PREPARATION OF LONG ALIGNED CARBON NANOTUBES AND STUDY ITS PHYSICAL PROPERTIES

Dissertation submitted in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

PHYSICS

By

Snehalata Sahu

412PH2112

Under the Supervision

Of

Dr. Pitamber Mahanandia

DEPARTMENT OF PHYSICS
NATIONAL INSTITUTE OF TECHNOLOGY,
ROURKELA
ODISHA-769008

2012-2014

Department of Physics

National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the work in the report entitled "**PREPARATION OF LONG ALIGNED CARBON NANOTUBES AND STUDY ITS PHYSICAL PROPERTIES**" by Snehalata Sahu, in partial fulfilment of Master of Science degree in PHYSICS at the National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance. The work is satisfactory to the best of my knowledge.

Supervised by

Date- 09-05-2014

Dr. P. Mahanandia

Place- Rourkela

Assistant Professor

Department of Physics

NIT, Rourkela

DECLARATION

I hereby declare that the project work entitled "**PREPARATION OF LONG ALIGNED CARBON NANOTUBES AND STUDY ITS PHYSICAL PROPERTIES**" submitted to the NIT, Rourkela, is a record of an original work done by me under the guidance of Dr. Pitamber Mahanandia, Faculty Member Department of Physics, NIT, Rourkela. This project work has not been performed on the basis for the award of any Degree or diploma/ associate ship/fellowship and similar project if any.

Snehalata Sahu

412PH2112

M.Sc. Physics

NIT, Rourkela

ACKNOWLEDGEMENT

I am most grateful to my advisor, Dr. Pitamber Mahanandia, for giving me the opportunity to work on an exciting project and for his encouragement and scientific guidance throughout my M.Sc. program. I wish to record my special thanks to Mr. Bamdev Das (M.Tech), Mr. Prakash Chandra Mahakul (Ph.D) and Miss. Kadambini Sa (Ph.D) for their valuable help in all respect of my project work. I would like to thank all the people who have contributed to this work.

I record my sincere thanks to Department of Ceramic Engeneering for extending all facilities to carry out the FE-SEM.

I express my sincere thanks to all the faculty members of Department of Physics, NIT Rourkela who have made direct or indirect contribution towards the completion of this project.

It gives me an enormous pleasure to thank all my friends and all the research scholars of the Dept. of Physics. In particular, I would like to thank my parents for their unconditional love and patience.

ABSTRACT

Carbon nanotubes (CNTs) of about 6 μm long have been successfully prepared by a simple pyrolysis technique. The precursors used for the synthesis of nanotubes through pyrolysis technique are pyridine (carbon source material) and ferrocene (catalyst). The synthesized CNTs have been characterized by X-ray Diffraction (XRD), field-emission scanning electron microscopy (FESEM) and High-resolution Transmission Electron Microscopy (TEM) and Raman Spectroscopy. The aligned carbon nanotubes were dissolved in polymethyl methacrylate (PMMA) polymer in a solution and silver contacts were made to study the effect of CNTs on electrical properties of PMMA. The I-V characterization of the PMMA-CNTs was performed to study its electrical properties. A linear current-voltage characteristic was obtained. The change in resistance with and without diffusion of polymer in carbon nanotubes were calculated from the I-V curve.

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

1.1 Introduction to Carbon nanotubes

CNT is a tubular form of carbon with diameter as small as 1nm. Its length varies from few nm to μm. The configuration of CNT is equivalent to a two dimensional graphene sheet rolled into a tube. Iijima first reported the carbon nanotubes in 1991 that were obtained by DC arc discharge method of a graphite electrode in helium gas in the carbonaceous deposits on the cathode [1].

Due to their unique structural, mechanical, electrical and thermal properties, carbon nanotubes have emerged as a potential candidate for applications in various fields such as sports equipments, energy storage, sensors, actuators, electronics and in other fields that are yet to be explored by scientists.

1.2 Types of CNTs

The crystalline structure of CNTs can be characterized by the chiral vector C within a corresponding graphite sheet plane. $\mathbf{C = m\,a + n\,b}$ (m, n ∈ N) where a and b are basis unit vectors. The length defines the perimeter and the angle θ_o the helicity (chirality) of the nanotube [2].

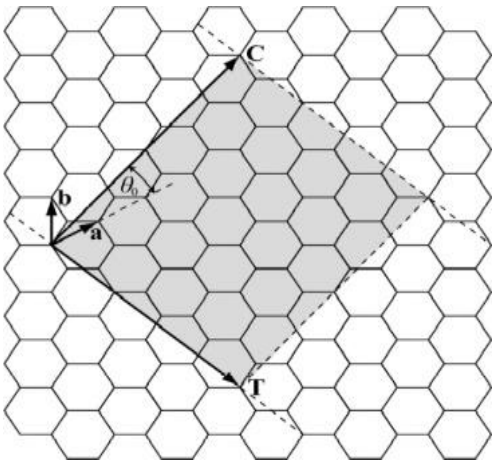

Fig 1.1 A carbon nanotube described by basis vectors a and b, chiral angle θ_o, chiral vector C and translational vector T [3].

Based on their chirality, CNTs can be classified into three types:

1. Armchair CNTs (n = m, $\theta_o = 30^o$): They are metallic and have no band gap.
2. Zigzag CNTs (m = 0, n > 0, $\theta_o = 0^o$): They are semiconductors with a finite band gap
3. Chiral CNTs ($0 < |m| < n$, $0 < \theta_o < 30^o$) : They are also semiconductors with a finite band gap.

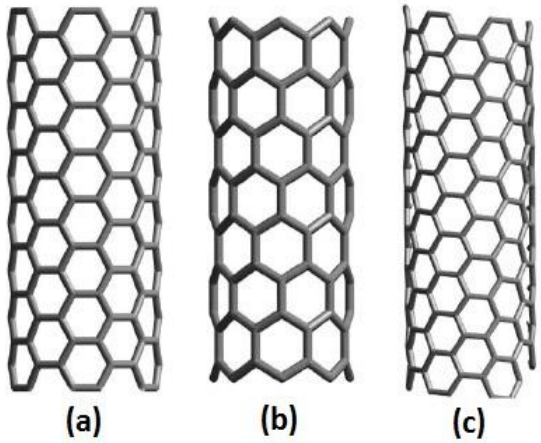

Fig 1.2 Classifications of CNTs: (a) Armchair CNTs, (b) Zigzag CNTs, and (c) Chiral CNTs

Based on their structure, nanotubes are categorized into two types:

1. Single-walled nanotubes (SWCNT): They consist of a single graphite sheet enveloped into a cylindrical tube.
2. Multi-walled nanotubes (MWCNT): They comprise an array of SWCNTs nanotubes that are concentrically nested like rings of a tree trunk.

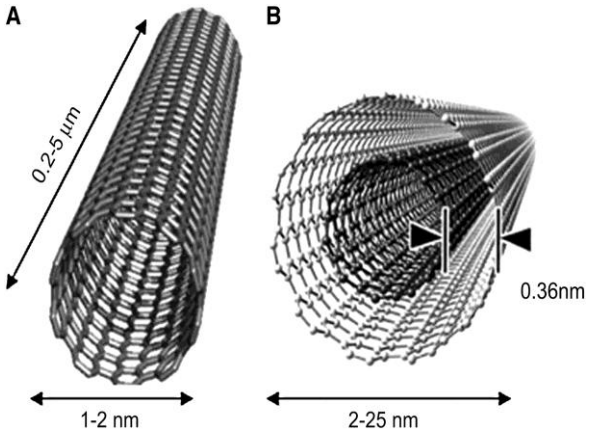

Fig 1.3 Schematic diagram of (a) SWCNT and (b) MWCNT showing typical dimensions of length, diameter, and separation distance between two graphene layers in MWCNTs [4].

1.3 Properties and Applications of CNTs

Carbon nanotube properties depend on how the graphene sheets are rolled into tube. The orientation of the crystal lattice with regard to the axis of the tube, known as chirality, determines the electronic band structure, and therefore the conductance. The dependence of the electronic properties on the structure implies that mechanical deformations can alter the band structure [5]. This results in electromechanical effects such as piezo-resistance and electrostatic actuation, which may lead to nanotube-based mechanical sensors and actuators.

CNTs have extremely low electrical resistance. They can carry the highest current density [6] of any known material, measured as high as 10^9 A/cm^2. Nanotubes can serve as extremely fine electron guns. This property can be utilised in cathode ray tubes (CRTs) as thin high-brightness low-energy low-weight displays known as field emission displays.

In terms of mechanical properties, nanotubes are among the stiffest (Young's modulus) and strongest (Yield strength) materials yet observed. Their Young's modulus is 0.64 TPa, roughly five times greater than steel. They are also quite flexible and can return to their original shape after bending and buckling. They can withstand large strains of up to 6-10 %, which corresponds to yield strength of 37 GPa, compared with ~300 MPa for steel [7]. They have led to interesting applications, including using nanotubes as a flexible, durable, high-aspect ratio atomic force microscope (AFM) tip and electromechanical memories. CNTs are also being used to reinforce ceramics and metal matrices. As a result of interaction between nanotubes and polymer, property improvements with CNTs include enhanced tensile modulus, fatigue behaviour, tensile and compressive strength, electrical conductivity as well as anisotropic optical properties.

1.4 Synthesis Techniques of CNTs

The nature and quality of CNTs depend on the method of production which controls. The basic prerequisites for the formation of CNTs are an active catalyst, a source of carbon and adequate energy. A metal catalyst is necessary for the growth of the CNTs in all methods used for synthesis of CNTs. Catalysts that are used to prepare CNTs usually include transition metals as a single such as Fe, Co, Ni or Mo [8] or mixture of two catalysts such as FeNi, PtRh and NiY. The catalyst activation is determined in relation to the melting temperature and the boiling temperature thus the melting and boiling temperature of a catalyst can be one of the vital factors in the synthesis of SWCNTs. The nanotube diameter

depends on the catalyst particle size. CNT lengths are typically limited to a few millimetres because the catalyst lifetime is usually less than one hour.

The common methods used for the synthesis of CNTs are arc discharge, Flame Synthesis, laser ablation , High Pressure Carbon Monoxide synthesis (HiPCO), Chemical Vapour Deposition (CVD), Pyrolysis and Plasma-enhanced CVD (PECVD).

Carbon nanotubes synthesized by arc discharge and laser ablation processes are high on purity but these methods are not effective for large scale production of MWCNTs. CVD and PECVD are best approach for low-cost and large-scale synthesis of high quality aligned CNT materials in the temperature range of 700-1200 ^{o}C [9].

The **Chemical Vapour Deposition** (CVD) is a process in which hydrocarbon vapours are thermally decomposed over transition metal catalyst particles. The gases that result from hydrocarbon vapors and catalysts pass over a hot surface and undergo chemical reactions. The chemical reactions resulting in the substrate surface leads to a solid deposit in the form of black carbon nanotubes. Chemical vapor deposition (CVD) is the dominant mode of high-volume CNT production [10]. However, large-scale CVD methods yield contaminants that can influence CNT properties and often require costly thermal annealing and/or chemical treatment for their removal. These steps can introduce defects in CNT sidewalls and shorten CNT length.

In case of PECVD, plasma is created which leads to a reduction in the activation energy for depositing the nanotubes. In PECVD, the electron impact activates the molecules whereas in CVD the energy needed to activate the gas molecules are provided by thermal means. Both these processes require rigorous control of parameters such as the furnace temperature, total reaction time, continuous supply of source materials, and flow rate of catalyst amount. Above all, the main disadvantage is the overall cost. The pyrolysis technique is the simplest technique as it eliminates the complex and expensive machinery that are associated with other methods. We have successfully synthesized MWCNTs by following this method. Complicated control of parameters is not required in pyrolysis because CNTs synthesis can be completed in one step. The preparation of metal supported catalyst that consume much time and are tiresome can also be avoided [11].

CHAPTER 2

LITERATURE SURVEYS

2.1 Literature Survey of Synthesis of CNTs

Before proceeding for the synthesis of carbon nanotubes we have gone through several literatures that describe different techniques associated with the CNTs production and applications, few of which are given in the following:

1. Sumio Iijima, Nature 354, 56 - 58 (07 November 1991), discovered a technique of preparing a new type of finite carbon structure that consists of needle-like tubes. The tubes were produced through an arc-discharge evaporation method. The needles grow at the negative end of the electrode used for arc discharge. Electron microscopy reveals that each needle consists of coaxial tubes of graphitic sheets, ranging in number from 2 upto about 50. Their diameter ranges from 4-30 nm in diameter and upto 1μm in length.

2. Hyeon Hwan Kim, Materials Science and Engineering B 133 (2006) 241–244, have shown that the carbon nanotubes (CNTs) can be synthesized using a DC arc discharge process in an air atmosphere. Multi walled carbon nanotubes could be synthesized in the deposit area of the cathode even in an air atmosphere in absence of inert gas. The single walled carbon nanotubes were not detected in the soot area despite using the same process conditions as in the inert gas. In addition, the quantity of amorphous carbon and other nanoparticles in the process chamber was remarkably reduced by this technique. This shows that arc discharge process is a practicable method for the large scale CNT fabrication.

3. Guang-Yong Xiong, Carbon 44, 967-973 (2005) devised a method in which the nanotubes were grown on single crystal Magnesium Oxide by chemical vapour deposition method. A thin film of catalyst (iron) was coated on MgO by magnetron sputtering. Then annealing of catalyst was done to form nanoparticles and the CNts were grown by CVD method. Different substrates of MgO resulted in different length of CNTs.

4. P.Mahanandia, Nanotechnology 19 (2008) 155602 paper on nanotubes synthesis describes a simple pyrolysis technique developed to synthesize aligned arrays of multi-

walled carbon nanotubes (MWCNTs) in a single-stage furnace at 700 ◦C. In this technique, no carrier gas was used. This technique has many advantages such as low cost machines, no complicated involvement of parameters, no need of metal supported catalyst compared to other techniques such as chemical vapour deposition (CVD) and PECVD. Carbon source materials used are xylene, cyclohexane, pyridine, camphor, hexane, toluene, and benzene for the pyrolysis separately with the catalyst source material ferrocene.

1.2 Motivation

There are many synthesis techniques for carbon nanotubes. Though these techniques have been useful for CNTs but there are also some demerits in it. Therefore, our main objective is to synthesize CNTs by a simple and effective pyrolysis technique. The pyrolysis technique reduces the production cost and allows easy operation as no complicated parameters are involved unlike CVD, PECVD and other methods. Efforts have been made to prepare CNTs polymer composite and many properties have been studied. However, till now diffusion of a polymer in CNTs in solution have not been studied and performed. Therefore, our main motive is to study the electrical properties of CNTs by diffusing a polymer into it.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Synthesis of long aligned CNTs

Syntheses of CNTs have been carried out using a single-step pyrolysis technique. It consists of a single stage furnace with reaction quartz tube.

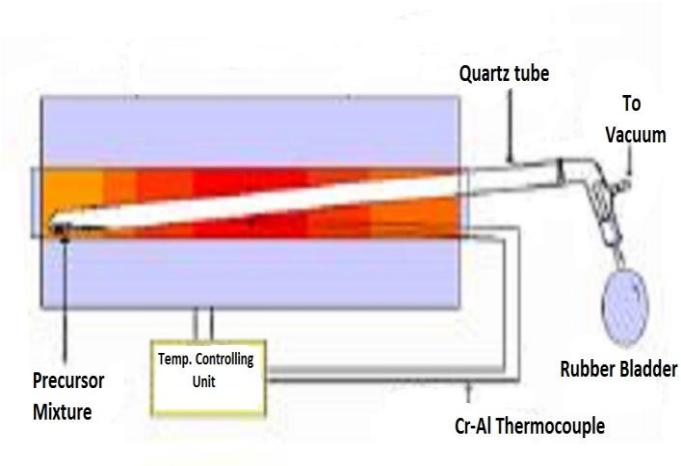

Fig. 3.1 Schematic diagram of the single-stage pyrolysis technique [12]

The precursors used for the synthesis of carbon nanotubes are pyridine and ferrocene. The quartz tube of diameter 1cm and length 70 cm with one end closed was first cleaned through acetone. Then, pyridine of around 2 ml and catalyst source material ferrocene that weighs around 18 mg was taken in the quartz tube. Rubber bladder was connected in the other end of quartz tube to collect harmful residual gases that are formed in the process. The whole assembly is placed inside the furnace. The precursor mixtures were heated up to pyrolysis temperature 900^{o}C. The reaction was continued for 4 hours and then cooled down to room temperature. The reaction quartz tube was taken into the safety hood to remove the bladder [13] as the gases collected (which may be either CO or CO2) may cause harmful effects.

3.2 Diffusion of PMMA polymer in CNTs

A solution of 18 mg poly-methyl methacrylate (PMMA) and 50 ml toluene is prepared and left for few hours to allow PMMA to get dissolve in toluene. CNT bundles of diameter 75 nm and length 1mm were taken and put in the above solution and were left for 2-

3 days. Sonication was done for 5 seconds of the prepared solution (Be careful while sonicating, does not allow the CNT bundles to break). CNTs were taken out from the solution and were allowed to dry for 2-3 days. The CNTs were dried by putting them on the SiO_2 substrate. Then, contacts were made by using silver paste and thin copper wires. The contacts were made by putting a small drop of silver paste on the two ends of the CNTs/PMMA.

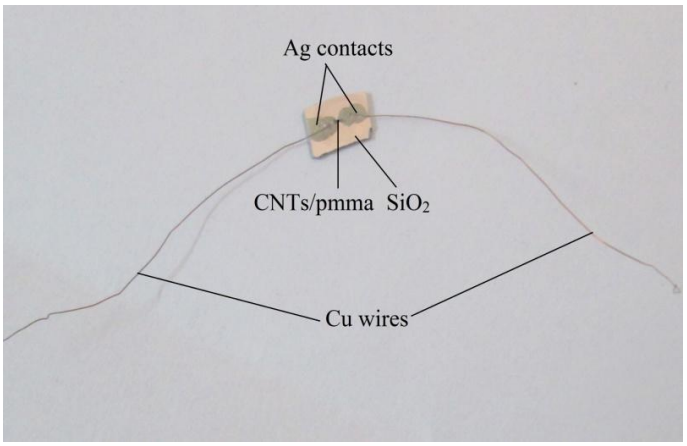

Fig. 3.2 CNTs/PMMA Device fabrication

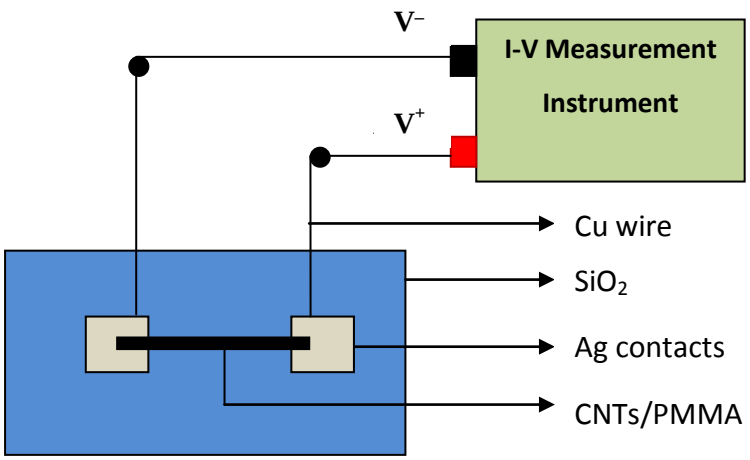

Fig. 3.3 Schematic of the arrangement for electrical measurement of CNT/PMMA

The following characterization techniques were used to study the structural, morphological and electrical properties of long-aligned CNTs:

3.3 X-Ray Diffraction (XRD)

The physical properties of CNTs greatly depend on how sheets have been rolled up, the tube and length diameter, aspect ratio (ratio between diameter and length of CNT)

and the nanotube's morphology. X-ray methods offer information about the structure of nanotubes at different length scales from the single nanotube to the nanotube bundle [14].

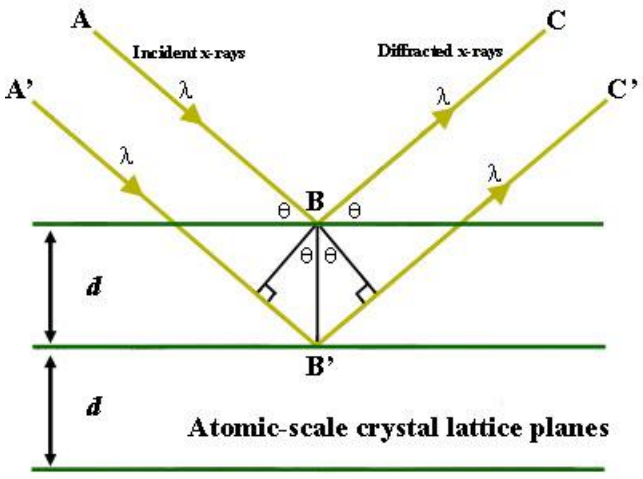

Fig. 3.4 X-ray diffraction [15]

X-ray diffraction (XRD) is a versatile, non-destructive analytical technique which provides the information regarding the crystal structure of a substance. When x-ray beam with a characteristic wavelength λ strikes the solid with an incident angle θ then the scattered radiation is determined by Bragg's law. The x-ray diffractometer works on the principle of Bragg's law. The general relationship between the wavelength of the incident X-rays, angle of incidence and spacing between the crystal lattice planes of atoms is known as Bragg's Law and expressed as:

$$n\lambda = 2d\sin\theta$$

where, λ = wavelength of the incident X-rays in angstroms

d = interplanar spacing of the crystal in angstroms

θ = angle between the incident rays and surface of the crystal

3.4 Field Emission Scanning Electron Microscope (FE-SEM)

The morphology, dimensions and orientation of CNTs can be easily revealed by using scanning electron microscope (SEM). In SEM, a beam of highly energetic electrons strike the sample. The secondary electron, back scattered electrons, are ejected from the sample. The electron interacts with the atoms that make up the sample producing signals that are collected at the detector. This signal contains information about the samples

surface, electrical conductivity, topography and composition. FESEM uses field emission gun that produces a cleaner image, less electrostatic distortions and spatial resolution less than 2 nm (that means 3 or 6 times better than SEM) [16].

3.5 High Resolution Transmission Electron Microscope (HRTEM)

The HRTEM images give information about the type of CNTs whether single or multi walled by scanning atom by atom under high resolution. The diameter can also be found from the HRTEM images. It directly images the atomic structure of the sample. It can provide structural information at better than 0.2 nm spatial resolution [17].

3.6 Raman Spectroscopy

It is a non destructive analysis of the CNT samples. Raman spectroscopy is considered an extremely powerful tool for characterizing CNT which gives qualitative and quantitative information on its diameter, electronic structure and distinguishes metallic and semiconducting material as well as chirality. Raman spectra can also reveal the information about the removal of structural and amorphous present in the nanotubes after purification [18].

3.7 I-V Characterization

The I-V measurement of CNTs and CNTs/PMMA polymer was done by Keithley 2400 instrument [19]. This instrument can act both as a voltage source and as a current source. A constant voltage was applied to the material and current was measured. This instrument gives a plot between current vs voltage in Y-axis and X-axis respectively.

Fig. 3.5 Keithley 2400 for I-V measurement

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 X-Ray diffraction Analysis

The powder XRD pattern (Cu Kα λ= 1.5406 A˚) of long aligned CNT samples prepared by the pyrolysis of pyridine and ferrocene is shown in figure 4.1. From the figure, it is shown that a prominent peak occurs at $2\theta = 26.4^{o}$ which corresponds to the (0 0 2) reflection of carbon. The interplanar distance is found to be 0.335 nm.

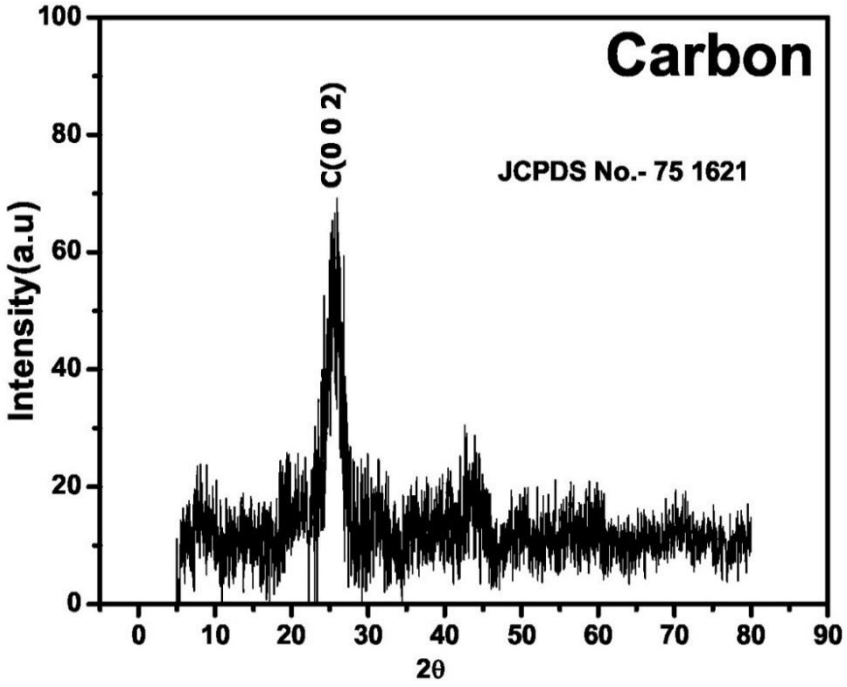

Fig 4.1 XRD pattern of synthesized carbon nanotubes

4.2 Field Emission Scanning Electron Microscope (FE-SEM) Analysis

The FE-SEM images of synthesized CNTs from pyridine using ferrocene as catalyst and CNTs used for PMMA polymer diffusion are shown in figure 4.2 and 4.3 respectively. Figure 4.2 shows that the CNTs synthesised from pyrolysis technique with some amorphous carbon as impurities were around 6 µm long. The carbon nanotubes with resolution of 500 nm show that the nanotubes are hollow inside closed at one end. Figure 4.3 shows that the carbon nanotubes used for electrical study were long aligned and around 1.5 mm in length.

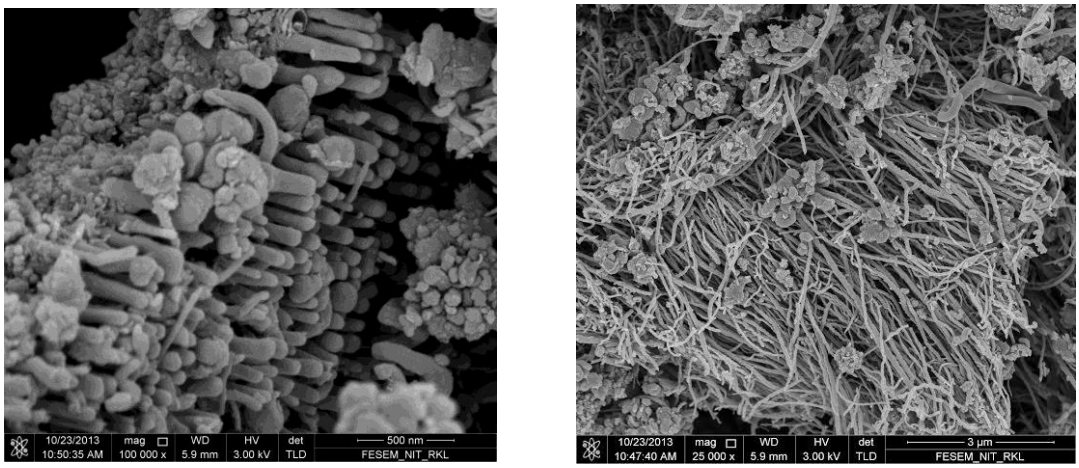

Fig. 4.2 FESEM image of as-synthesized carbon Nanotubes

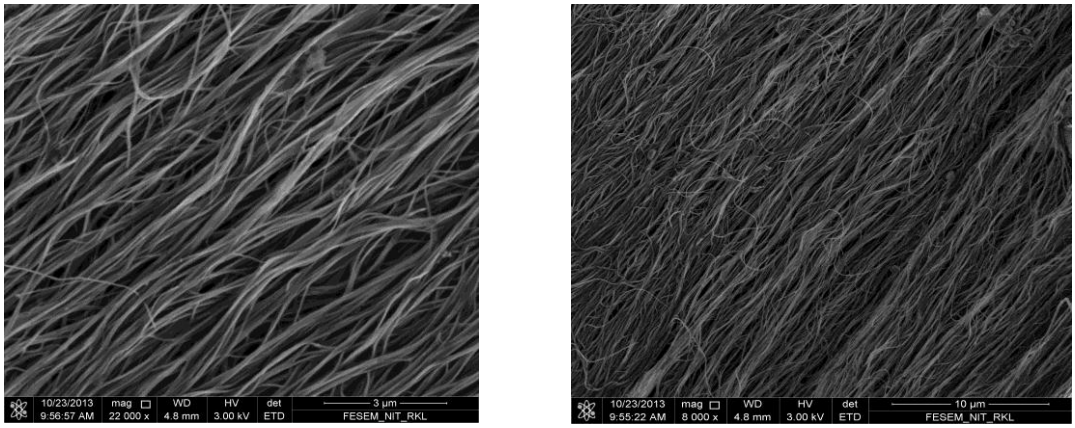

Fig. 4.3 FESEM image of millimetre long carbon nanotubes

4.3 High Resolution Transmission Electron Microscope (HRTEM) Analysis

The HRTEM image of long aligned carbon nanotube is shown in figure 4.4. This figure shows the synthesized carbon nanotubes used for diffusion purpose are multiwall in nature with a diameter of **~75** nm.

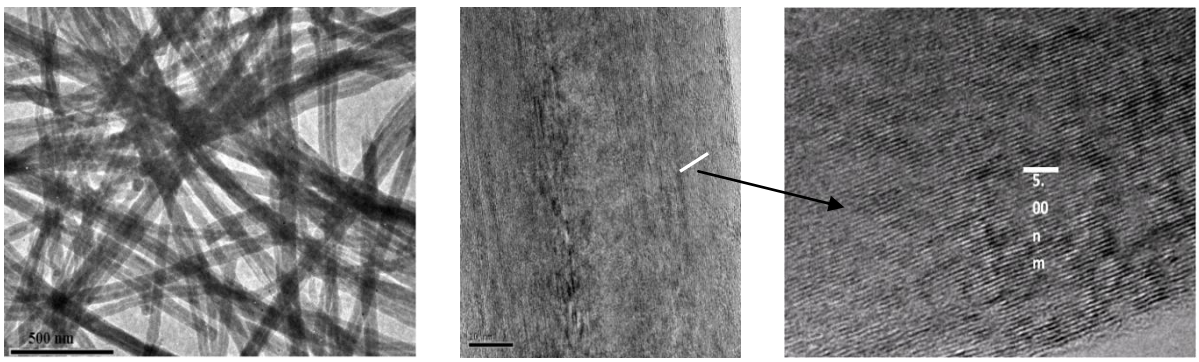

Fig. 4.4 HRTEM image of long aligned CNTs at different resolution

4.3 Raman spectra Analysis

The Raman Spectra (as shown in figure 4.5) show the occurrence of peaks at 1380 cm^{-1} and 1572 cm^{-1} corresponding to disorder (D-band) and graphite (G-band) bands, respectively. The former is an indication of the presence of defective material and the latter one refers to the well-ordered graphite [20].

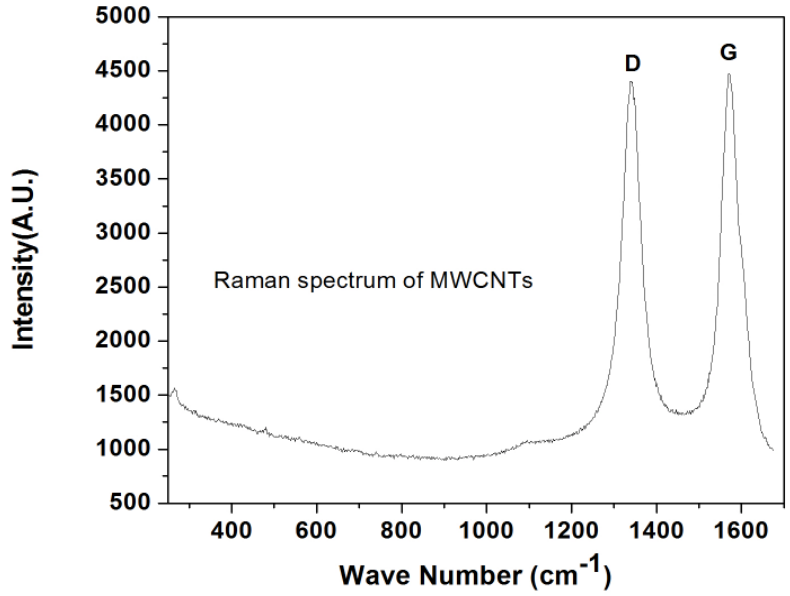

Fig. 4.5 The Raman Spectra of as synthesized CNTs

4.4 I-V Measurement

The current-voltage (I~V) characteristics graph of multi-walled carbon nanotubes (MWCNTs) without polymer and with polymer is shown in figure 4.6 (a) & (b), respectively. From the figure, it is shown that the current increases linearly with applied voltage for both MWCNTs without and with PMMA polymer at room temperature. It confirms that both the materials show ohmic behaviour. The resistance of CNT bundles without polymer and with polymer is found to be 4.6Ω and 1.5KΩ from the I-V characteristics.

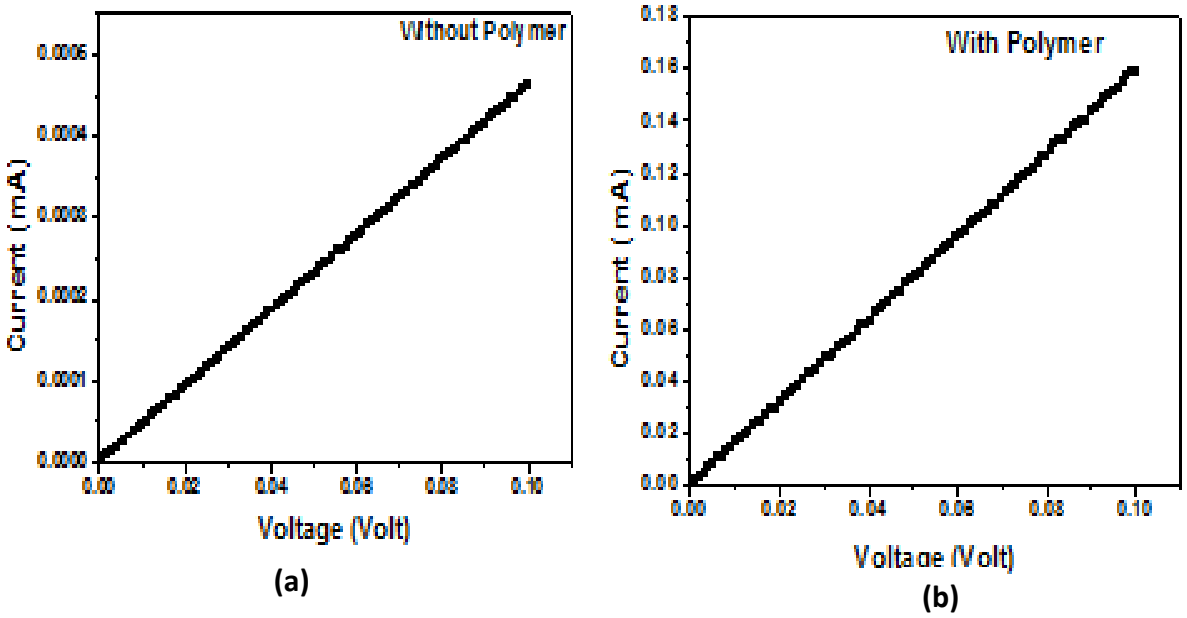

Fig 4.6 (a) & (b) shows the current voltage characteristics graph of multi-walled carbon nanotubes (MWCNT) without polymer & with polymer respectively

CONCLUSION

We have synthesized the aligned arrays of multi-walled carbon nanotubes by using a simple and effective pyrolysis technique. The technique is a one-step process in which carrier gas and pre-deposited metal catalysts are not required. The production cost is also low compared to other methods (CVD, PECVD). The synthesized CNTs were found to be few micrometers long with high aspect ratio of around 1000:1. The Raman spectra show that the prepared carbon nanotubes through pyrolysis contain few amorphous impurities that can be removed by purification either by oxidation or acid treatment.

The CNTs used for electrical study with PMMA polymer were found to be multi-wall in nature with diameter around 75 nm and length around 1 mm. The I-V characteristics shows that diffusion of PMMA in MWCNTs increases the resistance of CNTs. Increase in resistance is due to the diffusion of polymer in the CNTs that obstruct the flow of electrons in one direction along the axis of nanotube.

REFERENCES

[1] Iijima S, Helical microtubules of graphitic nature, *Nature* 354 56 (1991)

[2] S. B. Sinnott and R. Andreys. "Carbon Nanotubes: Synthesis, Properties, and Applications". *Critical Reviews in Solid State and Materials Sciences* 26 (3) 145–249 (2001)

[3] http://en.wikipedia.org/wiki/File:CNTnames.png

[4] http://jnm.snmjournals.org/cgi/content-nw/full/48/7/1039/FIG1

[5] Belluci S., Carbon nanotubes: Physics and applications, *Physica Status Solidi* (c) 2 (1): 34-47 (2005)

[6] Sander J. Tans, Alwin R. M. Verschueren, Cees Dekker, *Nature* 393 (1998) 49

[7] Yu, M.-F.; Lourie, O; Dyer, MJ; Moloni, K; Kelly, TF; Ruoff, RS, "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load". *Science* 287 (5453): 637–640 (2000)

[8] Xu, B., Guo, Ju., Wang, X., Liu, X., & Ichinose, H. (2006). Synthesis of carbon nano-capsules containing Fe, Ni or Co by arc discharge in aqueous solution. Carbon, 44-2631

[9] Li W Z, Xie S S, Qian L X, Chang B H, Zou B S, Zhou W Y, Zhao R A and Wang G *Science* 274 1701, 1996

[10] M. Endo, T. Hayashi, Y.-A. Kim, Large-scale production of carbon nanotubes and their applications. *Pure Appl. Chem*. 78, 1703 (2006)

[11] [12] P.Mahanandia and Karuna Kar Nanda, A one step technique to prepare aligned arrays of carbon nanotubes, *Nanotechnology* 19 155602, 2008

[13] Mahanandia P, Vishwakarma P N, Nanda K K, Prasad V, Barai K, Mondal A K, Sarangi S, Dey G K and Subramanyam S V 2008 *Solid State Commun*.145 143

[14] Shaijumon M M, Rajalakshmi N, Ryu H and Ramaprabhu S 2005 *Nanotechnology*16518

[15] http://serc.carleton.edu/research_education/geochemsheets/BraggsLaw.html

[16] http://areeweb.polito.it/ricerca/carbongroup/fac_fesem.html

[17] http://www.dstuns.iitm.ac.in/microscopy-instruments.php

[18] Li Yet al 2004 *Nanotechnology*15 1645

[19] http://www.tevetllc.com/documents/pdf/keithley/2400_Series_Broc.pdf

[20] Jahanshahi, M., Raoof, J., Hajizadeh, S., & Seresht, R. J. (2009). Synthesis and subsequent purification of carbon nanotubes by arc discharge in NaCl solution. Phys. *Status Solidi A*, 1, 101-105.