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INTERACTIONS OF ELECTRON BEAM WITH SPRING LIKE MWCNT's SYNTHESIZED BY CVD METHOD

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Abstract

Multi-walled carbon nanotubes (MWNT's) are prepared by using a thermal catalytic-chemical vapour deposition (CVD) using acetylene gas as precursor and powdered nickel as catalyst. Argon gas is used as carrier gas and the growth characteristics of MWCNTs were controlled using flow rate, Ar/C2H2 ratio and temperature. The interaction of electron beam with MWNT's is investigated using a scanning electron microscope in the regime of 5 to 30 keV. The structural details of the MWCNTs were studied using x-ray diffraction and FTIR spectroscopic analysis. Interestingly, the nanotubes have grown as helical/spiral coils with multi-terminal junctions as Y or H were observed. The FTIR analysis showed C-C, C=C, C-H bending and stretching modes at 1100, 1531, 1593, 924, 2924 cm-1confirming the presence of multiwalled carbon nanotubes. Further, the XRD analysis showed sharp reflections of (002), (101) and (110) planes. The electron beam interaction with multiwalled carbon nanotubes showed axial joining of tubes. The carbon atoms found to have displaced from the surface of MWCNTs create vacancies and disordered rings of carbon structures. These disordered rings of two different nanotubes joined together as they bend due to potential field.

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*Keywords:*Multi Walled Carbon Nanotubes; MWNT's; Chemical Vapour Deposition; CVD

1. Introduction

Chemical Vapour Deposition process is one of the most popular and desired processes for the synthesis of Carbon Nanotubes as it offers much control for a selective production of nanotubes with desired properties. The other

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methods like Electric Arc Discharge method and Laser Vaporisation methods involve high temperatures and the formation of nanotubes is rapid. This does not allow us to control the output product. The Chemical Vapour Deposition technique operates at a temperature range of 600^0 C-1200^0 C whereas the other processes like arc discharge method are done at temperatures as high as 3000^0 C. Through this process large number of Carbon Nanotubes can be produced as the fabrication process can be very convenient. The process control, ease of handling and regulation of the output product, low energy requirement, better efficiency in terms of cost and purity gives the Chemical Vapour Deposition technique an advantage over all other processes for the production of Carbon Nanotubes. This process is obviously a better choice for mass producing Carbon Nanotubes, given the other methods are a bit complicated and rapid.

Based on the pyrolytic decomposition of hydrocarbons mainly benzene (C6H6), acetylene (C2H2) and methane (CH4), the Thermal CVD technique can be carried out in a relatively low temperature range. The other types of CVD processes are Plasma Enhanced Chemical Vapour Deposition (PECVD) and Alcohol Catalytic Chemical Vapour Deposition (ACCVD). The source of carbon used in this process is a gaseous hydrocarbon compound which is passed on to the catalyst which is usually in a nano particle powder form. The catalyst is usually dispersed on a substrate and the temperature is raised by using a heated coil or plasma. In the conventional CVD method, the production process is carried out in a tube furnace. Here introduce the paper, and put a nomenclature if necessary, in a box with the same font size as the rest of the paper. The paragraphs continue from here and are only separated by headings, subheadings, images and formulae. The section headings are arranged by numbers, bold and 10 pt. Here follows further instructions for authors.

2. Experimental Procedure

In this paper we report the synthesis of Carbon Nanotubes using Thermal Chemical Vapour Deposition technique. The entire process was carried out in an electrical tube furnace of inner diameter of 2.5 cm and length 60cm. The gas used as the source for carbon is acetylene (C2H2) gas. Nickel metal powder (99.7% pure) is used as a catalyst and it is placed in a boat crucible made of Alumina (Al2O3) which acts as a substrate in the process. This helps in increasing the surface area of the catalyst as the powder is evenly distributed inside the boat crucible. The temperature inside the furnace is raised up to 850^0 C and is maintained at this temperature, for the ceramic tube to also attain the same temperature and then the boat crucible with catalyst is introduced into the ceramic tube. The gas pipe with the cork at the end is then attached to one end of the tube and the other end was left open. The Argon gas is used to dilute the Acetylene gas and also to provide an inert atmosphere during the formation of the nanotubes.

As we tried using Acetylene gas without the inert atmosphere, it formed amorphous carbon every time and there weren't any nanotubes.

The pressure inside the tube is atmospheric pressure as one end of the tube is left open. The flow rate of acetylene gas is kept way low in compared to the argon gas flow. The argon gas was first let into the tube for some time to flush out any air present inside the tube and to create an inert atmosphere inside. Then the acetylene gas was let into the ceramic tube for up to 5 min. The slow growth of the nanotubes can be carefully observed from the open end of tube.

During this process the acetylene gets decomposed into carbon and hydrogen. The hydrogen gets escaped from the open end of the tube whereas the molecular carbon thus formed gets converted into atomic level carbon due to the heat energy supplied. The energy supplied is sufficient to break the bonds in the molecular carbon resulting into an atomic level carbon which then gets diffused towards the substrate. The nucleation of the individual carbon atoms starts on the surface of the catalyst and the growth takes place from there.

Jourdain V. et al. (2002) explained the growth mechanism for the growth of carbon nanotubes. The first step involves the formation of Nano sized metallic particles on the substrate. The second step involves the dissociation of the hydrocarbon molecules on the surface of the metal catalyst particle to liberate hydrogen and carbon, which then gets dissolved into the particle. In the third step the diffusion of the carbon particle through the metal particle and precipitation takes place. The termination of the nanotube growth is achieved due to over coating and deactivation of the catalyst that takes place.[12]

In general, the nanotube growth mechanism in the Chemical Vapour Deposition process involves the dissociation of hydrocarbon molecules catalysed by the transition metal, and the saturation of carbon atoms in the metal

nanoparticle. The precipitation of carbon from the catalyst surface leads to the formation of long, tubular carbon solids in a sp2 hybridised structure. The diameters of the nanotubes can be controlled by varying the size of the catalyst particles. [11]

After 5 minutes the gas flow is stopped, and the boat crucible is removed out from the tube immediately to prevent any further reactions. The furnace is then shut down and is allowed to cool on its own.

The carbon deposits on the inner walls of the tube can be removed by heating the tube without any gas flow as the carbon gets combusted in presence of oxygen.

Fibrous cotton like product is obtained in the boat crucible which was carefully removed and analysed using a Scanning Electron Microscope. The sample wasn't handled without any pressing and the sample is stuck on to the carbon tape for analysis in SEM by dissolving it in Ethanol.

3. Results and Discussion

3.1. Scanning Electron Microscope (SEM) Analysis

Figure-1, 2 show Scanning Electron images of Carbon Nanotubes synthesized during the CVD process. Figure-1 shows the long nanotubes that are produced at a magnification of 250X and an accelerating voltage of 25kV. The thickness and length of the nanotubes produced are inconsistent throughout the sample. The nanotubes aren't linearly aligned in one direction; rather they are random and tangled, probably due to the handling. The sample is transferred into storage by scraping off from the surface of the substrate.

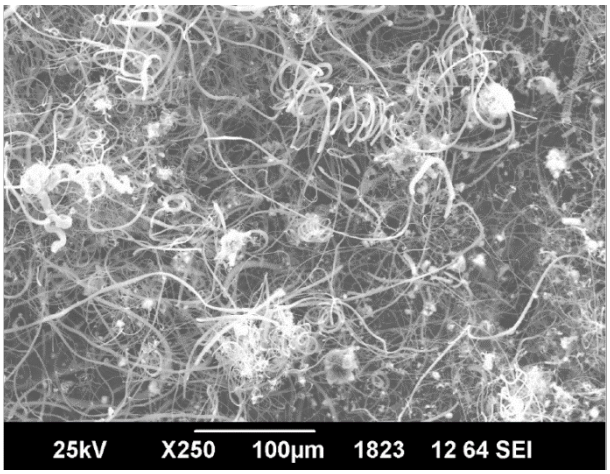

Figure 1- SEM image of CNT sample (Ni, 850C, 1 atm)

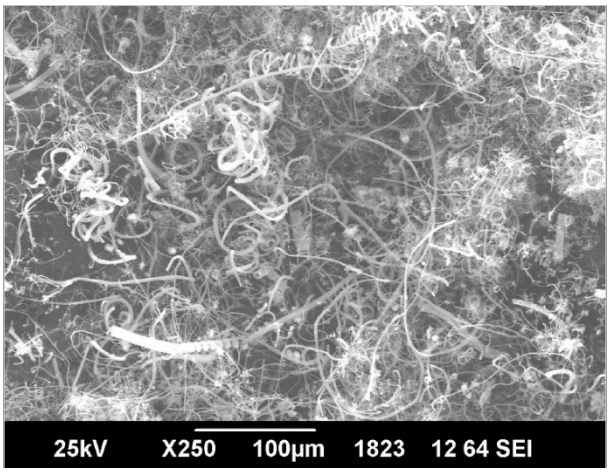

Figure 2- SEM image of CNT sample (Ni, 850C, 1 atm)

Figure-2 is to particularly represent a very long nanotube that is observed during the analysis and also a Carbon Nano coil that is produced which is basically a helical structure with a varying pitch throughout its length. The magnification and the accelerating voltage are same as that of the Figure-1.

Figure-3 shows that the long and thin tube in the left-bottom corner of the image was originally two separate nanotubes which got attached to form one single nanotube when the electron beam is focused on to that area. The two separate tubes moved towards each other and then got attached just when focused, while the images were being observed live in the display from SEM. This image is taken at a magnification of 600X and an accelerating voltage of 25kV.

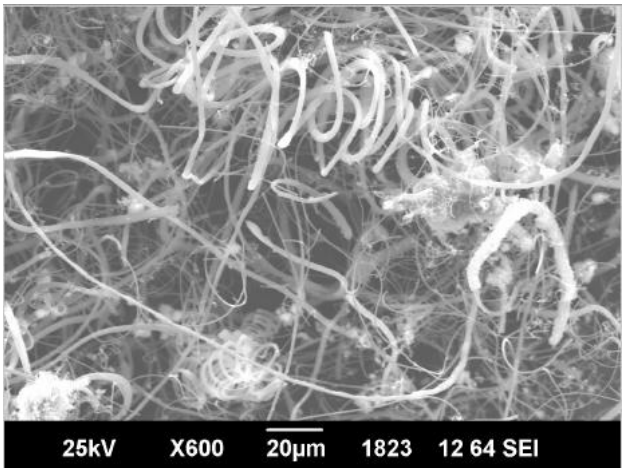

Figure 3- SEM image of CNT sample (Ni, 850C, 1 atm)

Figure-4 is also to indicate the same phenomenon as observed in the Figure-3. The thick bent tube was actually above and away from the thin straight tube when originally observed and when the focusing is done slowly and carefully this time the thick tube slowly moved towards the thin tube and ultimately got attached to it. This image is taken at a magnification of 3000X and an accelerating voltage of 25kV.

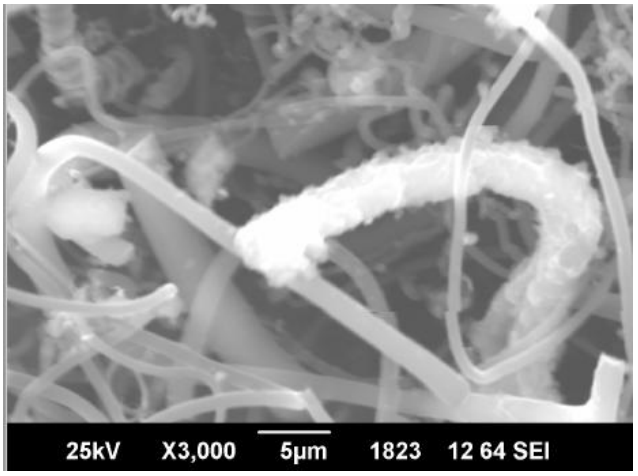

Figure 4- SEM image of CNT sample (Ni, 850C, 1 atm)

Some studies have shown that the joining of the carbon nanotubes when irradiated with high intensity electron beam due to the formation of amorphous carbon at the joint. This amorphous carbon comes from the carbon present in the air.

Florian Banhart has stated that the amorphous carbon that gets deposited at the joining of the nanotubes depends on the amount of the impurities present at the region. Hydrocarbon molecules from the air and other environments are attracted by CNT's as they are by most other specimens. At room temperature, these molecules are highly mobile on almost all surfaces. Once such molecule migrates into the area that is irradiated with an electron beam of sufficient energy, dissociation under the beam leads to the transformation into amorphous carbon, which is immobile and remains in the irradiated area. [1].

But all of this joining happened when they are put together intentionally and irradiated at the joint with an electron beam and the joint itself is not a perfect joint to be exact. The nanotubes don't actually coalesce but instead the joint is soldered by the amorphous carbon that gets deposited at the joint where there is an impurity or a defect. The phenomenon of the nanotubes moving and coming closer or attaching to each other to form one single nanotube, as observed in our study hasn't been studied.

SEM uses a high intensity electron beam to practically scan the surface of the specimen pixel by pixel.The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition. The intensity of the electron beam increases when it is focused at a particular area and that means that the number of electrons that touch the specimen increase.

Bin LI et al states that the electrons from the electron beam collide with the nucleus of the carbon atom and transfer the momentum on to the carbon atom. Most of the times the electron gets deflected at a small angle, but some electrons are back scattered. Most of the collisions are of elastic type in which the carbon atom may get knocked off from the hexagonal rings of the nanotubes. Only a small fraction of carbon atoms was knocked out of their positions as interstitials or sputtering atoms leaving the nanotube to the open space. The loss of atoms led to a reconstruction of the network from a purely hexagonal to a coherent structure containing also non-six-member rings, which produced Stone−Wales defects by forming pentagon−heptagon pairs and thus brought shrinkage to the tube wall. In addition, the removal of carbon atoms left vacancies in the tube walls and also shrank the tube. The small amount of atom loss was responsible for the bending of the shells rather than that of the whole nanotube. Usually it leaves a deformation in the nanotubes. [2].

So,it can be attributed that due this vacancy, the nanotubes get attracted towards each other and form new bonds with the nearest nanotubes to fill up the vacancies, i.e., new covalent bonds form between carbon atoms from the hexagonal ring structures of both the nanotubes.

Figure-5,6 show spiral like Carbon Nanotubes formed in the boat crucible. The nanotubes are intertwined and are twisted randomly with no clue of any growth pattern. By further analysis of the rigidity and tensile properties of these coil like structures the application of some nanostructures to bind or in some structural applications. Figure-5 is taken at a magnification of 1000X and Figure-6 at a magnification of 2500X whereas the accelerating voltage is kept at 25kV for both the cases.

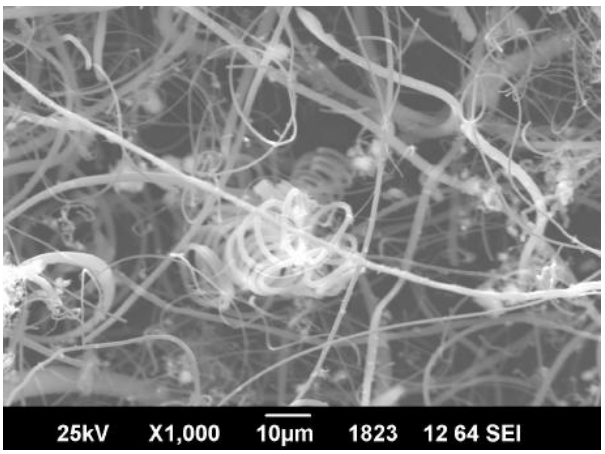

Figure 5- SEM image of CNT sample (Ni, 850C, 1 atm)

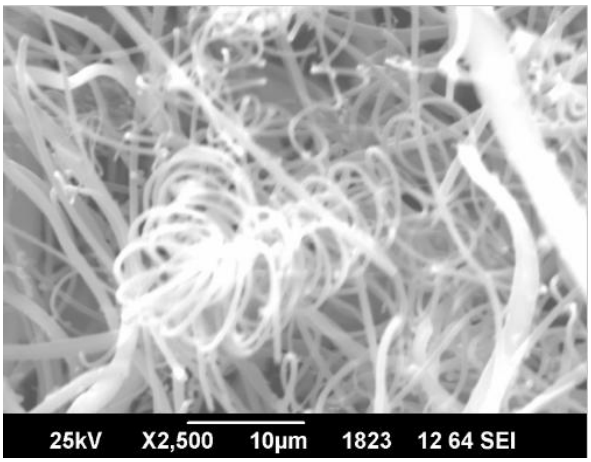

Figure 6- SEM image of CNT sample (Ni, 850C, 1 atm)

Figure-7, 8, 9 show spring shaped Carbon Nano Coils that can be produced through the Chemical Vapour Deposition process. It proves that some complex mechanical structures can also be made from Carbon Nanotubes. These can be used in some structural applications of some Nano structures if all the properties are properly analysed.

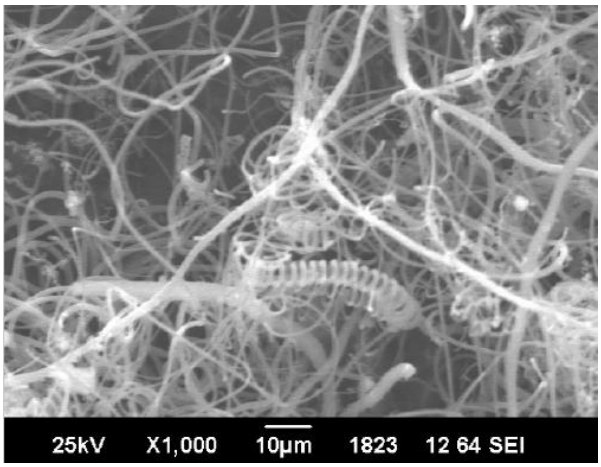

Figure 7- SEM image of CNT sample (Ni, 850C, 1 atm)

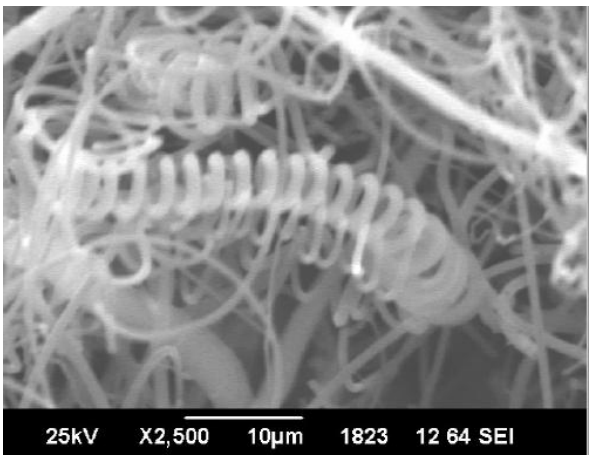

Figure 8- SEM image of CNT sample (Ni, 850C, 1 atm)

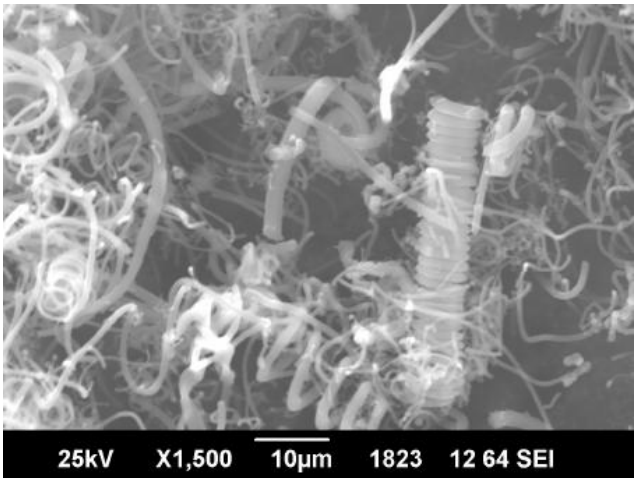

Figure 9- SEM image of CNT sample (Ni, 850C, 1 atm)

3.2. X-Ray Diffraction (XRD) Analysis

The graph-1 shows the XRD data of the corresponding sample. Clearly intense sharp peaks indicating the Multi Walled Carbon Nanotubes (MWNT's) can be observed. Along with the CNT's, peaks corresponding to amorphous carbon and the catalyst can also be seen. An XRD pattern is a sum of the diffraction patterns produced by each phase in a mixture. From XRD patterns we can determine the type of crystalline phases present in the mixture, quantity of each crystalline phase present in the mixture and we can also determine if any amorphous material is present in the mixture. Experimental XRD data can then be compared to reference patterns to determine what phases are present in the mixture. A phase is a specific chemistry and atomic arrangement where each phase produces a unique diffraction pattern. Usually amorphous materials do not produce sharp diffraction peaks.

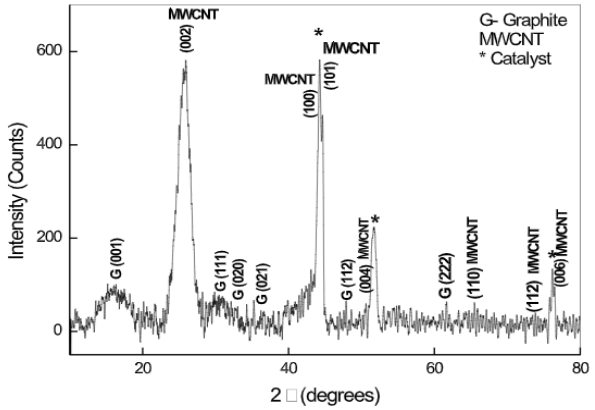

Fig.10: XRD diffractograms of spring type MWCNT synthesized using CVD technique

3.3. Fourier Transform infrared (FTIR) Analysis

The FTIR analysis of the MWNT sample has shown some N-H bonds (both bending and stretch) and Nitrile bonding's, probably due to the Nitrogen present in the atmosphere as the synthesis was carried out in atmospheric conditions. It has also shown C=H (bending), C-H (both bending and stretch). C-O (stretch), O-H bonds were also observed along with C=O (stretch) bonding's. Carbenes were also noted in the FTIR spectrum data. The C-H, C-C bonds and the C=C bonding indicate a clear presence of Carbon Nanotubes.

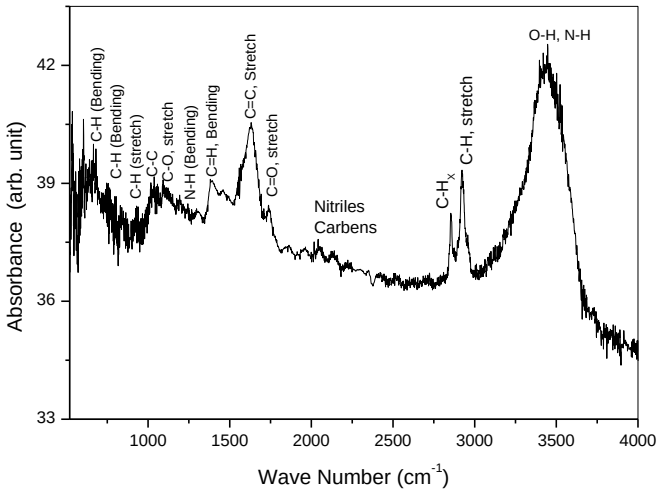

Fig.11: FTIR Spectrum of MWCNTs

4. Conclusions

Carbon nanotubes have been synthesized by using CVD method at 850^0 C using a Ni catalyst and Alumina (Al2O3) as substrate and acetylene as the source for carbon. A unique behaviour of the nanotubes moving towards nearby nanotubes, when irradiated by a high intensity electron beam, is observed. Two nanotubes joining axially to form one long nanotube is also been observed. The benefits of CVD method in the production of complex shaped CNT's like Carbon Nano Coils- spirals, springs like structures have also been analysed. CVD method is very useful in mass producing carbon nanotubes and also a very efficient process which doesn't require high temperatures and also provide better control over the synthesizing parameters.

(1)

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