Fabrication of Carbon Nanotubes and Investigating the Characteristics

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ABSTRACT

Carbon nanotubes (CNT) are the fantastic nano-material which exhibits a very low thermal expansion and high current capability. It has a wide variety of methods for synthesis. One of the most reliable and best suited is Arc Discharge method. Multi walled CNT (MWCNT) are synthesized in an experimental setup. Soot deposited is in mixture form of nanoparticles and hence it is purified and MWCNT are separated and collected. XRD analysis and TEM images are taken for CNT. MWCNT are coated on the silica substrate through DIP coating. Dispersion of CNT is handled and the resistivity and morphology of cnt dip coated are studied. The change in resistivity is determined by the graph plotted through Four Point Probe method. Investigation concludes that the MWCNT developed is suitable for contacts in transistors and miniature sensors for fabrication due to its low resistivity.

General Terms

Carbon Nanotubes, synthesis, purification and characterization

Keywords

Carbon nanotubes, Arc discharge method, synthesis, purification, characterization – XRD, SEM, TEM.

1. INTRODUCTION

Nowadays our world is full of innovation and intelligence. To suit the expectation nanotechnology is a mandatory. Substance at mass behaves different in nanoscale. There is a wide change in characteristics of materials. Nanoscale development is a Most innovative and efficient field, carbon nanotubes are the best option for contacts and nanoscale fabrication.

CNTs have been a subject of fascination for many scientists and engineers. They have received considerable interest in research due to their unique atomic structure/dimensions and exceptional properties.

Interconnects made by copper, aluminum at nanoscale fabrication doesn't have the unique properties of cnt such as low thermal expansion [1] and high current density [2] enables it to suitable for such precise capabilities. CNT due to its structure and conductivity properties it has become an effective research and development area.

Nanotubes have a cylindrical structure and it can be synthesized through different methods. Synthesis of CNT is done basically through Arc discharge method. Arc discharge method is Easy & best suited for laboratory preparation which yields High purity Multi Walled Carbon Nanotubes (MWCNT). It is comparatively cheaper than Laser method and easier than Chemical method.

In this arc discharge method the carbon soot is produced which has nanotubes, nano particles etc.., the carbon soot cannot be used as such so it is purified. Purification yield pure CNT and efficient nanotubes. This process includes grinding, soaking, filtering, drying and cooling.

Characterization is the conformation of CNT and justification of nanotubes structure, size and morphology. The X-Ray diffraction method is done to prove the presence of Graphite. The Travelling Electron Microscope (TEM) displays the size of the nanotubes.

This paper exhibits the best, easy and well suited methodology for multi walled CNT synthesis, purification and characterization. Results and discussion conforms the presence of multi walled carbon nanotubes to a length of 100nm and a diameter of 10nm are produced. Since CNT is a well suited for high conductive in nature and low thermal expansion in further research dispersion and conductivity may be possible.

2. SYNTHESIS

There are various types suited for CNT preparation. Laser method, chemical method, arc discharge method and plasma torch method.

Since arc discharge method [3] is well suited for multi walled CNT it is taken into consideration. Also it yields more CNT and comparatively more economy.

Arc discharge method parameters are listed. Basically this method yield a high purified multi walled CNT.

- Material used   : Graphite rod
- Rod Size (Anode)   : 30cm length & 11mm diameter
- Disc Size (Cathode) : 50 x 10 mm disc
- Atmosphere   : Nitrogen
- Current   : 150 Amperes
- Voltage   : 30V DC
- Speed   : 10 rpm

The experimental setup includes nitrogen filled chamber with water cooling system, servo motors and DC Power supply. Fig 1 illustrates the experimental setup.
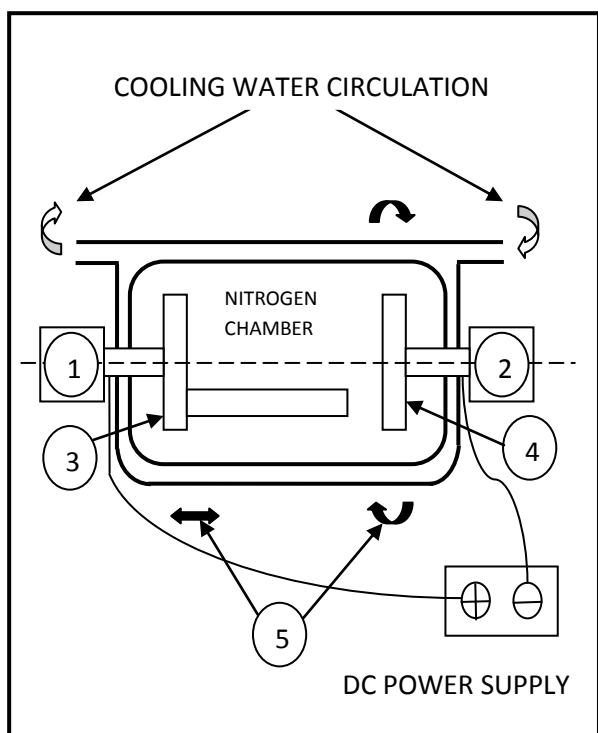
Fig 1: Schematic of Arc Discharge Method

Legends:

      1 – Servo Motor

      2 – DC Motor (10 RPM)

      3 – Graphite Rod as Anode

      4 – Graphite Disc as Cathode

      5 – Direction of Rotation

Initially the chamber was vacuumized to 600mm of Hg (Mercury) pressure (0.799 bar). Nitrogen was purged to maintain 1kg / cm^2 (0.980 bar). Graphite rod was drilled with 4mm diameter hole and the hole was filled with Nickel (Ni) & graphite powder which acted as a catalyst in a ratio of 1:1.

Nickel as a catalyst [4] & [5] is corrosive resistant, heat resistant and controlled expansion alloy. The Melting point and boiling point is comparatively low when compared with other catalyst such as Iron (Fe) and Cobalt (Co). The cost is also less when compared with cobalt alloy.

A DC Power supply is connected to both electrode and disc. Electrode act as Anode and Rotating graphite disc at 10 RPM was used as cathode.

When the specified voltage and current is applied and the gap between anode and cathode is maintained to 1mm, arc generated between two electrodes (Graphite). Cooling water was circulated to remove the heat.

During discharge carbon atoms sublimate from anode and gets deposited on cathode. A carbonaceous deposit rich in MWCNT (Multi Walled Carbon Nanotubes) grow up.

A servo motor moves the anode forward when the anode gets consumed, in order to maintain the electrode gap constant. Soot deposited on the graphite (cathode) was continuously removed using a thin blade.

By using this thin blade the cathode is always maintained free of deposited material which is constantly removed from the high temperature reaction region.

The collected carbon soot is cooled at room temperature.

3. PURIFICATION

Carbon soot contains nanotubes, fibers, particles etc.., this soot cannot be used as such hence it has to be purified. Purification undergoes basically grinding, soaking, filtering, drying, cooling, treating, filtering and heating. Purification steps are represented in a block diagram. Fig 2 illustrates the block diagram of purification.
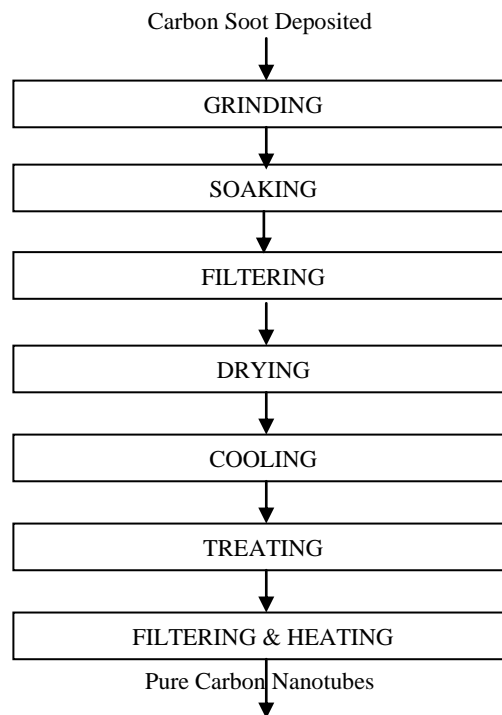

Fig 2 – Purification Block Diagram

3.1. Grinding

Pestle and Mortar is used for grinding the carbon soot. Due to discharge the carbon nanotubes are bonded together and to get the carbon nanotubes in powder it is grinded to a fine powder.

3.2. Soaking

De-ionized water is used for soaking. This helps in removing suspended particles in the grinded soot. The soaking is done for one hour.

3.3. Filtering

High quality Ashless filter papers of grade 42 used to filter the soot. The diameter is 125mm circle filter paper and Cat no 1442 125 which is well suited.

3.4. Drying and Cooling

The filtered soot is kept in an oven at 120°C. The time the soot is kept is one hour. Then the mass is cooled at room temperature.

3.5. Treating, Filtering and Heating

The soot is treated with toluene solvent for 3hours at a ratio of 1:3. The CNT are again Filtered and Heated in an oven at 85°C for 1hour. Again the treated soot is heated in air tubular furnace at 480°C for 3 hours followed by air cooling.

4. DISPERSION

Dispersion [6] is a method of splitting combined carbon nanotubes. Multi walled Carbon nanotubes (MWCNTs) obtained are compressive together and for coating it has to be individualized and hence they are taken and treated with sulfuric acid (H_2SO_4) at 30%wt concentration in water for 15 min at 60ºC in an oven. The treated cnt is washed in distilled water for 3 times and filtered in the Ashless filter paper. The filtered cnt is dried in oven for 10 min.

75mg of cnt is dispersed in 50ml of acetone and sonically treated for 8 hours. Similarly 50mg of cnt is dispersed in 100ml of acetone and sonically treated for 8 hours. CNT dispersed solution is obtained and made ready for coating and it is shown in fig 4.

Parameters for CNT Dispersion:

- MWCNT   –   125mg

- H_2SO_4 –   30ml

- Acetone solvent (C_3H_6O)   –   200ml

- Oven   –   50 - 60°C

- Distilled water   –   500ml

A 15 ml of dispersed MWCNT in acetone solvent at different percentage is collected and stored in an air tight bottle. Fig 5 shows the different percentage dispersed cnt.
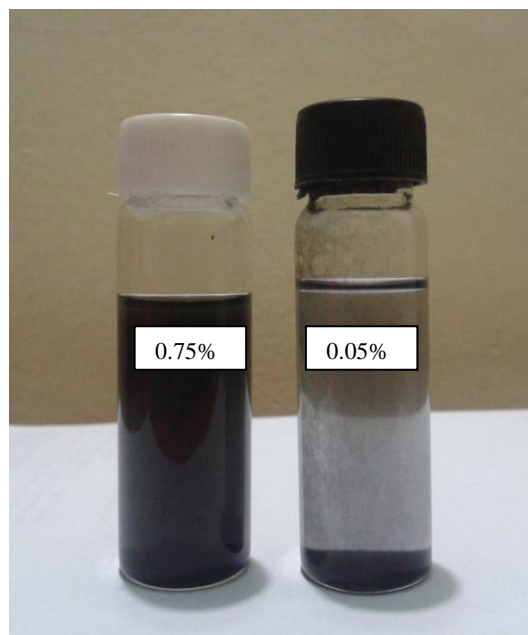

Fig 4 – CNT dispersed in Acetone

Fig 5 – 0.75% & 0.05% dispersed MWCNT

5. COATING

There are many coating techniques possible such as spin coating, DIP coating [6], Ion Implantation etc.., DIP coating is an easy and reliable which involves solvent dispersion.

Parameters for DIP coating:

- Ethanol absolute   – 30ml

- Distilled water   – 1000ml

- Substrate   – Fused Quartz / Silica

- DIP coating machine & Oven

The substrate is pre-cleaned through ethanol absolute. It is sonically treated for 1 hour and washed with distilled water 3 times. Now the substrate is dipped in the dispersion liquid for 5 min for first cycle and then dried in oven at 50ºC.

5 samples are taken and after first cycle one sample is removed from oven. For second cycle again the four samples are dip coated and dried in oven. After drying again one sample is removed.

Similarly from one cycle to five cycle dip coated sample are attained. Through this dip coating cycles the cnt coating thickness is varied from 100nm to 250nm. Fig 6.a and Fig 6.b shows the DIP coating of carbon nanotubes in silica substrate. SEM image shows the CNT is coated on silica and it is connected together to form the electrical conductivity.
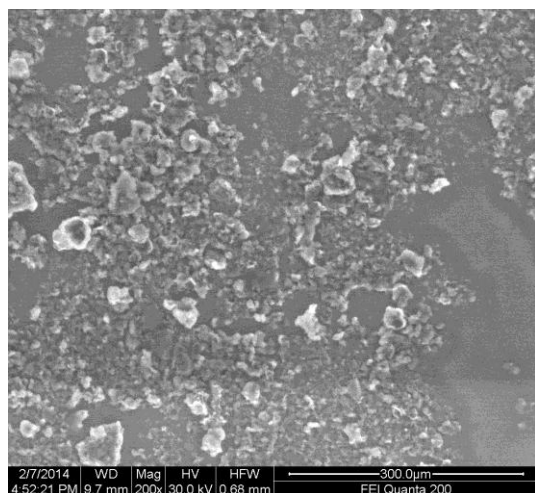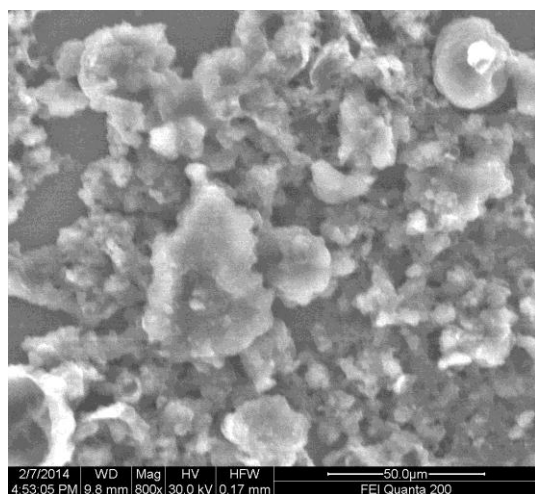
Fig 6.a. 500µm SEM image of Dip coated CNT

Fig 6.b. 50µm SEM image of Dip coated CNT

6. CHARACTERISATION

Carbon nanotubes are to be characterized by its size, structure, resistivity etc.., Characterization of CNT involves mainly

- XRD analysis

- TEM image morphology

- Four point Probe Method

6.1. XRD Analysis

X-ray crystallography tool or XRD analysis [7] is used to determine atomic and molecular structure. The atoms cause the beam of X-rays to diffract in many directions. Depending on angles and intensities of diffracted beams the crystallographer produces a 3D picture of density of electrons.

The electron density shows mean positions, chemical bonds and disorder of atoms in the crystal. The first decade used this method to determine the atom size, lengths, chemical bonds types; atomic-scale in various minerals, alloys etc.., It is still a great method to characterize atomic structure of new materials. It is also suited to the properties of material.

The measurement is made through a crystal mounted to goniometer and precisely rotated to bombard with X-rays which produces the diffraction pattern or reflections. Two

dimensional images are converted to 3D using Fourier transforms for the samples.

The diffracted pattern are plotted to identify the availability of carbon nanotubes. Fig 7 illustrates the XRD analysis chart. From XRD it was observed that produced CNTs are crystalline in nature graphitic (002) peak corresponding to the pure graphitic reflection
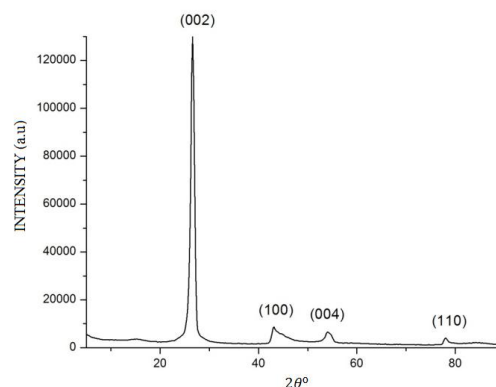

Fig 7 – X-Ray Diffraction pattern for MWCNT

6.2. Transmission Electron Microscopy (TEM) Analysis:

It is a technique where a beam of electrons are transmitted through the specimen as it passes through. The image formed due to interaction of electrons are magnified and focused to an imaging device like fluorescent screen on a layer of the film or detected in CCD camera.

Its capability of imaging is significantly higher than light microscopes, owing to very less de Broglie wavelength of electrons. This helps the instrument user to examine fine details like a single column of atoms.

It can measure thousands of times smaller than the smallest resolvable object in light microscope. It forms a major analysis method of range in scientific fields for both physical and biological sciences.

The TEM [8] image of the Carbon nanotubes at two different scales is illustrated in Fig 8 and Fig 9. While analyzing the nanometer scale of the MWCNT it indicates the Carbon nanotubes are 99% pure.

The Fig 8 shows morphology analysis shows that the MWCNT are properly synthesized. The nanotubes length are measured and found to be approx 100nm.

Since CNT is a conductive in nature it can be used for contacts in fabrication. Further scaled image of the CNT is also done and the diameter of the nanotubes is measured and it is approx 10nm. Fig 9 shows the 50nm scaled image.
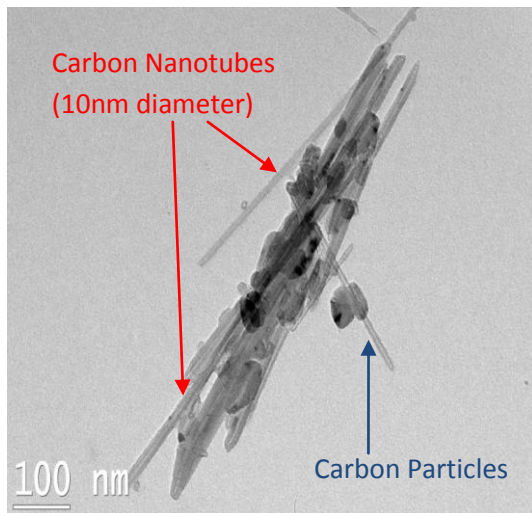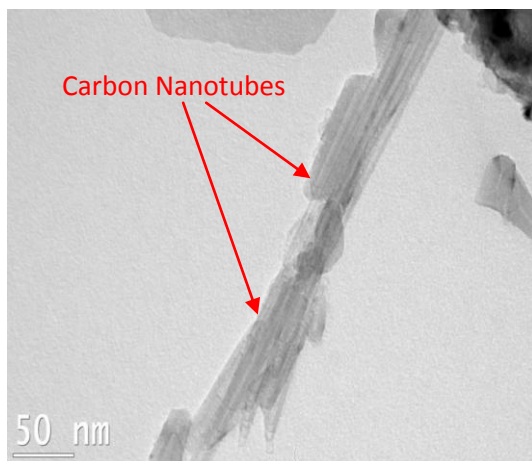
Fig 8 – 100nm scale TEM image of MWCNT

Fig 9 – 50nm scale TEM image of MWCNT

6.3 Electrical Resistivity of CNT

Electrical resistance of cnt is a factor to analyze the conductivity. Depending on the resistance of the CNT it can be classified. To calculate the resistivity four point probe method [9] & [10] is used the purpose of it is to measure the resistivity of any semiconductor. It measures either bulk or thin film specimen, which has different expression. It has four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs to minimize sample damage.

A current source which has high impedance is used to supply current through the outer two probes. A voltmeter measures the voltage across the inner two probes to find the sample resistivity. For a very thin layer s<<1mm we have current rings instead of spheres. Deriving and solving we get the equation,

Resistivity, $R = [\pi/\ln(2) * t * (V/I)]$

Where,

t = thickness of the coating (t=100nm)

V = Voltage of the layer coated

I = Current of the layer coated

Fig 10 shows the I-V characteristics. On solving, the resistivity of the cnt is measured as 11m ohms, which

represent it is highly conductive. The resistivity when compared with a reference papers [11] & [12] the cnt got is having low resistivity. Hence it is very well suited for high conductivity sensors or interconnects.
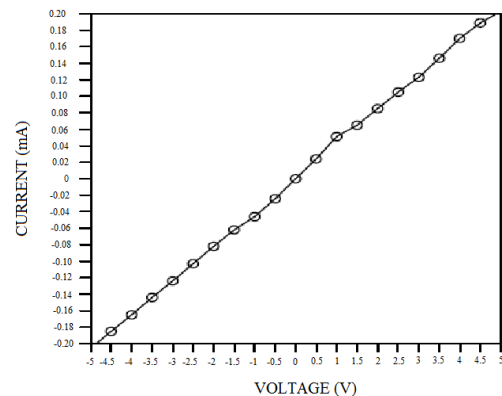

Fig 10 – I-V curve for Electrical Resistivity

7. RESULTS

Synthesis of multi walled carbon nanotubes through Arc Discharge method give a promising result and are so reliable. The results show that the MWCNT are synthesized properly and the carbon nanotubes are having a length of 100nm and diameter of 10nm. Resistivity is found as 11m ohms and can be used as contacts and sensors used in hydrogen chamber.

8. DISCUSSION

Since carbon nanotubes having a cylindrical structure it can be used for composite mixture. A Future approach with composites will be analyzed in further research Tran's conductance of cnt will also be concentrated in further research.

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