Chapter 8

Characterization and Properties of Carbon Nanotubes

Sanjeev Kumar[*1], Sapna Jain[2], Bhawna Yadav Lamba[3], Pankaj Kumar[4]

[1-4]Department of Chemistry, University of Petroleum and Energy Studies
Bidholi, Energy Acres, Dehdradun, 248007, India

[*1]sanjeevkumar.dubey2@gmail.com; [2]sapnaj22@gmail.com; [3]byadav@ddn.upes.ac.in; [4]pkumar@ddn.upes.ac.in

I. INTRODUCTION

Carbon has always grabbed the attention of scientist due to its high abundance and interesting nature. Carbon is accomplished of establishing many allotropes due to its valency and special property called Catenation. The last few years have beheld the various inventions, developments and small to large scale production of allotropes of carbon with size range in nanometers. Carbon nanotubes (CNTs) are one of them. The size of CNTs is greater or equal to fullerenes but smaller to graphite. Their shape is tubular. It may also be termed as ultra-thin carbon fibre with diameter in the nano scale and length with micrometer size. They have emerged as novel and potential carbon material for practical point of view and they will directly be related to wide range of application in field of nanotechnology.

CNTs can be envisioned as rolled hexagonal carbon networks that are plugged by pentagonal carbon rings. There are two kinds of carbon nanotubes:

(i) single-walled (SWNTs) and

(ii) multi-walled (MWNTs).

Both types of CNTs have wide-ranging electronic, thermal and structural properties. Different characterization techniques are available to analyse their structure and properties.

In this chapter we will specifically focus research investigation on the different properties of CNTs and the different characterization techniques used for analysis of the properties. The account of characterization methods such as SEM, TEM, X-ray diffraction, infrared and Raman spectroscopy are discussed in detail.

II. CHARACTERIZATION AND PROPERTIES

Accurate characterization techniques are needed that can probe surface, chemical and structural properties of CNTs [1].

A. Molecular Structure

We know that CNT is a cylindrical molecule composed of carbon atoms. The structure of a typical SWCNT is illustrated in Fig. 1.

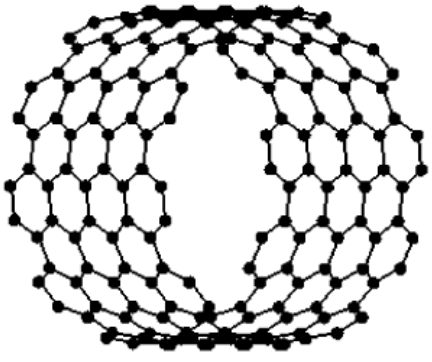


Fig. 1 Molecular structure of CNT

SWNT has a hexagonal pattern that repeats itself in a regular pattern in the space to give the whole CNT. Here is in this periodic arrangement of the carbon atoms, each atom is bonded to three adjacent carbon atoms. The bonding present in the molecule is accountable for the structure. One *s*-orbital and two *p*-orbitals combine to form three hybrid orbitals. So, it is sp^2 hybridized. Each hybrid orbital is at 120 °to each other within a plane, as shown in Fig. 2 [2].

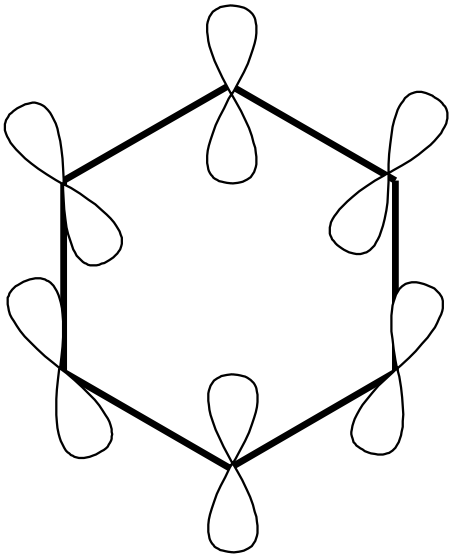


Fig. 2 Basic hexagonal bonding structure for one graphite layer

This covalent bond is formed due to head on overlapping of orbitals is a strong bond which is also referred to as the σ – bond. It is responsible for the extraordinary mechanical properties of CNTs. In addition, the out-of-plane bond, the π-bond, formed due to sideways overlapping is weak bond. The interaction between the layers of MWCNTs and bundles of SWCNTs is due to the presence of weak π-bond. The bonding in CNTs is not pure sp^2 as when the graphene sheets are rolled to form tubes rehybridizaion takes place and it results into formation of a mixture of σ and π orbitals.

B. Optical Property: Infrared (IR) and Raman Spectroscopy

IR spectroscopy works on principle of interaction of electrical component of electromagnetic wave with the dipole moment change in a molecule due to vibrational motions. It gives different bands due to stretching and bending of bonds in a molecule. Thus, IR spectroscopy can detect characteristic vibrational modes and hence can recognize varied organic functional groups on a CNT surface. The different functional groups show various stretching and bending vibrations, in and out of the plane. However, quantitative measure about the functional group concentrations cannot be excerpted and peaks are often hard to distinguish from background features. Furthermore, IR spectroscopy cannot detect some functional groups whose presence has been identified by some other analytical techniques. However, IR can determine the bonding strength between CNT and functional groups present on them.

Raman spectroscopy is based on scattering of light which brings change in frequency of light. The scattering process can be thought of as the incoming photon raising the molecule to a virtual exited level. Raman spectroscopy is based on inelastic scattering of monochromatic radiation. During this process, energy is switched between the photon and the energy levels of molecule. The molecule may gain energy and will scatter photon with lower energy or it may give energy to it, so that the scattered photon is of higher energy than the incident photon.

The Raman interaction leads to two possible outcomes, these are as follows (Fig. 3):

- *Stokes line*: it is the line observed when the molecule absorbs/gains energy and the emitted photon has a lower energy than the incident photon.
- *Antistokes line*: the molecule loses energy and the emitted photon has a higher energy than the incident photon.

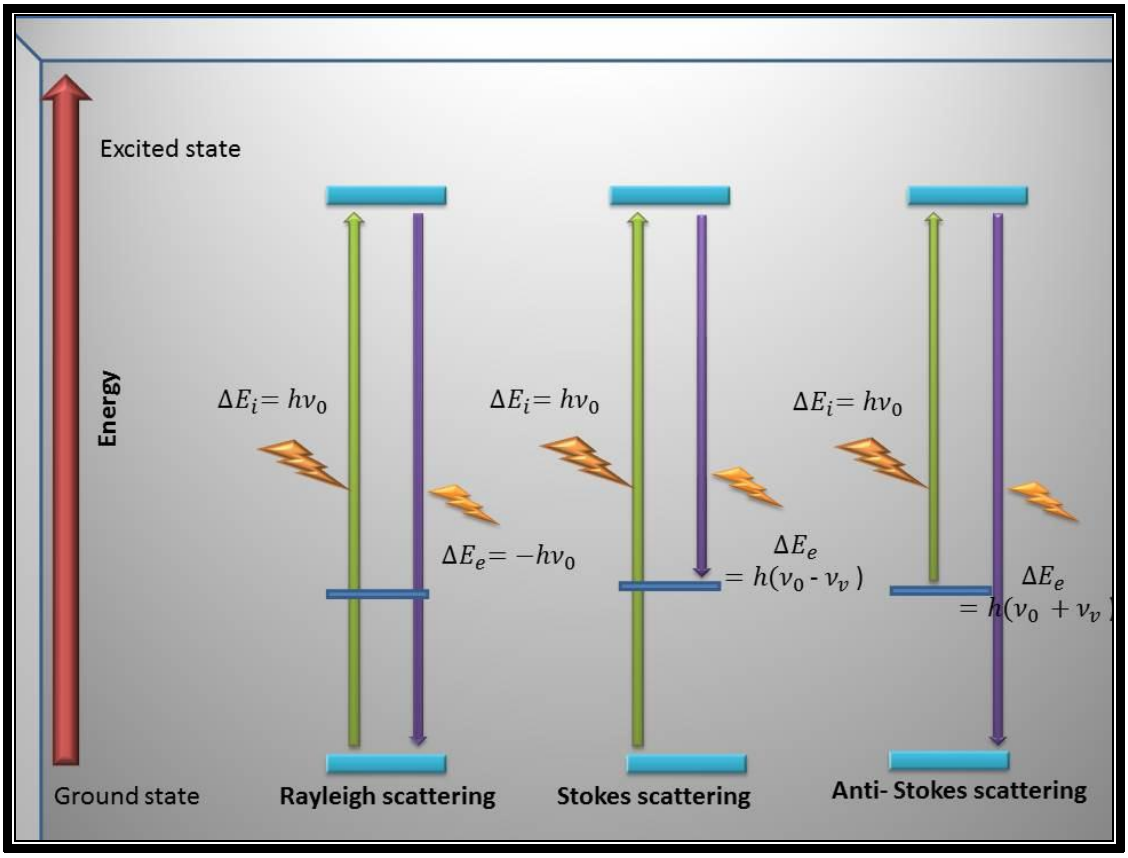


Fig. 3 Energy level diagram for Raman signals

The difference in energy of photons incident is due to change in the rotational and vibrational energy level of the molecule interacting with the light. It gives a good idea about the energy levels of molecule studied by the Raman spectroscopy, which is considered to be one of the most powerful tools for characterization of CNTs. It is a comparatively fast method and does not require the preparation of sample for testing. It can also be called as a non-destructive analysis method in which the compound remains intact.

With the help of Raman scattering, we can study the quality of the material, the microscopic structure of the carbon nanotube, and quantum confinement (both phonon and electron).

It is generally used to quantify quality of the carbon nanotube powders. Since the electronic structure depends on the chirality of a given nanotube, experimental optical probes of the electronic structure can reveal much information about the diameter, chirality, and metallic or semiconducting nature of a SWCNT sample. In the following sections, two important optical spectroscopic techniques that are used to characterize SWCNTs are introduced.

After applying suitable purification procedure, the Raman spectrum of a purified sample will appear as shown in Fig. 4. The Raman-active vibrations of the tangential modes all into two groups: (i) the high-energy modes (HEM) below 1600 cm^{-1} and (ii) the D mode, near to 1350 cm^{-1}.

The most characteristic features for CNTs can be summarized as follows:

1. The high frequency peaks which are the characteristic of CNTs.
2. The low-frequency peak < 200cm^{-1} characterizes the presence of SWNT, which depends upon the radius of CNT.
3. The D mode which assigns the residual and ill-organized graphite.

The optical properties of CNTs refer to absorption, photoluminescence (fluorescence) and Raman interactions.

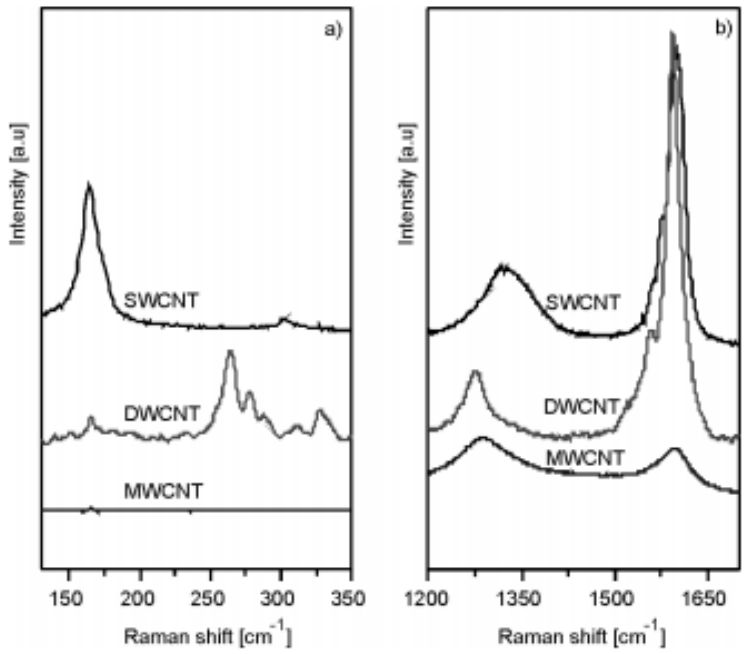


Fig. 4 Raman spectra of SWCNT, DWCNT and MWCNT

C. Structural Property: XRD and Neutron Diffraction

X-Ray Diffraction (XRD) gives information about the structural morphology of crystalline materials by their diffraction pattern. It is based on the dual wave/particle nature of X-rays and relies on the relationship between density of materials and absorption of X-rays. X-ray crystallography ascertains the positions of atoms in the lattice. Normally, the X-ray beam is kept immovable in a particular direction and the X-ray spectrum is recorded by rotating the crystal through a wide range of angles. Each detected X-ray signal corresponds to a coherent reflection, called "Bragg reflection" from successive planes of the crystal for which Bragg's law is satisfied and refers to the following equation [3]:

$$2d\sin\theta = n\lambda \quad (1)$$

where,

d is the spacing between the planes,

θ is the angle that X-ray beam makes with respect to the plane,

λ is the wavelength of the X-rays, and

n is an integer.

X-ray crystallographic methods can elucidate the structural information at different micro and nano length scales viz. from the single nanotube to the bundles of carbon nanotube and also applied to elucidate the inner structure of crystalline solids.

X-rays can be obtained from different sources including basically either X-ray generators or synchrotron facilities. The wavelength of X-ray produced depends on the nature and type of anode metal used. For example the characteristic spectral lines of wavelength 154 pm is obtained by the use of copper as anode material. The X-ray beam ejected reaches the sample and gets diffracted, the diffracted intensity is collected by a suitable detector (CCD camera, photographic film etc.). By knowing the experimental conditions (sample to detector distance, size of the detector, wave length of the X-rays) the diffraction pattern can be obtained as a graphic of the diffracted intensity.

The XRD pattern of CNT shows two peaks near to 25 °and 42 °corresponding to the interlayer spacing of the CNT (d_{002}) and d_{001} reflection of the carbon atoms, respectively. The asymmetry of band near 42 ° may be attributed to trubostratic nature of nanotubes (Fig. 5).

In the XRD of carbon nanotubes, we observe a strong and sharp peak corresponding to $2\theta = 26.3$ °. This is a significant characteristic and important feature which corresponds to a d-spacing of 3.39 Å. This is typically found in graphite or multiwalled carbon nanotubes ($d_{(002)}$) 3.4 Å). In some research work, a similar peak is observed, however it is so weak to say that it was attributed to the remaining graphite particle introduced during the arc discharge or laser ablation. In contrast, Futaba et al. also found a similar but very broad peak, whose broadness arises from the imperfect long-range order of the

SWNT sample with an average intertube spacing of 9 Å.

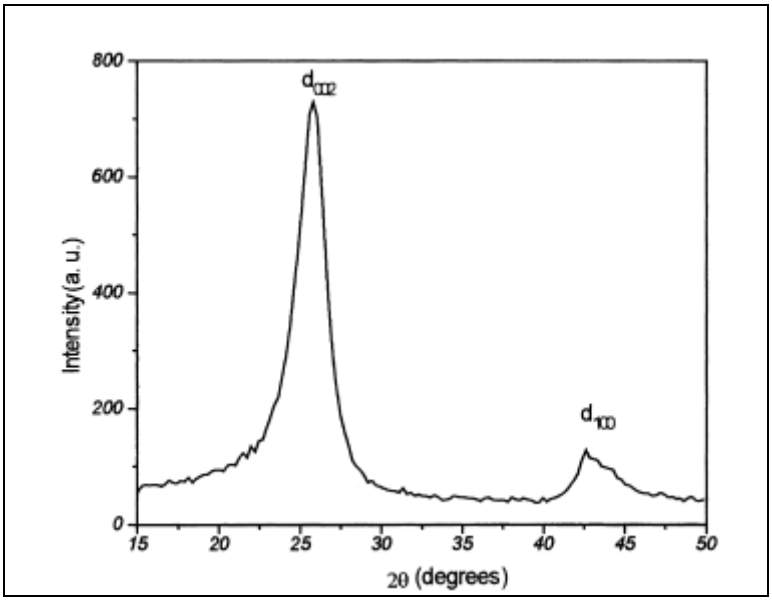


Fig. 5 The XRD of CNT

Neutron diffraction is similar to XRD and follows the same Bragg's law that describes XRD. A neutron diffraction measurement requires a neutron source (like nuclear reactor) which ejects neutrons and they show wave phenomenon. When a beam of neutrons is slowed down and selected properly by their speed, the neutrons with a wavelength near one Angstrom can be diffracted by atoms in a solid material. However, unlike X-ray, the neutrons directly interact with the nucleus of CNT and not with the electron clouds. So we may obtain strong response from atoms with low atomic number even. In this respect it could be considered as better technique than XRD, giving precise data for atomic position in the structure. So we can obtain the structural information of aligned CNTs from neutron diffraction technique.

As shown in the Fig. 6a-c, the neutron diffraction pattern from CNTs has some characteristics that can be related to graphite and some that can be related to activated carbons. The (002) and (004) reflections for graphite can be attributed to the inter-layer spacing and are present for the nanotubes but displaced to lower Q-values, indicating an increase in the spacing. All *(hk0)* peaks for the nanotubes have an asymmetric profile and there are no *(hkl)* peaks due to the lack of correlations between layers, which can be related to disorder of turbostratic graphite. In the measurements of neutron diffraction some residual intensity for the *(hkl)* peaks is believed to be characteristic of CNTs.

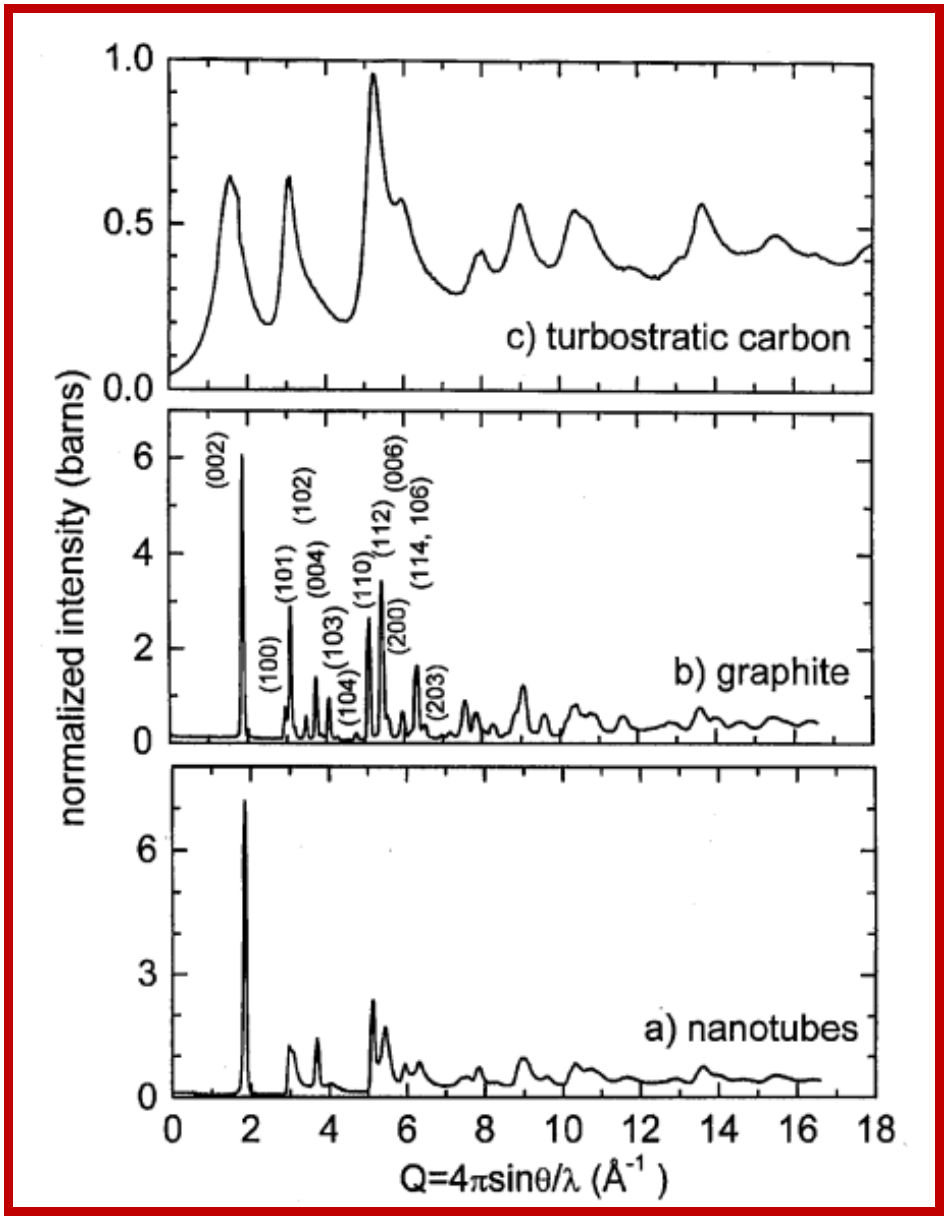


Fig. 6 Neutron diffraction pattern for structure of: (a) CNT, (b) Graphite and (c) activated carbon samples [4]

D. Surface Morphology: Scanning Electron Microscopy

Scanning Electron microscopy is an indispensable characterizing technique for any kind of nanomaterial. It divulges morphology, orientation and provides direct observation of size, shape and structure of CNTs. SEM Voltage usually ranges from 1 to 30 keV, this voltage is preferred to liberate surface electron. SEM consists of filament which is generally made of tungsten or lathanium hexaboride. This will be connected with voltage source. The gun will give adequate current to release electrons into the vacuum. The emitted electron will interact with the surface of the sample with very high energy and a secondary electron will get liberated from the surface of the sample. This ejected electron and the back scattered electron is taken on a photographic plate giving detailed surface morphology of the sample.

Fig. 7 gives six SEM images of a carbon nanotube sample. These images were recorded at different magnifications to envision the overall sample and the morphology of the tubes and their arrangement. In this particular study, the sample contains bundles of aligned nanotubes, and contains relatively small amount of the unwanted particles [5, 6].

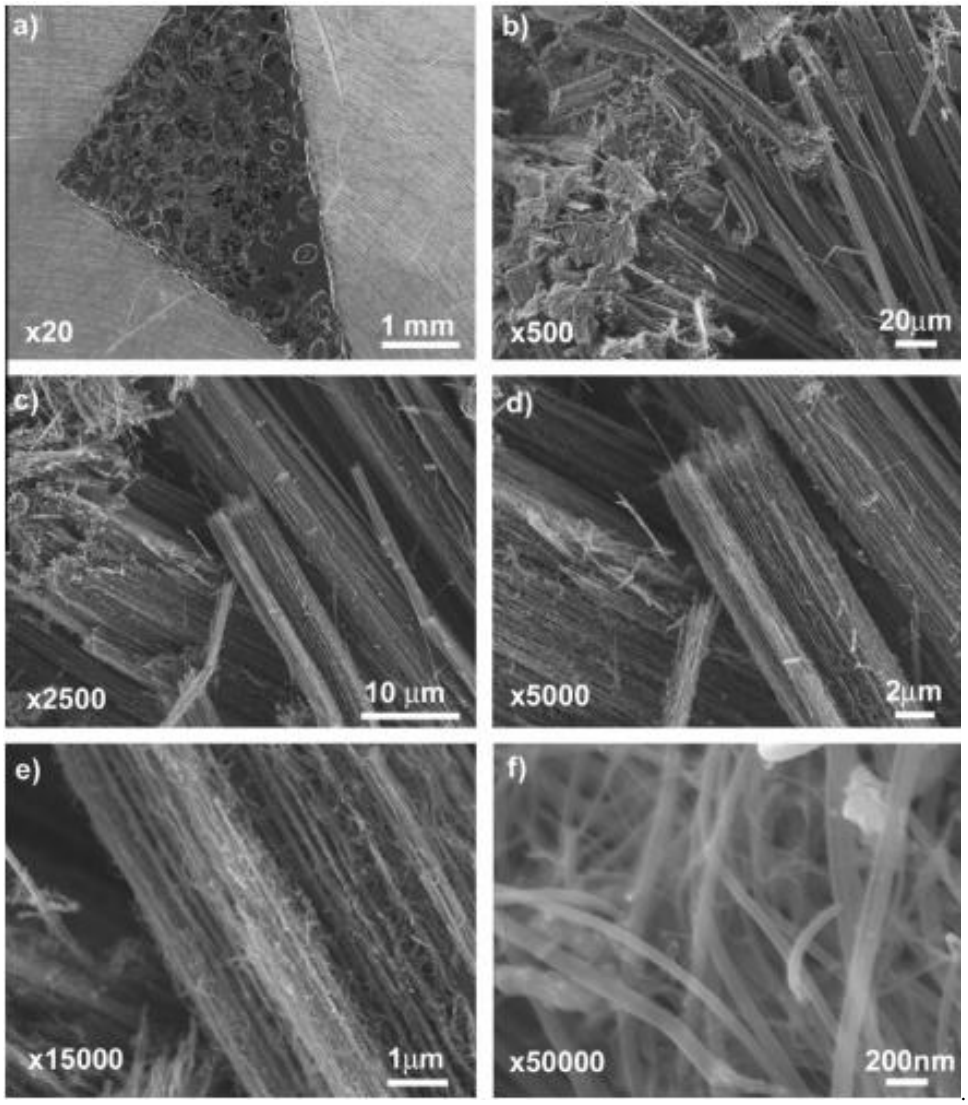


Fig. 7 SEM images for CNT [5, 6]

E. High Resolution Transmission Electron Microscopy (HR-TEM)

In transmission electron microscopy (TEM), a beam of electrons is transmitted through an ultra-thin specimen of material under investigation. The beam of electrons interacts with the sample as it passes through. Due to this interaction of electrons with the specimen, an image is formed, magnified and then focused on an imaging device viz. photographic film or any fluorescent screen (Figs. 8 and 9).

An emission source is required in TEM, which may be a lanthanum hexaboride (LaB_6) source or a tungsten filament. A thin tungsten filament is used which may be as thin as hairpin or may be like a small spike-shaped filament. In case of LaB_6 sources, small single crystals are used. The source gun is connected to a high voltage (100-300kV) and sufficient current is given leading to emission of electrons from the source. The emission of electrons is either due to thermionic or field electron emission into the vacuum. The electron beam can be further focused to the desirable size and location for subsequent interaction by the use of upper lenses. The transmitted electron images will be magnified and focused on a layer of photographic film.

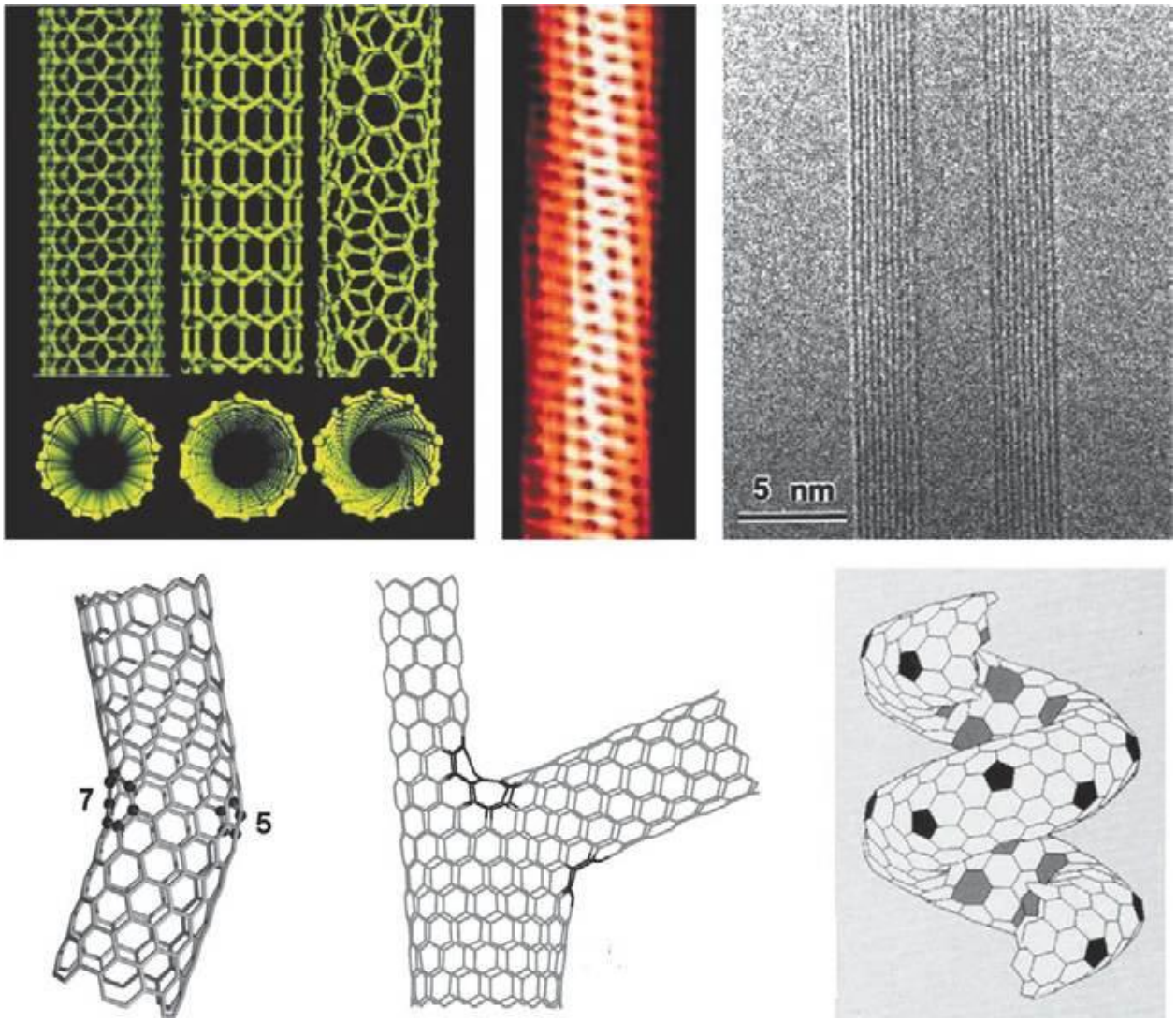
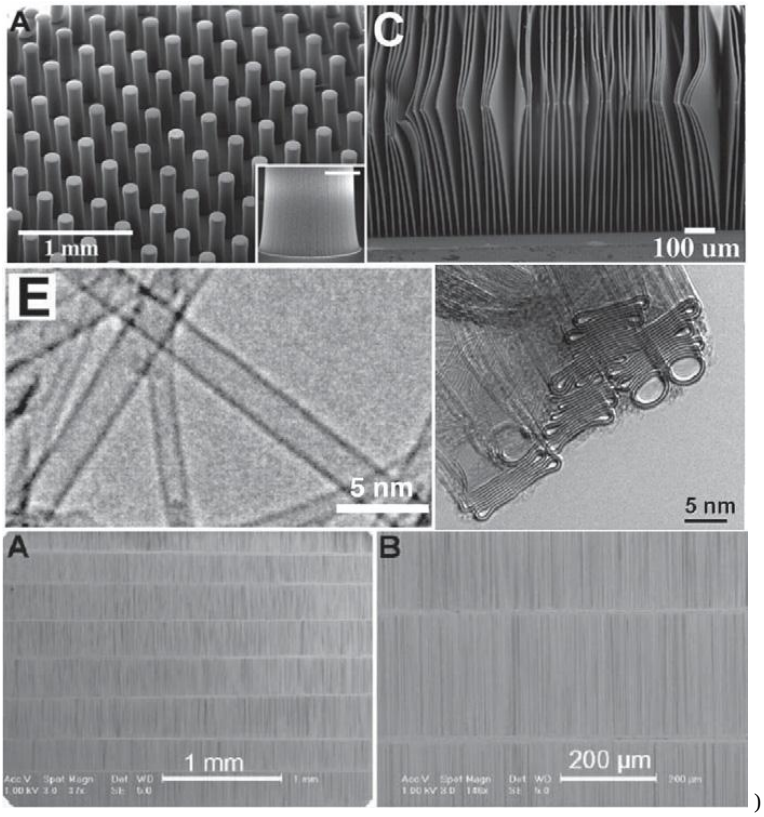


Fig. 8 TEM image of a MWNT [7]



)

Fig. 9 High-resolution TEM image of the SWNTs [7]

III. CONCLUSION

In the present chapter the characterization techniques are discussed. We can use infrared spectroscopy to identify the functional groups present on the modified CNTs, also infrared spectroscopy is frequently used for determination of impurities remaining from synthesis or molecules capped on the nanotube surface. The optical characterization can be accomplished by the use of Raman spectroscopy, in which we observed noteworthy peaks related to SWCNT and their diameter. Due to non-tedious sample preparation, it is considered as one of the best characterization techniques. Along with it is a comparatively fast and non-destructive analysis method for CNTs.

The technique of XRD is used to extract information about the interlayer spacing, the structural strain and the impurities present. Scanning electron microscopy (SEM) is a powerful technique used to reveal morphology, orientation and gives direct observation of size, shape and structure.

We can determine the nanotubes helicities with high resolution images. Several features such as chiral indices, intershell spacing, and helicity can also be obtained by transmission electron microscopy. For a precise characterization of carbon nanotubes, all these skills discussed here cannot be used discretely but must be used in harmonizing ways.

REFERENCES

[1] V. Shanov, Yeo-Heung Yun, and M. J. Schulz, "Synthesis and Characterization of Carbon Nanotube Materials," *Journal of the University of Chemical Technology and Metallurgy*, vol. 41, iss. 4, pp. 377-390, 2006.

[2] M. F. L. De Volder, S. H. Tawfick, R. H. Baughman, and A. J. Hart, "Carbon Nanotubes: Present and Future Commercial Applications," *Science*, vol. 339, iss. 6119, pp. 535-539, 2013.

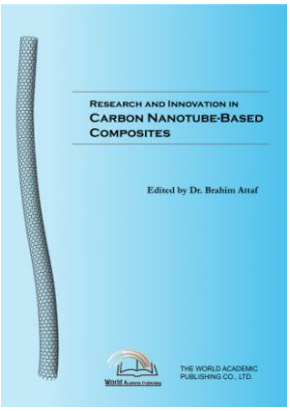
[3] C.P. Poole, Jr. and F.J. Owens, *Introduction to Nanotechnology*, 400 pages, ISBN: 978-0-471-07935-4, John Wiley & Sons, May 2003.

[4] J. Dore, A. Burian, and S. Tomita, "Structural studies of carbon nanotubes and related material by neutron and X-ray diffraction," *Acta Physica Polonica A*, vol. 98, iss. 5, pp. 495-504, 2000.

[5] J. H. Lehman, M. Terrones, E. Mansfield, K. E. Hurst, and V. Meunier, "Evaluating the characteristics of multiwall carbon nanotubes," *Carbon*, vol. 49, pp. 2581-2602, 2011.

[6] T. V. Le, H. T. Nguyen, A. T. Luu, M. V. Tran, and P. L. M. Le, "$LiMn_2O_4$/CNTs and $LiNi_{0.5}Mn_{1.5}O_4$/CNTs Nanocomposites as High-Performance Cathode Materials for Lithium-Ion Batteries," Acta Metallurgica Sinica(English Letters), vol. 28, iss. 1, pp. 122-128, 2015.

[7] M. Zhang and J. Li, "Carbon nanotube in different shape," *Materials Today*, vol. 12, iss. 6, pp. 12-18, 2009.



Research and Innovation in Carbon Nanotube-Based Composites
Edited by Dr. Brahim Attaf

ISBN 978-0-9889190-1-3

Hard cover, 136 pages

Publisher: The World Academic Publishing Co. Ltd.

Published in printed edition: 30, December 2015

Published online: 30, December 2015

This book of nanoscience and nanotechnology provides an overview for researchers, academicians and industrials to learn about scientific and technical advances that will shape the future evolution of composite materials reinforced with carbon nanotubes (CNTs). It involves innovation, addresses new solutions and deals with the integration of CNTs in a variety of high performance applications ranging from engineering and chemistry to medicine and biology. The presented chapters will offer readers an open access to global studies of research and innovation, technology transfer and dissemination of results and will respond effectively to challenges related to this complex and constantly growing subject area.

How to cite this book chapter

Sanjeev Kumar, Sapna Jain, Bhawna Yadav Lamba, Pankaj Kumar (2015). Characterization and Properties of Carbon Nanotubes, *Research and Innovation in Carbon Nanotube-Based Composites*, Dr. Brahim Attaf (Ed.), ISBN 978-0-9889190-1-3, WAP-AMSA, Available from: http://www.academicpub.org/amsa/

World Academic Publishing - Advances in Materials Science and Applications