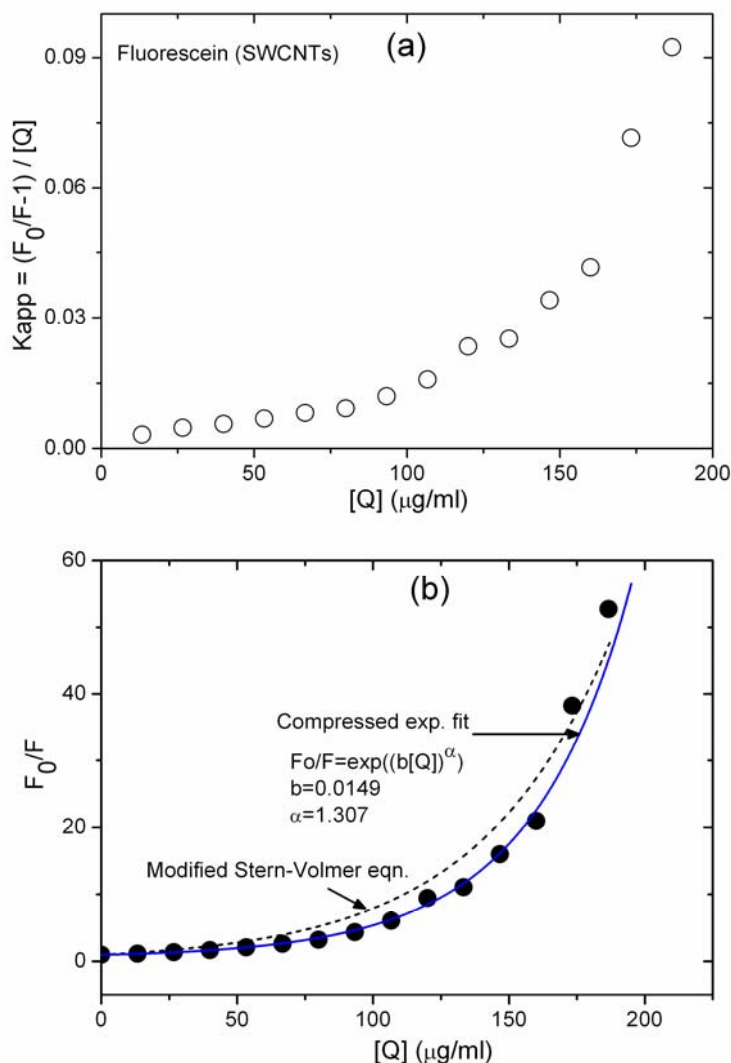


Figure 7-9: (a) $(F_0 / F - 1)$ as a function of $[Q]$ showing non-linear behavior. (b) Comparison of “modified Stern-Volmer equation” and observed compressed exponential behavior for quenching of fluorescein PL with SWCNTs.

contribution to the observed quenching is extremely small as compared to the static contribution. However, for the defective SWCNTs, our results follow a compressed-exponential growth behavior due to the long cylindrical structure of the quenchers (in this case CNTs), in contrast to the small volume of spherical shape of the quenchers as assumed in ‘sphere of action’ model. We believe that due to presence of defects on the

CNT surface, the quenching efficiency is extremely high that follows a faster-than exponential behavior with $\alpha=1.307$, as compared to the modified Stern-Volmer equation with $\alpha=1$. In case of SWCNTs-700 °C, it was found to follow $\alpha=1.032$, while MWCNTs follows perfectly the modified Stern-Volmer equation ($\alpha=1$). Though a compressed-exponential growth is uncommon in physical systems, recently Baouchaud and Pitard suggested a specific model for compressed-exponential that can occur from local rearrangement of molecules or micro-collapse of particles [349]. Such rearrangement of molecules is quite plausible in case of adsorption of fluorophores on CNTs with highly reactive sites due to presence of defects. Rhodamine 6G and Quinine sulphate also shows the similar behavior. In case of Quinine sulphate exponential and modified form of Stern-Volmer equation (eqn. 7) gives equally good fit. Exponential dependence of eqn. (7) comes from Poisson distribution for the probability of finding a volume V with n quencher given by $P(n) = \frac{\lambda^n}{n!} e^{-\lambda}$. Where λ is the mean number of quenchers per volume V . We approximately estimated the radius of sphere of action using the parameter obtained from fitting Eqn. (6). We calculated approximately the number of SWCNTs/ cm³ added in each step as follows:

Step1: Number of carbon atoms required to form a typically (8,0) SWCNTs of length 10 nm was calculated using nanotube modeler software (from JCrystal software [350]). It requires 760 carbon atoms. Thus to form a (8,0) SWCNT of 15 μ m length 114×10^4 carbon atoms are required.

Step2: Since 6.022×10^{23} carbon atoms weights 12.011 gm. Thus 114×10^4 carbon atoms (required to form 15 μm (8,0) SWCNTs) would weight

$$\left(\frac{12.011}{6.023 \times 10^{23}} \right) \times 114 \times 10^4 \text{ gm} = 227 \times 10^{-13} \mu\text{gm}.$$

Step3: 40 μl addition of dispersed SWCNTs to 3 ml of fluorophore solutions weights 13.33... μgm of SWCNTs added in each step.

Step4: Number of carbon nanotubes added in each step equals to

$$\frac{13.33 \dots \mu\text{gm}}{227.33 \times 10^{-13} \mu\text{gm}} = 5.864 \times 10^{11} \text{ CNTs}.$$

Step5: Mean number of quenchers per volume is estimated

$$\lambda = \left(\frac{5.865 \times 10^{11}}{3 \times 1000} \right) \text{ CNTs} / \text{cm}^3 = 1.955 \times 10^8 \text{ CNTs} / \text{cm}^3.$$

Further using $\lambda = 1.955 \times 10^8 \text{ SWCNTs} / \text{cm}^3 \times \pi r^2 h = 0.0149$, the radius of sphere of action equals to 1.271 μm typically for a 15 μm long SWCNTs. Since SWCNTs are cylindrical in nature, if we assume quenching action volume cylindrical, the action radius comes out to 1.271 μm . The large radius of sphere of action represents more efficient quenching. The large sphere of action for SWCNTs arises from the extended geometry, facilitating a number of adsorption sites, and possibility of quenching of large number of fluorophore molecules by a single SWCNTs molecule.

Fig. 7-10 shows effect of MWCNTs on photoluminescence of fluorophores and comparison of quenching efficiency of MWCNTs with SWCNTs. Fig. 7-10 (a) shows typical decrease in PL intensity of Fluorescein with increasing concentration of MWCNTs. Fig. 7-10 (b) shows Stern-Volmer plot for quenching of Fluorescein with

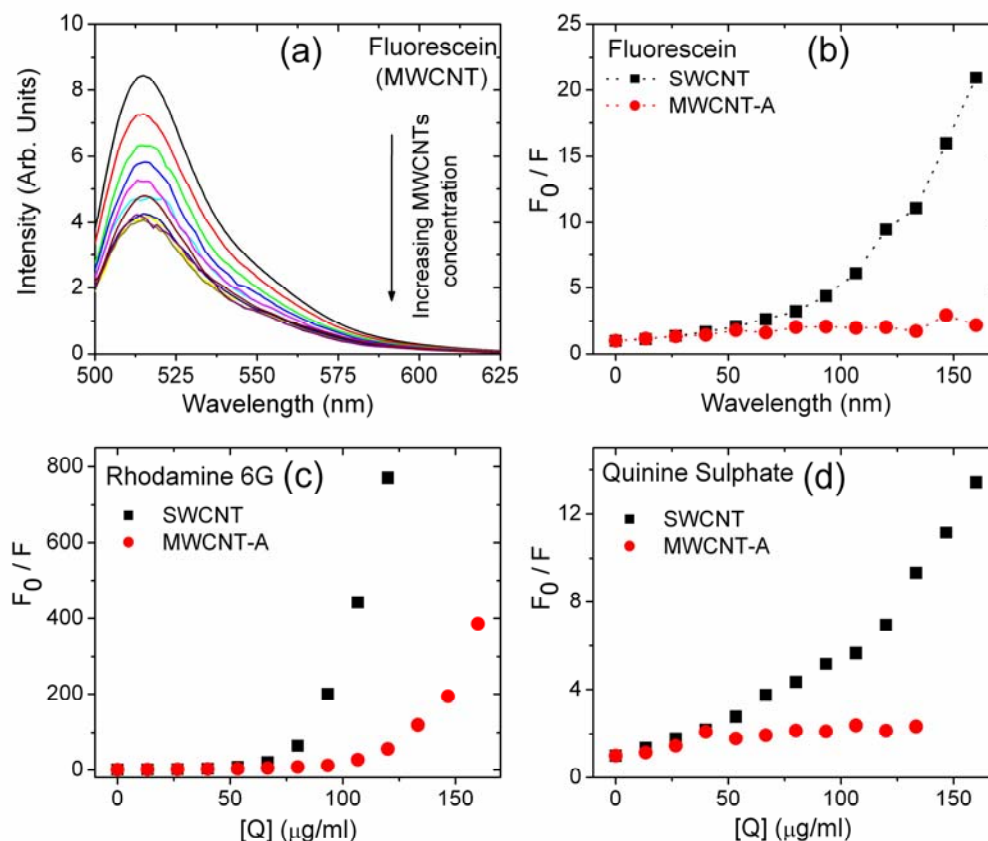


Figure 7-10: (a) Change in PL intensity after addition of MWCNTs. (b) Stern-Volmer plot of quenching of Fluorescein with SWCNT and MWCNTs-A (c) Stern-Volmer plot of quenching of Rhodamine 6G with SWCNTs and MWCNT-A (d) Quenching of Quinine sulphate using SWCNTs and MWCNTs-A.

MWCNTs and its comparison with SWCNTs. SWCNTs show large F_0/F as compared to MWCNTs. Similarly Fig. 7-10 (c) and Fig. 7-10 (d) shows comparative quenching capacity of SWCNTs and MWCNTs for Rhodamine 6G and Quinine sulphate respectively. Quenching efficiency of MWCNTs is comparatively lower than the SWCNTs, except for Rhodamine 6G the quenching efficiency of MWCNTs was significant. This is in agreement with absorbance data in Fig. 7-6 (d), where almost equal adsorption was observed for SWCNTs and MWCNTs-A. It is important to note that

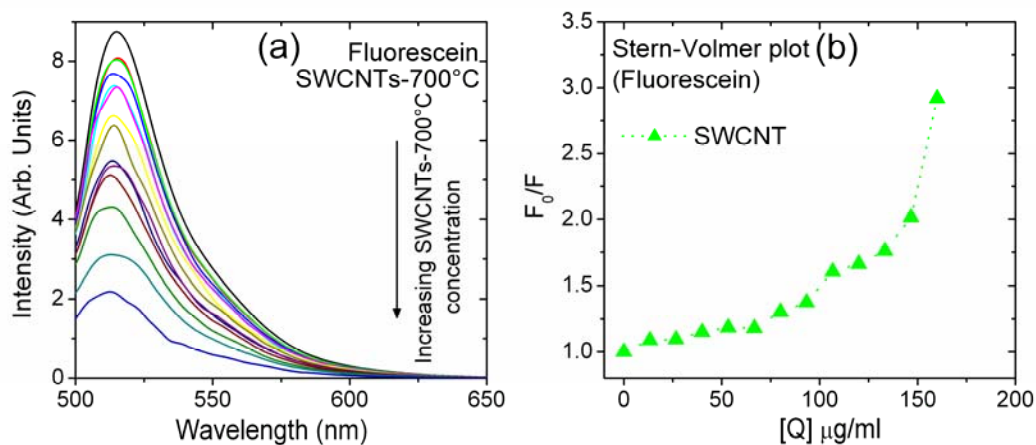


Figure 7-11: (a) PL quenching of Fluorescein with SWCNTs-700 °C (less defects) (b) Stern-Volmer plot of quenching of Fluorescein with SWCNT-700 °C.

F_0 / F value is quite high for Rhodamine 6G as compared to Fluorescein and Quinine sulphate at even comparatively lower concentration of SWCNTs. Very high quenching

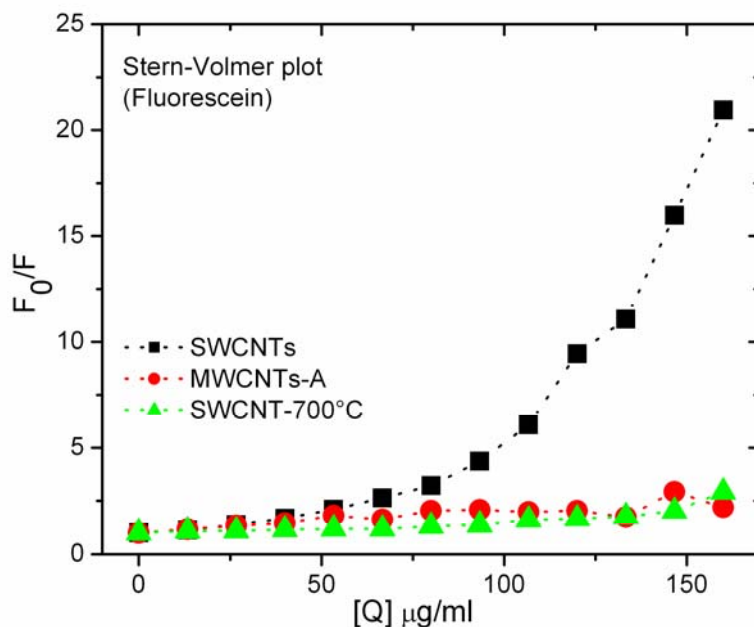


Figure 7-12: Comparison of quenching efficiency of SWCNTs (having defects), SWCNT-700°C (less defects) and MWCNT-A.

efficiency observed in case of Rhodamine 6G is due to higher adsorption. Fig. 7-11 (a) shows the PL quenching using SWCNTs-700°C, which contains much lesser defects than the SWCNTs. Fig. 7-11 (b) shows the Stern-Volmer plot of quenching of Fluorescein using SWCNTs. We have experimentally shown that SWCNTs-700°C contains fewer defects as compared to SWCNTs [346]. It is very interesting to note that the defect free SWCNTs shows only ~ 65.6% quenching efficiency as compared to that of unannealed SWCNTs (98.1%) and it is the lowest among all samples. Fig. 7-12 shows the comparison of quenching efficiency of SWCNTs (defective), SWCNTs-700°C (defect free) and MWCNTs. Although SWCNTs-700°C shows higher adsorption of fluorescein [Fig. 7-5], but it shows much lower quenching efficiency. This shows structural defects control the

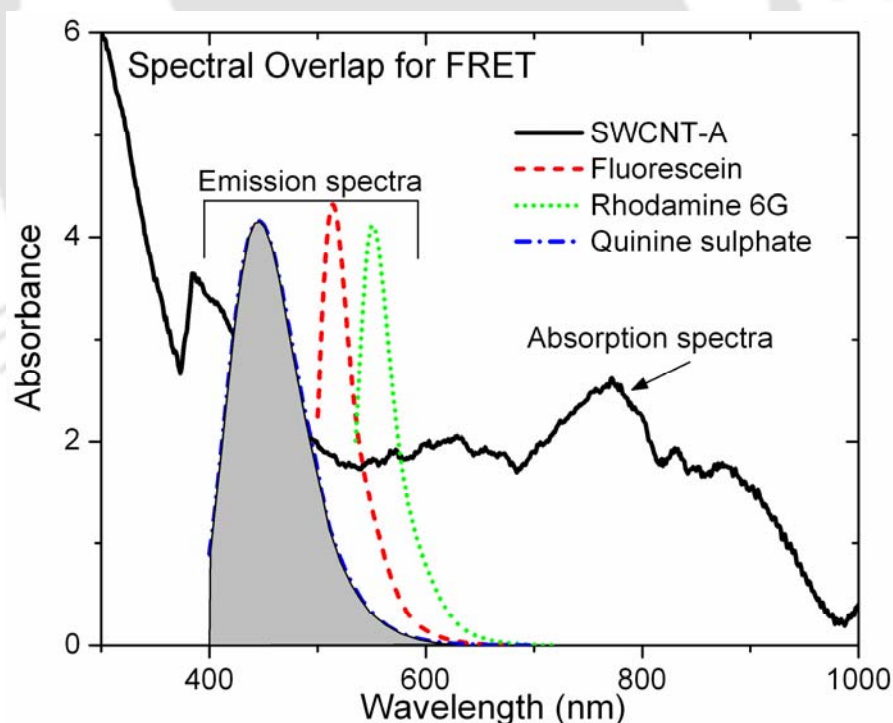


Figure 7-13: Schematic of the overlap region of absorption spectra of SWCNTs and emission spectra of Fluorescein, Rhodamine 6G and Quinine sulphate, essential condition fulfilled for FRET.

quenching process of Fluorophores. This is one of the important findings of the thesis.

Fig. 7-13 shows the overlap between absorption spectra of SWCNTs used and emission spectra of all the three fluorophores studied to explore the possibility of FRET. Interestingly the absorption range of SWCNTs overlaps with the emission range of studied fluorophores, indicating a strong possibility of FRET.

To understand the role of structural defects and dangling bonds, other carbon forms present as impurity in detail towards quenching of fluorophores, effect of Graphite,

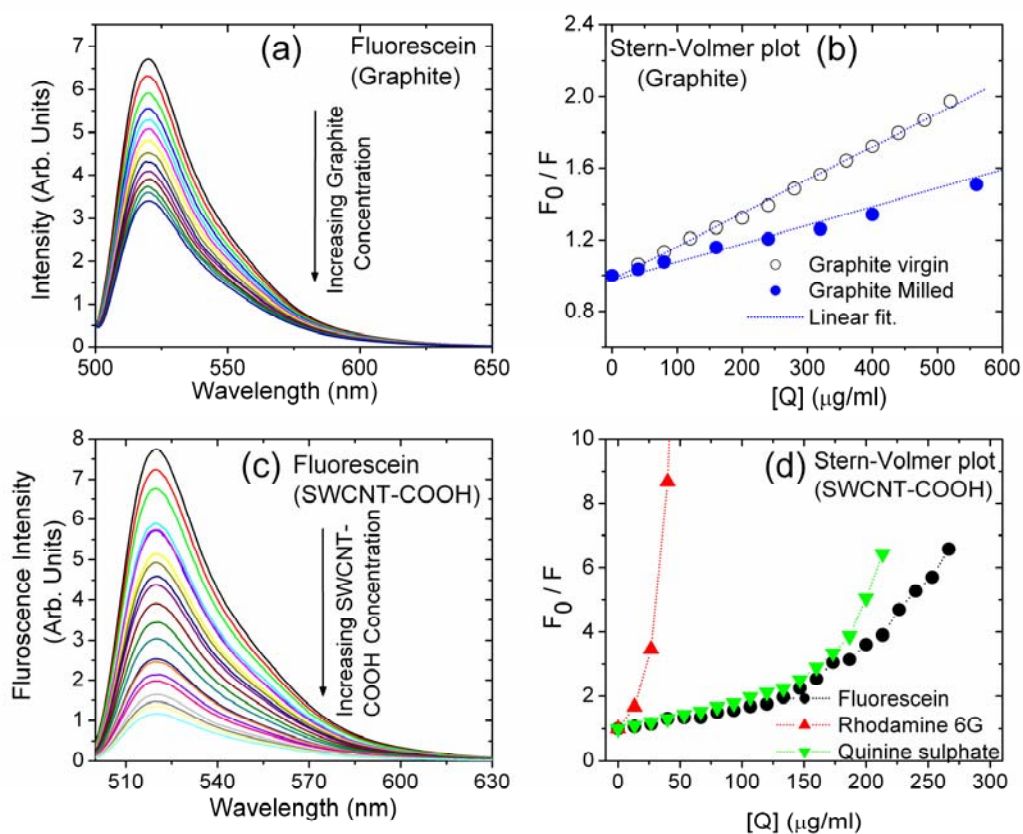


Figure 7-14: (a) PL quenching of Fluorescein using Graphite (b) Stern-Volmer plot for quenching using virgin graphite and milled graphite. (c) Quenching using acid functionalized SWCNTs (SWCNT-COOH) and (d) Stern-Volmer plot for comparison of quenching of Fluorescein, Rhodamine 6G and Quinine sulphate using SWCNTs-COOH.

SWCNTs functionalized with carboxylic acid group, activated charcoal and MWCNTs-2 (which had extremely low metal content [345]) was studied. Fig. 7-14 (a) quenching of PL intensity of Fluorescein using Graphite and Fig. 7-14 (b) shows corresponding Stern-

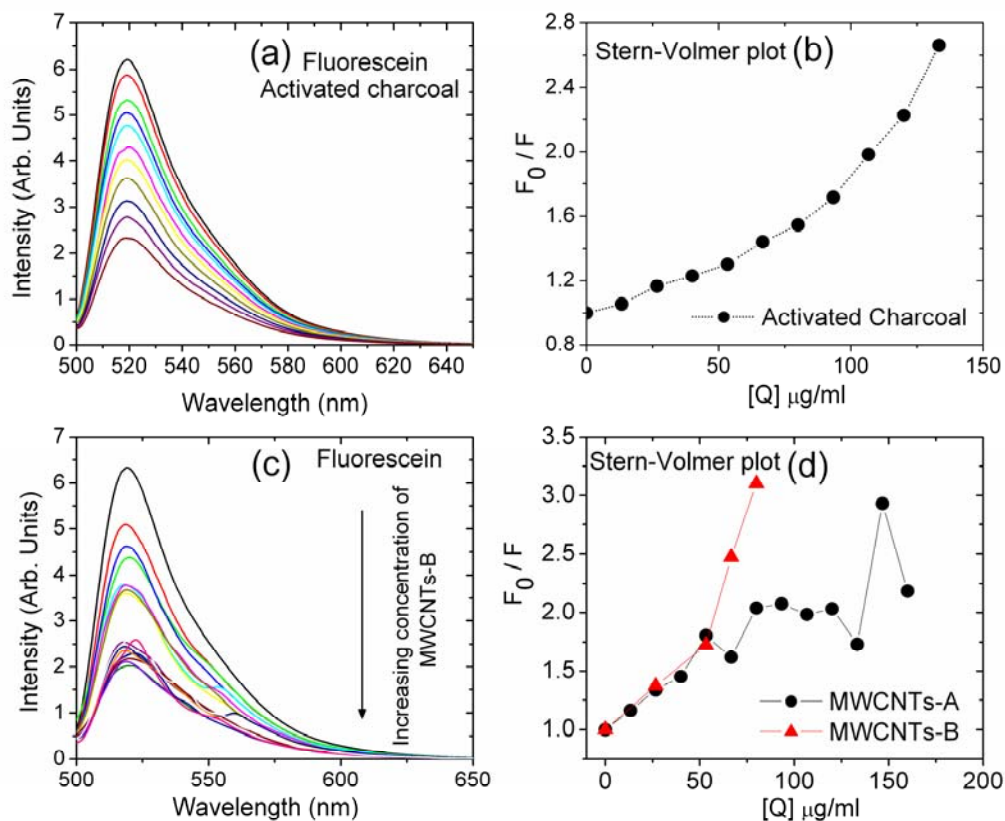


Figure 7-15: Stern-Volmer plot of quenching of Fluorescein using (a) activated charcoal and (b) for two types of MWCNTs namely MWCNT-A and MWCNT-B.

Volmer plot. Stern-Volmer plot shows F_0/F varies linearly with increasing [Q] i.e concentration of dispersed graphite. Graphite shows linear stern volmer plot in contrast to the carbon nanotubes. In this case only static quenching is involved. For graphite, the value of F_0/F observed experimentally (~ 2) is much lower than the SWCNTs and MWCNTs for same concentration. Ball milled graphite also shows linear Stern-Volmer

plot with slightly smaller value of F_0 / F . Ball milled graphite shows slight decrease in quenching efficiency due to decrease in sp^2 content, required for π - π interaction. Ball milling of graphite do not enhance quenching effect of graphite. This indirectly proves that structural defects in CNTs act as sites of enhanced dipole required for surface energy transfer in case of carbon nanotubes. In case of graphite due to absence of any absorption peaks (zero band gap, conductor) do not show any significant improvement of quenching efficiency contrary to the SWCNTs. Fig. 7-14 (c) shows the effect of SWCNTs functionalized with carboxylic group on PL intensity of Fluorescein. In this case all the dangling carbon bonds are satisfied after functionalization with COOH group. Fig. 7-14 (d) shows the Stern-Volmer plot for SWCNT-COOH quenched Fluorescein, Rhodamine 6G and Quinine sulphate. Quenching efficiency of SWCNT-COOH was found to be much lower than the as procured SWCNTs, but higher than the vacuum annealed SWCNTs-700°C containing fewer defects. Experiment with SWCNT-COOH shows that dangling bonds are important for quenching. Decrease in the amount of dangling bonds leads to decrease in the value of F_0 / F in case of COOH-SWCNT. Even SWNT-COOH shows higher quenching efficiency for Rhodamine 6G than the Fluorescein and Quinine Sulphate due to surface adsorption, as discussed before. Fig. 7-15 (a) shows the Stern-Volmer plot for a well known adsorber activated charcoal. It is interesting to observe that F_0 / F value is quite low (only ~ 2.8) in case of activated charcoal as compared to SWCNTs. Visibly the PL quenched by carbon nanotubes does not recover whereas, activated charcoal gives a turbid solution and Graphite powder does not quench efficiently. In case of Graphite, PL recovers back after some time showing again the green emission from Fluorescein.

Another possible mechanism of quenching could be Surface energy transfer (SET) from fluorophores to metal nanoparticles. SET originates from the interaction of the electro-magnetic field of the donor dipole with the free conduction electrons of the accepting metal. Metal nanoparticle Iron, Nickel, Cobalt nanoparticles which were used in the synthesis of carbon nanotube as catalyst has also got quenching properties [351]. In nanotube sample the metal residue was estimated to be 2 % by weight using Thermogravimetric (TGA), and Energy dispersive X-ray (EDX) analysis. EDX shows the presence of Cobalt and Molybdenum. These metal nanoparticles were used as catalyst during growth and even after purification it was not completely removed as observed in transmission electron microscope. We studied the extent of quenching due to these metal nanoparticles as well as their salt solution and found that decrease in PL intensity extremely low with the salt. We also studied quenching effect of two MWCNTs having different amount of metallic impurities. Fig. 7-15 (d) shows comparative study of MWCNTs-A and MWCNTs-B (containing lower metallic impurities) on F_0 / F . MWCNTs-A shows lower value of F_0 / F as compared to MWCNTs-B. It is interesting to note that MWCNTs-B contains very low amount of metallic residue but shows comparatively higher value of F_0 / F . From our ESR studies it is found that MWCNTs-B have more dangling bonds than MWCNTs-A, and hence larger quenching efficiency for MWCNTs-B is justified.

Static quenching may arise due to formation of non-fluorescent complex between defect sites (generated during acid purification of carbon nanotubes) and the fluorophores. Non-covalent attachment of dye occurs through hydrophobic interaction [327]. Since we did not observe any significant new peak in Uv-Vis spectra after addition of nanotubes,

thus the binding may occur through a non-covalent π -stacking interaction. Some of the earlier reports discard the quenching through energy transfer to the CNTs [352], while recent studies shows that a small number of extra holes or electrons in carbon nanotube can quench excited states through a non-radiative Auger recombination mechanism [353].

7.3.3 Time Resolved Photoluminescence (TRPL)

TRPL measurements were performed to isolate contribution of dynamic quenching. Fig. 7-16 (a) shows typical TRPL spectra for Fluorescein and Rhodamine 6G showed single life time 4.05 ns and 4.12 ns respectively before quenching, whereas Quinine sulphate required two exponential to fit representing two life times 20.541 ns (channel-1) and 0.893 ns (channel-2), Channel-1 accounting for 98.9 % of the process. Fig. 7-16 (b) shows variation of τ_0 / τ with concentration of SWCNTs, MWCNTs-A, SWCNTs-700 °C (less defective) and graphite. Error in the calculated PL life time measurements was only 0.1 %. It is interesting to observe the τ_0 / τ roughly increases with increasing concentration [Q], rather than remaining constant at $\tau_0 / \tau = 1$ (condition for a perfect static quenching). Moreover, it is does not follow the relation $F_0 / F = \tau_0 / \tau$ (condition for a perfect dynamic quenching). τ_0 / τ shows an intermediate behavior. This clearly indicates involvement of combined dynamic and static quenching. Dynamic component is more prominent in SWCNTs than the SWCNTs-700°C and MWCNTs, and it hardly shows any variation in case of graphite as compared to nanotubes. This is because number of dangling bonds in SWCNTs (defective) is comparatively higher than the SWCNTs-700°C and MWCNTs. Fig. 7-16 (c) shows decrease in the life time for Quinine sulphate and Fig. 7-16 (d) for Rhodamine 6G respectively.

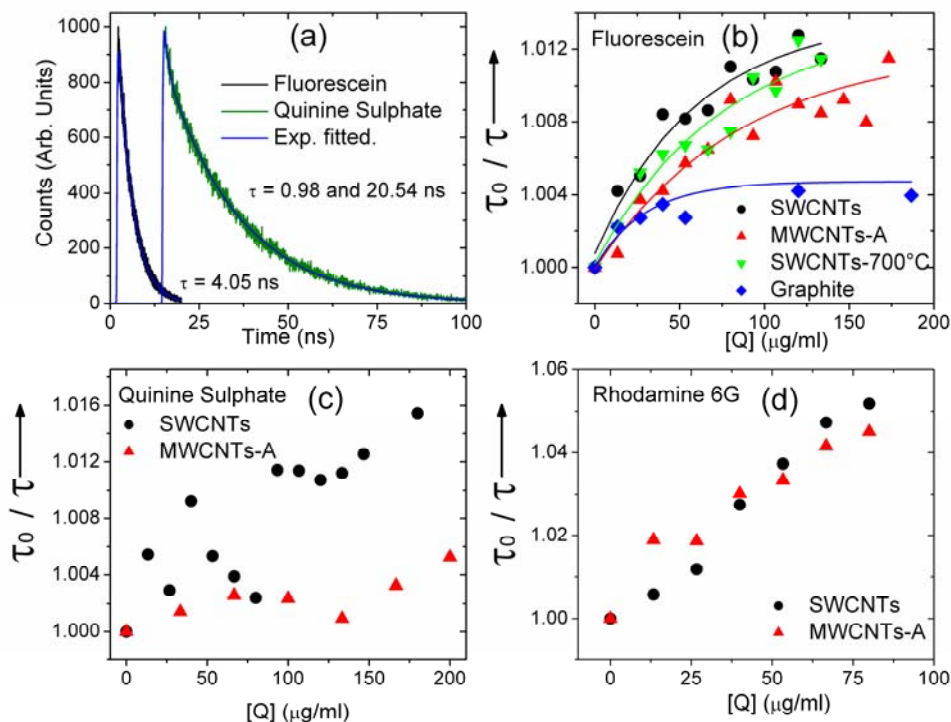


Figure 7-16: (a) TRPL spectra of Fluorescein and exponential fit to the PL decay curve of Fluorescein ($\tau = 4.05$ ns) and Quinine sulphate ($\tau = 0.98$ ns and 20.54 ns, two exponential components required) (b) Change in the ratio time constants with concentration. Monotonic decrease in the fluorescence life time was observed for Fluorescein, Rhodamine 6G and Quinine sulphate. (c) Variation in the ratio of decay time (τ_0/τ) of PL of Quinine sulphate with concentration of SWCNTs and MWCNTs-A. (d) Variation (τ_0/τ) of Rhodamine 6G with concentration of SWCNTs-A and MWCNTs-A.

7.3.4 Surface adsorption of fluorophores on nanotube

Adsorption is a process where a solid is used for removing a soluble substance from the water. Every kind of carbon has its own adsorption isotherm. Fig. 7-17 shows the variation of amount of fluorophore with the changing concentration of CNTs. For adsorption analysis, using Beer-Lambert's (eqn. 8) law the concentration of fluorophore was estimated in the solution before and after addition of carbon nanotubes.

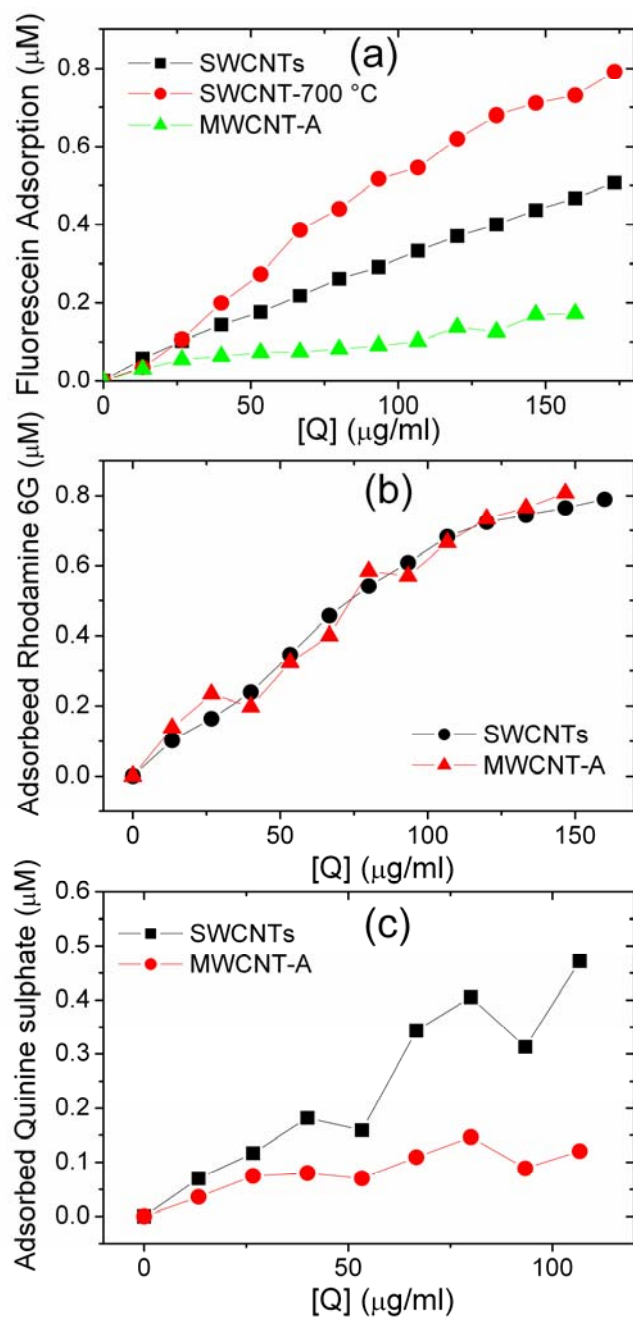


Figure 7-17: Adsorption isotherms for (a) Fluorescein (b) Rhodamine 6G and (c) Quinine sulphate using SWCNTs, SWCNTs-700 °C and MWCNTs-A. In case of Fluorescein and Quinine sulphate adsorption linearly increases with increasing concentration of nanotubes, while in Rhodamine 6G it saturates at higher concentration of CNTs as shown by plateau region in Fig. (b)

$$c = \frac{A}{\alpha l} \quad (7-8)$$

Where A (Absorbance) is known experimentally from absorption spectra, value of extinction coefficient α (cm^{-1}/M) is known from literature [347] and l is the length of the quartz cuvette used for experiment (10 cm). Adsorbed amount of fluorophore (q_e) was estimated after subtracting the value of concentration of fluorophore before and after addition of CNTs in each step. Weight of the fluorophore adsorbed [A] was calculated by dividing the number of micro-moles to the molecular weight, 332.31 gm for fluorescein, 479.02 gm for Rhodamine 6G and 391.47 gm for Quinine sulphate. Fig. 7-17 (a) shows amount of fluorescein adsorbed by SWCNTs, vacuum annealed SWCNTs-700°C and MWCNTs. It is interesting to note that amount of fluorescein adsorbed by vacuum annealed SWCNTs-700°C is more than the SWCNTs (virgin), and MWCNTs shows the least adsorption for same weight. Although SWCNTs shows lesser adsorption but shows strong quenching effect and this clearly shows that structural defects play a major role for PL quenching. This is a novel finding from our experiment. Fig. 7-17 (b) shows the change in the weight of adsorbed Rhodamine 6G with increasing concentration of carbon nanotubes. Contrary to the Fluorescein and Quinine sulphate, Rhodamine 6G is equally adsorbed by both SWCNTs and MWCNTs. Another interesting observation, adsorption of Rhodamine 6G does not linearly increase with increasing concentration of CNTs, it reaches saturation indicating very little amount of Rhodamine 6G molecules left in the solution. Fig. 7-17 (c) shows the variation of amount of Quinine sulphate adsorbed with concentration of CNTs, which is almost linear increase with [Q]. Similar to the fluorescein, Quinine sulphate is less adsorbed by MWCNTs than SWCNTs. Higher slopes of adsorption isotherms shown in Fig. 7-17 indicates a high affinity of fluorophores

towards nanotubes samples. A plateau value approaching at higher concentrations shows a complete surface coverage and hardly any Rhodamine 6G molecules left in the solution.

The adsorption isotherms have been analyzed using both Langmuir (left side) and Freundlich models (right side) to understand further the nature of interaction between fluorophores and nanotubes as shown in Fig. 7-18. Langmuir isotherms model represents monolayer adsorption of molecules on the surface, whereas the Freundlich isotherm represents multilayer adsorption of molecules on the surface. Langmuir isotherm is expressed as

$$[A] = \frac{Q_m b [Q]}{1 + b [Q]} \text{ or, } \frac{[Q]}{[A]} = \frac{1}{Q_m b} + \frac{1}{Q_m} [Q] \text{ (Linear in [Q])} \quad (7-9)$$

and Freundlich isotherm is expressed as,

$$[A] = K_f [Q]^{1/n} \text{ or, } \log [A] = \log K_f + \frac{1}{n} \log [Q] \text{ (Linear form)}, \quad (7-10)$$

where, $[A]$ is the amount of fluorophore adsorbed by $[Q]$ weight of CNTs. Q_m represents maximum adsorption capacity, K_f Freundlich affinity coefficient and n represents Freundlich exponent factor (n). From Fig. 7-18 linear line profile is expected if it follows a particular isotherm either Langmuir isotherm or, Freundlich isotherm. Fig. 7-18 (a) and (b) shows Langmuir and Freundlich isotherms respectively for Fluorescein adsorbed on SWCNTs and SWCNTs-700°C. Behavior of Langmuir isotherm in this case is far away from being linear, whereas Freundlich isotherm shows an excellent fit to the data points giving $R^2 = 0.997$. The value of slope and intercept obtained linear fit to eqn. (10) i.e, $\log [A]$ vs. $\log [Q]$ give values of inverse of the Freundlich exponent factor (n) and

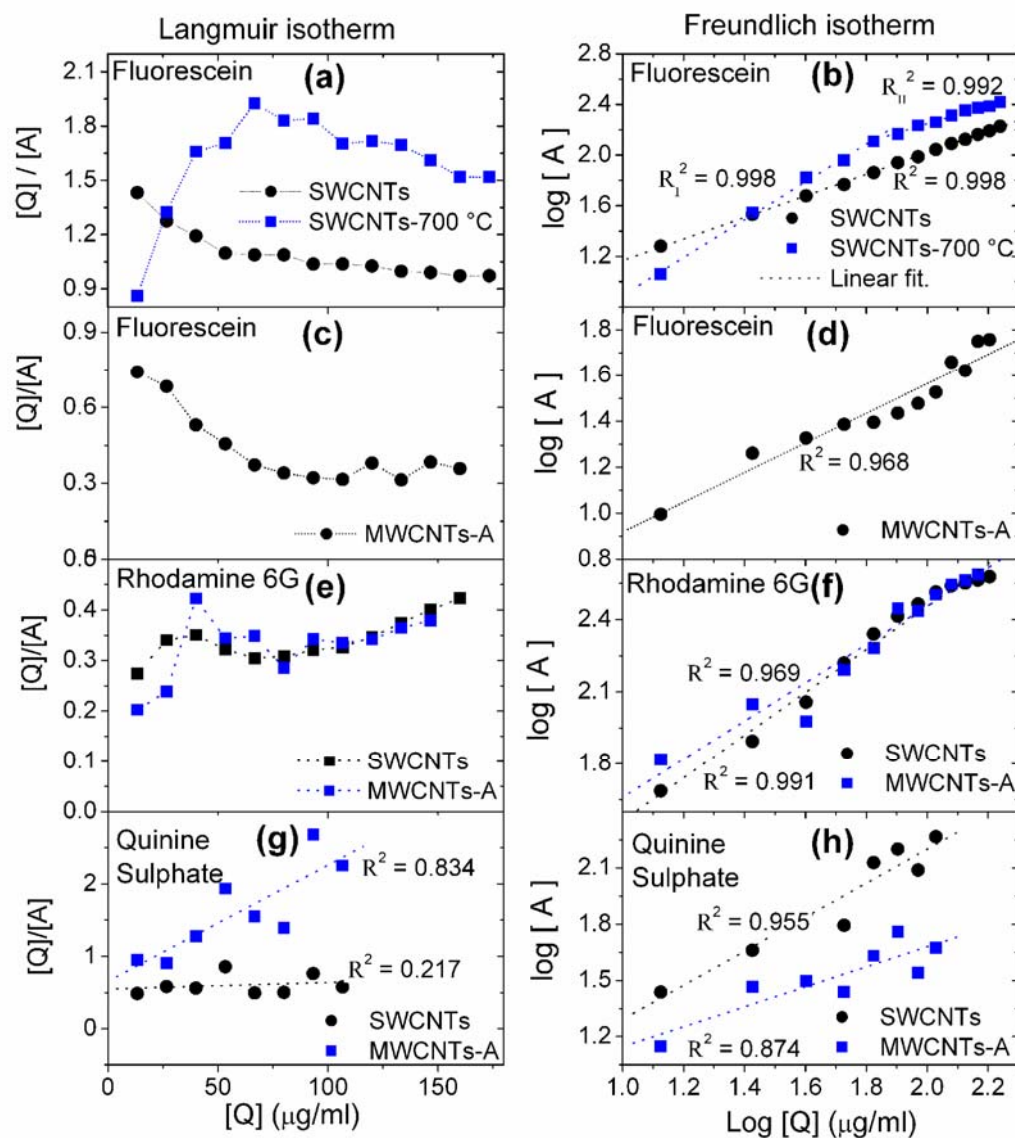


Figure 7-18: Langmuir (left side) and Freundlich isotherm (right side) models for adsorbed fluorophores on carbon nanotube surface. Adsorption of fluorescein on SWCNTs and SWCNT-700 °C surface is shown by (a) Langmuir isotherm and (b) Freundlich isotherm. Linear fit to the experimental data points are shown by dotted line. Freundlich isotherm model best fits to the experimental data points showing multilayer adsorption. (c) and (d) shows Langmuir and Freundlich isotherm for adsorption of Fluorescein on MWCNTs-A. Similarly (e) and (f) shows Langmuir and Freundlich isotherm respectively for adsorption of Rhodamine 6G on SWCNTs (●) and MWCNTs-A (■). Langmuir and Freundlich isotherm for adsorption of Quinine sulphate of the surface of SWCNT and MWCNT-A are shown in Fig. (g) and Fig. (h) respectively.

Log of Freundlich affinity coefficient K_f . Value of Freundlich exponent factor (n) comes out to be 1.174 for SWCNTs that indicates a contribution of adsorption, as it is within a range of 1-10.[354] In case of SWCNTs-700°C, adsorption behavior can be divided into two segments, one for lower concentration and other for higher concentration of nanotubes due to difference in interaction for adsorption in the two concentration ranges, both giving excellent $R_f^2 = 0.988$ and $R_{II}^2 = 0.992$ values,. For SWCNTs-700°C the value of n was found to be 0.66 for lower concentration region and 1.35 for higher concentration. High CNT concentration may influence the physical characteristics of the solid-liquid suspensions, such as by increasing the viscosity and inhibiting the diffusion. Fig. 7-18 (c) shows the Langmuir isotherm and Fig. 7-18 (d) Freundlich isotherm for MWCNTs-A. It is interesting to note that the behavior of MWCNTs-A is similar to the annealed sample SWCNTs-700°C in Langmuir isotherm, and it is not linear in behavior. This indicates Langmuir model poorly represents the physical process of adsorption in this case. On the other hand linear fitting for the Freundlich model shows $R^2 = 0.968$, indicating that quenching process does not perfectly follow the Freundlich model. In the case of adsorption of fluorescein on MWCNTs, the value of n was found to be 1.548. Similarly fitting for adsorption of Rhodamine 6G on nanotubes is shown in Fig. 7-18 (e) for Langmuir and Fig. 7-18 (f) for Freundlich isotherm. In the case of Rhodamine 6G as well Freundlich isotherm is nearly linear as compared to Langmuir isotherm giving $R^2 = 0.991$ and 0.969 for SWCNTs and MWCNTs. The value of Freundlich exponent factor for Rhodamine 6G adsorbed on SWCNTs was found to be 1.121 and 1.256 for MWCNTs-A. Fig. 7-18 (g) shows the Langmuir isotherm and Fig. 7-18 (h) shows the Freundlich isotherm for Quinine sulphate adsorption on carbon nanotubes. Interestingly, in this case

nature of both the isotherms were linear in nature, but Freundlich isotherm fits better as represented by $R^2 = 0.955$ and 0.874 for SWCNTs and MWCNTs. For adsorption of Quinine sulphate, the Freundlich exponent factor (n) was found to be 1.101 and 1.876 for SWCNTs and MWCNTs respectively. Thus from this study it is clear that adsorption of fluorophores on the carbon nanotubes take in the form of multilayer adsorption of molecules. Slight deviation observed from Freundlich model represents fluctuations arising from the probabilistic nature of adsorption sites leading to the slight non-linearity. Although there has been attempt to model this with non-linear models like Brunauer-Emmett-Teller model (BET) and Polanyi-Manes model (PMM) [355], but within the experimental error and taking consideration of various factor related to carbon nanotubes like structure, purity, dispersibility problem etc, Freundlich model is found to best represent the physical process of adsorption of fluorophores on the nanotube surface. Large value of Freundlich exponent factor (n) for SWCNTs shows higher adsorption on SWCNTs than the MWCNTs.

In agreement to our results, through adsorption isotherms modeling other studies on organic chemical adsorption on CNTs have shown that SWCNTs are heterogeneous adsorbents and Freundlich equation describes well the interaction between organic molecules and SWNTs [343]. Organic chemicals and CNT interactions shows adsorption heterogeneity and hysteresis due to simultaneous involvement of several mechanisms namely, π - π bonds, electrostatic interactions, and hydrogen bonds. In case of organic chemicals, the dominant mechanism was found to be different for different types of chemicals (such as polar and nonpolar) requiring different models to predict organic chemical-CNT interaction. The major factor affecting adsorption by CNTs is their suspendability, which strongly affects their mobility, exposure and risk in the

environment. Heterogeneous nature of adsorption has been explained in terms of (a) presence of high energy adsorption sites, such as CNT defects [356], functional groups [357], and interstitial and groove regions between CNT bundles [358] (b) due to condensation such as, surface and capillary condensation of gas or liquid adsorbates. We have observed that the three fluorophores studied here shows quantitatively different behavior towards SWCNTs, as shown by different quenching efficiencies, different isotherms for adsorption. This is due to the different affinities shown by different dyes depending upon the molecular geometry and charge. It has been reported that molecules with planar structure and high charge load are favored for the adsorption [359].

7.3.5 Discussion

In the absorption spectra of different fluorophores with and without CNT, absence of a strong red shift in the overall spectrum suggests that there is minimal complexation of the dye with the nanotubes [340, 360]. The structure / morphology dependent adsorption reveals that π - π stacking is the main driving force responsible for the dye-CNTs interactions. It has been reported that the planar molecules easily approach CNTs via a face-to-face conformation [359], which is favorable for π - π interactions between the conjugated aromatic chromophore skeleton and the nanotubes. On the contrary, the non-planar molecules are kept apart from CNTs due to spatial resolution, resulting low π - π interactions with the CNTs [359]. Through absorption studies we observed preferable adsorption for Rhodamine 6G. Relatively high value of quenching efficiency observed in the case of Rhodamine 6G is due to combined effect of high surface adsorption and FRET. Quantitative analysis of adsorption data shows multilayer adsorption of fluorophores on the nanotube surface as represented by Freundlich Model. Small deviation from the

Freundlich model represents probabilistic nature of surface adsorption of fluorophores on the nanotubes surface.

CNTs acts as an efficient quencher in various PH ranges, since the three fluorophores studied were prepared in different PH medium, fluorescein in alkaline medium, Rhodamine 6G in water and Quinine sulphate in acidic medium. The amount of fluorescein adsorbed by vacuum annealed SWCNTs-700°C is much larger than the unannealed SWCNTs (defective) and MWCNTs. MWCNTs shows minimum adsorption of fluorescein. We have shown in chapter-3 that unannealed SWCNTs contains large amount of defects that can be substantially removed by vacuum annealing at 700 °C [346]. These annealed samples have higher thermal stability and lower D-band intensity in Raman spectra [346]. SWCNTs (defective) show lesser adsorption but have stronger quenching capability. Thus surface adsorption can not properly account for the extent of quenching observed. Besides surface adsorption, role of other suspects like metallic nanoparticles and other forms of carbons particularly amorphous carbon and graphite present as impurities in CNTs samples were eliminated through controlled experiments. Experiment with two samples containing different amount of metallic impurities eliminates its role in large quenching effect observed. Other forms of carbon like graphite and activated charcoal shows very low (only ~ 3 %) quenching efficiency.

Thus, structural defects primarily control the PL quenching efficiency of SWCNTs for standard fluorophores. Stern-Volmer plot was found to be non-linear indicating combined effect of static and dynamic quenching effect. Presence of dynamic quenching contribution was confirmed from time resolved photoluminescence studies. TRPL studies shows monotonic change in PL lifetime with increasing concentration of quencher. Since the change in τ_0 / τ was very small in comparison to F_0 / F , we concluded negligibly

small contribution of dynamic quenching to the observed effect. Hence, static quenching plays the dominant role. Plot of $\left(\frac{F_o}{F}-1\right)\frac{1}{[Q]}$ versus $[Q]$ shows non-linear behavior in contrast to linear behavior expected for combined static and dynamic quenching. Such positive deviation in the Stern-Volmer plot is observed when the extent of quenching is large. Weak association between carbon nanotubes and fluorophores through π - π interaction do not form a ground state complex, instead it appears that static component is due to the quencher being adjacent to the fluorophore at the moment of excitation. These closely spaced fluorophore-quencher pairs are immediately quenched and thus appear to be dark complexes. This type of apparent static quenching is usually interpreted in terms of a “Sphere of action” within which the probability of quenching is unity. The modified form of the Stern-Volmer equation (eqn. 7) represents such situations. Experimental data point follows compressed exponential behavior, rather than the “Sphere of action” model. This is due to very small dynamic quenching contribution, leading to $K_D \approx 0$. Mathematically in such situation ‘modified Stern-Volmer equation’ given by eqn. 7 simplifies to experimentally observed compressed exponential form. Physically this represents the situation when the fluorophore and quencher are very close, there exists a high probability that quenching will occur before these molecules diffuse apart. As the quencher concentration increases, the probability that a quencher is within the first solvent shell of the fluorophore at the moment of excitation increases. Exponential dependence in eqn. (7) comes from Poission probability distribution for the probability of finding a volume V with n quencher. Compressed exponential form arises from the rearrangement of fluorophores on CNTs with highly reactive sites due to presence of defects.

A number of possible mechanisms have been reviewed by Tan et. al. for the deactivation of excited fluorophores resulting in effective quenching through energy transfer or photoinduced electron transfer in association with the property of the fluorophore, the conjugation mode, and the local environment [335]. It is thought that either energy transfer or electron transfer might contribute to such high quenching efficiency. It is believed that FRET is the dominant process responsible for the high efficiency of quenching observed experimentally. FRET is based on the concept of fluorophore as an oscillating dipole, which can exchange energy with another dipole with a similar resonance frequency. Structural defects in the SWCNTs increase the dipole moment and interact more efficiently with the fluorophore, giving rise to very efficient quenching effect observed experimentally.

SWCNTs are different from organic quenchers because they show superior quenching efficiency for a variety of fluorophores, with low background and high signal-to-noise ratio, along with other advantages derived from nanomaterials itself. SWNTs are suitable for biosensors compared to the organic quenchers because they are soluble / dispersible in water. Second they have ultrahigh surface area for loading as nanocarriers, including multiple molecules along the nanotube sidewall for multiplexed sensing. The combination of SWNTs with functional nucleic acids has potential to be used as biosensor. SWNTs could be intergrated into sensor arrays, for high throughput detection of multianalytes with good sensitivity and specificity.

7.4 Conclusions

Our study shows that defective SWCNTs act as an efficient fluorescence quencher. Surface defects or dangling bonds are believed to be responsible for the efficient

fluorescence quenching. Structural defects in the carbon nanotubes can increase the dipole moment and interact more efficiently with the fluorophore. Besides the surface adsorption, FRET is the dominant mechanism for the observed quenching. Stern-Volmer plot was found to follow compressed exponential behavior, which is close in behavior to “sphere of action” model used for the cases when extent of quenching is large along with molecular rearrangements. Exponential behavior observed is due to negligibly small contribution of dynamic quenching as confirmed from TRPL studies. Although the surface adsorption of fluorescein on less defective sample (SWCNT-700°C) was higher than SWCNTs (defective sample) but it showed lower quenching efficiency. Minor contribution of surface adsorption was found towards PL quenching, except Rhodamine 6G where we observed significant contribution of it leading to much higher quenching efficiency. Studies with other carbon materials such as graphite and activated charcoal show very low quenching efficiency (~ 49 %) for fluorescein. SWCNTs show quenching efficiency of 98.1 % for fluorescein, whereas less defective SWCNTs show 65.6% quenching efficiency. MWCNTs show quenching efficiency of only ~ 49 % similar to graphite and activated charcoal. Graphite shows very poor quenching efficiency and a linear Stern-Volmer plot. Comparative study with two MWCNTs sample containing different amount of metallic impurity and amorphous carbon eliminates any possibility of metallic nanoparticles towards observed quenching. This is the first report presenting comparative study of quenching efficiency of SWCNTs, MWCNTs and various other forms of carbon. Adsorption studies showed surface adsorption on carbon nanotubes follows Freundlich isotherm, indicating multilayer adsorption of fluorophores on the nanotube surface. The defect enhanced quenching efficiency and knowledge of interaction between commonly

used fluorophores and carbon nanotubes paves the way for numerous biological and optoelectronic applications.



Chapter -8

Summary and Conclusions

8.1 Summary and Conclusions

Carbon nanotubes (CNTs) contain various types of structural defects depending upon the growth conditions and growth method. Depending on the nature of defects, it influences the electronic and optical properties of CNTs to different extents. Defects in CNTs are usually undesirable since its presence may have detrimental effects on the reliability and performance of the electronic and optical devices. Control, modification and monitoring of defects are immensely important for the defect engineering in CNTs. Interestingly possibility of incorporation of controlled amount of desired type of defect through various methods opens a new era of single molecular electronic and active photonic devices. Inter-tube linkages formed by incorporation of pentagon-heptagon pairs results into semiconductor-metal or, semiconductor-semiconductor junctions which can be used as components in electronics or, active quantum electro-optical devices. Recently a few experimental studies have demonstrated defect enhanced electrical conductivity and its tunability, enhanced chemical sensitivity and quicker electrochemical response, enhanced dispersion in DNA solutions, control of transport properties of metallic atoms along the CNT surface. For understanding and utilization of defect engineered properties, spectroscopic and microscopic methods of characterization and identification of such defects is essential. However, very few studies have addressed the characterization of defects and diameter dependent properties in CNTs.

This thesis is an attempt in the direction of identification of defect related spectroscopic signatures of CNTs using Raman spectroscopy and EPR spectroscopy. Control and modification of defects in CNTs through vacuum annealing and ion irradiated

have been demonstrated and investigated by using XRD, TGA and Raman and EPR spectroscopy. Low energy ion-irradiations experiments were performed using four different ions at various fluences to investigate the possibility of defect engineering in SWCNTs and MWCNTs. We have demonstrated defect enhanced photoluminescence quenching efficiency of CNTs in several fluorophores, a property highly desirable for CNTs applications as biomarkers.

In spite of huge potential applications of MWCNTs, the knowledge of diameter dependent spectroscopic features are lacking in literature. We have systematically investigated diameter dependence of interwall separation, thermal stability and defects through HRTEM and spectroscopic features in XRD, Raman spectroscopy and EPR spectroscopy for MWCNTs of various diameters in the ranges 5-100 nm.

The major contributions of the present work are summarized below.

A. Methodological Contributions

This thesis presents a method for estimating diameter of MWCNTs through XRD and Raman spectroscopy. We have demonstrated a way to estimate different phases of carbon or forms of CNTs present in the sample by deconvoluting thermogravimetric curves with reverse Sigmoidal fitting as compared to the commonly used Gaussian fitting. A superior method of residual catalyst estimation has been demonstrated through magnetization measurements as compared to the commonly used method of thermogravimetric analysis.

B. Diameter Dependent Properties of MWCNTs

X-ray diffraction profiles show diameter dependent interwall separation due to decrease in $d(002)$ spacing as the diameter of the MWCNTs increases, in close agreement with the

HRTEM studies. Other diffraction peaks shows diameter dependence in terms of variation of intensity of (101) peak and FWHM of (100) peak. These results demonstrate the capability of XRD line profile analysis for understanding the intertube interactions for large diameter nanotubes and it further allows probing the strain and curvature effect for the small diameter nanotubes. From the observed diameter dependence of various spectral features, we have found that XRD is a very powerful non-destructive tool for characterization of MWCNTs.

We have presented a systematic analysis of the diameter dependent spectral features in Raman spectra of SWCNTs and MWCNTs. Deconvolution of the Raman spectra for different diameter MWCNTs show gradual decrease of the semiconducting component of the G^- band frequency with increasing diameter, explained on the basis of intertube interactions. Our studies clearly show that phonon spectra of low diameter MWCNTs are similar to that of the SWCNTs and for large diameter nanotubes, intertube interactions becomes significant. These results demonstrate the capability of Raman line profile analysis for understanding the intertube interactions for large diameter nanotubes and it also allows probing of strain and curvature effect in small diameter nanotubes.

A systematic diameter dependence of oxidative stability was observed for MWNTs associated with curvature effects and lattice strain. Role of defects in the oxidative stability was elucidated through studies of vacuum annealed samples. It was also shown that magnetic impurities (catalysts) do not influence the oxidative stability of SWCNTs/MWNTs. Similarly, a proper deconvolution of the EPR spectra show diameter dependent g-value for conduction electron spin resonance (CESR) peak originating from interaction between conduction electrons residing on nanotubes and conduction electron of

metal nanoparticles. The g-value of the ferromagnetic resonance (FMR) peaks shifts away from the free electron g-value with increase in the metal residue content, representing the amount of metal metallic residue content in the sample.

C. Spectroscopic Studies of Structural Defects

Our investigations on pristine and processed SWCNTs show new intermediate frequency modes (IFM) modes in the range $400\text{-}1200\text{ cm}^{-1}$ and additional feature in the range $1600\text{-}2400\text{ cm}^{-1}$ in Raman spectra. Few of the IFM modes observed at 479, 668, 704 and 870 cm^{-1} are common to all samples and are inherent to CNTs with structural defects. Laser induced defects shows modification of IFM modes giving rise to new IFM modes at 807, 867 and 929 cm^{-1} of varying intensity and widths depending upon defect density. IFM modes inherent to CNTs particularly 668 cm^{-1} peak shows modification of lineshape and Raman frequency with increasing defect density. Similarly, the defect related 929 cm^{-1} peak shifts towards higher frequency with increasing defect concentration. More interestingly, vacuum annealing assisted defect removal shows reduction in the intensity of IFM modes observed at 709 cm^{-1} and a broad peak in the region $756\text{-}1011\text{ cm}^{-1}$, while the characteristic peak of CNTs observed at 675 cm^{-1} sharpens with reducing defect density and it shifts towards lower frequency. Further, we have monitored the modification of IFM modes upon Ar^+ and N^+ ion-irradiation. Peak at 669 cm^{-1} disappears with increasing defect density created by N^+ ion irradiation, while new peaks at 804, 868 and 926 cm^{-1} evolve with the increasing defect concentration. Similarly, Ar^+ ion irradiation shows decrease in the intensity of CNT characteristic peak observed at 669 cm^{-1} and evolution of two new peaks at ~ 814 and 931 cm^{-1} related to structural defect. Besides these modes, SWCNTs shows a number of modes at 1724.3, 1909.2, 2173.5 and

2270.7 cm^{-1} , the intensity of these peaks decrease with structural improvement upon vacuum annealing, showing their origin from structural defects.

Room temperature photoluminescence (PL) bands observed at ~ 2.05 and ~ 2.33 eV for pristine SWCNTs and MWCNTs is argued to originate from the structural defects in CNTs. Similarly, after aniline functionalization, visible PL emission was observed at 2.06 eV and 2.21 eV from SWCNTs and at 2.03 and 2.19 eV from MWCNTs. PL excitation spectroscopy after aniline functionalization shows creation of a broad energy state in case of SWCNTs, while sharp energy states in case of MWCNTs. Such visible PL from CNTs is believed to arise from band gap opening of CNTs due to structural defects created during reflux reaction.

We have demonstrated a method for deconvolution of EPR spectra, to quantify the relative contributions from metallic impurities and conduction electrons CNTs. A sharp feature in EPR near $g = 1.998$ disappeared upon vacuum annealing confirming its origin as structural defects in CNTs. This is consistent with our understanding of origin of visible PL from structural defects in pristine CNTs. EPR studies on N^+ ion irradiated MWCNTs showed several new EPR active centers related to defects at $g = 2.462, 2.068, 2.074, 1.986, 1.9882$ and 1.913 . We have presented a systematic study of the temperature dependence of EPR line profile on samples having different amount of metal residues, which provides knowledge of the characteristic EPR features from CNTs and variation in the FMR lineshape originating from metal nanoparticles. Temperature dependent studies confirms that a Dysonian like sharp feature at $g = 2.000$ arises from conduction electrons residing on the nanotube walls, while paramagnetic defects gives rise to a Gaussian like feature at $g = 2.009$.

D. Defect Annihilation through High Vacuum Annealing

Vacuum annealing studies of pristine and ion irradiated SWCNTs and MWCNTs reveal that optimum annealing temperature for strain relaxation and structural defect removal is 700 °C for SWNTs and 500 °C for MWNTs. The difference in the nature and concentration of structural defects between SWNTs and MWNTs leads to different annealing temperatures required for defect annihilation.

E. Engineering of CNTs Using Ion-irradiation

Through systematic studies on the effect of ion irradiation in CNTs, we have found the optimum dose of irradiation for structural improvement for H^+ , C^+ , N^+ and Ar^+ ions. In case of H^+ irradiation, structure of SWCNTs improves upon 10^{12} ions/cm². H^+ irradiation at 30 keV only creates point defects. A dose of 10^{13} ions/cm² of C^+ , N^+ at 30 keV shows reduction in the defect density as reflected from improvement of I_G/I_D ratio. Improvement in the structure occurs due to the dynamic annealing effect of accelerated ions. Increase of irradiation energy to 80 keV shows lower reconstructive capability. In case of H^+ and C^+ and N^+ , a dose of 10^{12} and 10^{13} ions/cm² shows constructive behavior, while Ar^+ shows increase in the defect density upon 10^{12} ions/cm² irradiation dose. This is due to higher contribution of electronic energy loss in case of H^+ , C^+ and N^+ ions responsible for constructive effect on lattice defects. While nuclear energy loss dominates in case of Ar^+ ions, which is responsible for destructive effect. Electronic energy loss deposits energy after impingement leading to healing of defects through ion-irradiation induced dynamic annealing. Increase in the nuclear energy loss with increasing mass of incident ions leads to the increase in defect concentration and may lead to re-organization of lattice as observed in case of 10^{13} ions/cm² Ar^+ irradiated SWCNTs. For all ions further increase of

irradiation dose to 10^{14} ions/cm² leads to structural degradation and evolution of new forms of carbon. Irradiation induced defects and renucleation in case of SWCNTs leads to evolution of nano-spring like structures upon 10^{14} ions/cm² with 30 keV N⁺ ions.

MWCNTs show different response towards ion irradiation due to their different structure and lower self healing capacity. Ion irradiation in SWCNTs leads to formation of vacancies and Stone-Wales defects, whereas in MWCNTs it leads to formation of curved graphitic structure. In case of MWCNTs, ion irradiation shows formation of ion-tracks resulting in the stacking faults in the layers. These stacking faults introduce curvature in the walls of MWCNTs, which shows formation of fullerene like structures at 10^{12} and 10^{13} ions/cm² irradiation dose for all ions other than Argon. In case of Ar⁺ a dose 10^{13} ions/cm² leads to the renucleation of diamond like structure. Further increase of irradiation dose to 10^{14} ions/cm² shows formation of curved fullerene like structure in case of C⁺ ion-irradiation, amorphisation of wall of MWCNTs in case of N⁺ and Ar⁺ ions. In-situ study of structural modification of CNTs under electron beam in a HRTEM shows possibility of defect engineering locally.

F. Defect Enhanced Photoluminescence Quenching Effect of CNTs

Though systematic studies of absorption and PL emission, we have demonstrated that structural defects in SWCNTs primarily control the PL quenching efficiency for standard fluorophores. SWCNTs with surface defects were found to be highly efficient (~98%) quencher as compared to the SWCNTs and MWCNTs with fewer defects. Structural defects in the CNTs increase the dipole moment and interact more efficiently with the fluorophores through fluorescence resonance energy transfer. Fluorescence quenching was found to follow a faster-than-exponential behavior with increasing

concentration of CNTs due to large aspect ratio of the CNTs, while an exponential behavior is expected from the 'sphere of action model'. Co-presence of quenching through surface adsorption was also confirmed through absorption studies. Fluorophores are adsorbed on the CNTs surface in the multilayer form following Freundlich isotherm. Defective CNTs were found to adsorb less as compared to the perfect CNTs. We have demonstrated that control and manipulation of defects in CNTs would enable enhanced quenching efficiency of CNTs for various biological applications.

8.2 Scopes For Future Work

IN this work, we have attempted to obtain fingerprint of structural defects in SWCNTs and MWCNTs through spectroscopic studies. Possibility of defect engineering in CNTs through ion irradiation, laser annealing and vacuum annealing has been demonstrated. Finally, application of surface defects in CNTs for efficient fluorescence quenching of standard fluorophores has been demonstrated. Work presented in this thesis opens up several avenues for defect characterization and defect engineering in CNTs for future applications in nanotechnology. Scopes for future works related to this thesis are as follows.

1. In situ monitoring of evolution of structural defects in CNTs during vacuum annealing can be studied. Such studies would provide knowledge of nature and origin of a specific defect and its properties that would be useful for a specific application.
2. Spectroscopic fingerprint of structural defects can be more specifically assigned to a particular kind of structural defect by collecting optical spectroscopy signals using scanning near field optical microscopy, confocal Raman spectroscopy / PL

spectroscopy, surface enhanced Raman spectroscopy along with in situ monitoring of structural defects during ion/ electron beam irradiation.

3. More controlled ion irradiation experiments can be performed with focused electron beam or ion beam at low temperature for introducing a particular kind of defect in CNTs and its effect on electrical/optical properties.
4. High resolution microscopy such as aberration corrected transmission electron microscopy can be coupled with optical techniques to monitor and control the defects in CNTs. This can provide precise knowledge of optical identification of specific defects monitored in electron microscopy.
5. More precise experiments under controlled atmosphere can be performed on annealing of defects in CNTs.
6. For fluorescence quenching purpose, we expect the quenching efficiency to depend upon the nature of CNTs whether it is metallic or semiconducting. We expect different mechanisms of energy transfer for them. This has to be tested on experimental grounds.
7. Defect engineered properties in CNTs can be utilized for bio-sensing applications and there is huge scope for future work in this direction.
8. Finally, these studies can be extended to graphene, the new material of choice. There have been a number of recent attempts reported in literature to understand defect induced modification of properties of graphene.

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