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Carbon Nanotubes from Unconventional Resources:
Part A: Entangled Multi-Walled Carbon Nanotubes and
Part B: Vertically-Aligned Carbon Nanotubes

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Additional information is available at the end of the chapter

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1. Part A: Entangled Multi-walled carbon nanotubes

1.1. Introduction

Nanotechnology is a topic attracting scientists, industrialists, journalists, governments and even a common people alike. Carbon nanotubes (CNTs) and other carbon nanostructures are supposed to be a key component of this nanotechnology. Having realized its tremendous application potential in nanotechnology, a huge amount of efforts and energy is invested in CNT projects worldwide. Till date, the art of CNT synthesis lies in the optimization of parameters for selected group materials on a particular experimental set-up. As viewed from the perspective of green chemistry, sustaining the environment implies sustaining the human civilization. The long-term key of a sustainable society lies in stable economy that uses energy and resources efficiently. Therefore, it is high time to evaluate the existing CNT techniques on these parameters.

Let us examine three popular methods of CNT synthesis viz Arc discharge, Laser-vaporization and CVD method. Arc-discharge method, in which the first CNT was discovered [1], employs evaporation of graphite electrodes in electric arcs that involve very high temperatures around 4000º C. Although arc-grown CNTs are well crystallized, they are highly impure. Laser-vaporization technique employs evaporation of high-purity graphite target by high-power lasers in conjunction with high-temperature furnaces [2]. Although laser-grown CNTs are of high purity, their production yield is very low. Thus it is obvious that these two methods score too low on account of efficient use of energy and resources. Chemical vapor deposition (CVD), incorporating catalyst-assisted thermal decomposition of hydrocarbons, is the most popular method of producing CNTs, and it is truly a low-cost and scalable tech-
nique for mass production of CNTs [3]. Unfortunately, however, till date only purified petroleum products such as methane, ethylene, acetylene, benzene, xylene are in practice, as precursor, for synthesizing CNTs. Apart from petroleum based hydrocarbons, carbon nanotubes have been synthesized from polymers, metalloccenes and domestic fuels such as kerosene and liquefied petroleum gas [4-7].

According to the principle of green chemistry, the feed stock of any industrial process must be renewable, rather than depleting a natural resource. Moreover, the process must be designed to achieve maximum incorporation of the constituent atoms (of the feed stock) into the final product. Hence, it is the time’s prime demand to explore regenerative materials for CNT synthesis with high efficiency. This well-valued material of biotechnology research was successfully brought to nanotechnology research with the first report of CNTs from natural precursors in 2001. Since then, investigators involved with this environment-friendly source of CNTs and established the conditions for growing multiwalled nanotubes (MWNTs), single-wall nanotubes (SWNTs) and vertically aligned MWNTs on the suitable catalytic support by a simple and inexpensive CVD technique. Researchers prepared good quality of Multi-walled carbon nanotubes (MWNTs) and vertically aligned ones by thermal decomposition of turpentine oil and Camphor [8,9]. Andrews et al. synthesized pure Single-walled carbon nanotubes (SWNTs) by catalytic decomposition of camphor and its analoges [10]. Ghosh et al. prepared single-walled carbon nanotubes from turpentine oil and eucalyptus oil [11]. We have succeeded in growing of CNTs from pine oil [12] and methyl ester of Jatropha curcas oil [13], a botanical hydrocarbon extracted from plant source, having boiling point around 200 - 280º C. Being a green-plant product, these oils are eco-friendly source and can be easily cultivated in as much quantity as required. Unlike any fossil/petroleum product, there is no fear of its ultimate shortage as it is a regenerative source. These sources are readily available, cheap and also user-friendly for chemical vapor deposition due to its volatile and non-toxic nature.

United states Environmental Protection Agency has developed 12 principles of green chemistry [14] that explain what the green chemistry means in practice. Using those definitions as a protocol, we can evaluate the CNT precursor materials such as Pine oil, Methyl ester of Jaerotha curcas oil and Methyl ester of Pongamia pinnata oil, as follows.

Prevention : With the highest CNT-production efficiency, plant based precursor complies with waste-prevention rule significantly.

Atom Economy : Botanical hydrocarbons gets maximum incorporation of its constituent atoms into the final product, CNTs.

Less Hazardous Chemical Synthesis : All the substances involved in this technique (carbon source, catalyst and support material) possess little or no toxicity to human health and the environment.

Designing Safer Chemicals: Our final product is common-grade CNTs that are apparently safe. Safer Solvents and Auxiliaries : The only auxiliary used in our method is the metal catalyst that are apparently safe.
Design for Energy Efficiency: By virtue of a low-temperature atmospheric pressure CVD process, the energy requirements of our technique are significantly low.

Use of Renewable Feedstock: The raw material is purely a regenerative material; so there is no danger of depleting a natural resource.

Reduce Derivatives: No derivative is formed in this technique; solely catalyst-assisted in-situ decomposition of plant based precursor leads to CNTs.

Catalysis: It is a purely catalytic process, no stoichiometric reagents are involved.

Design for Degradation: CNTs as such are non-biodegradable; however, their intentional degradation can be achieved by introducing certain functional groups.

Real-time analysis for pollution Prevention: This technique as such should be fully compatible with real-time analysis for pollution prevention, if executed at an industrial laboratory.

Inherently Safer Chemistry for Accident Prevention: Substances and their form used in our process are chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.

In this chapter the authors discuss the morphology of the carbon nanostructures produced using Pine oil, Methyl ester of *Jatropha curcas* oil and Methyl ester of *Pongamia pinnata* oil as natural carbon precursors by spray pyrolysis method, a modified chemical vapor deposition method. It is similar to chemical vapor deposition method, the only difference is the vaporization and pyrolysis of carbon source occurs simultaneously in spray pyrolysis whereas in CVD it is a two step process. Since these precursors evaporate at relatively higher temperatures, spray pyrolysis method was adopted for synthesis of CNTs. The results show that the morphology closely correlates with precursor concentration and the authors propose that the effect is related to the competition between rate of decomposition of precursor and the diffusion of carbon species through the catalyst particle.

1.2. Experimental Methods

A catalytic supporting material Fe, Co and Mo with silica (Fe:Co:Mo:SiO₂ = 1:0.5:0.1:4) was prepared by wet impregnation method [15]. Appropriate quantities of metal salts (Merk) i.e. Fe(NO₃)₃, 6H₂O, Co(NO₃)₃, 3H₂O and (NH₄)₆Mo₇O₂₄, 4H₂O were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merk). The solvent was then evaporated and the resultant cake heated to 90-100 °C for 3 h, removed from the furnace and ground to fine power. The fine powders were then calcined for 1 h at 450 °C and then re-ground before loading into the reactor. The prepared catalyst was directly placed in a quartz boat and kept at the centre of a quartz tube which was placed inside a tubular furnace. The carrier gas nitrogen was introduced at the rate of 100 mL per minute into the quartz tube to remove the presence of any oxygen inside the quartz tube. The temperature was raised from room temperature to the desired growing temperature. Subsequently, the carbon precursor was introduced into the quartz tube through spray nozzle and the flow was maintained at the rate of 0.1 - 0.5 ml/min. Spray pyrolysis was carried out for 45 minutes and thereafter furnace was cooled to room temperature. Nitrogen atmosphere was maintained throughout the experiment. The morphology
and degree of graphitization of the as-grown nanostructures were characterized by high resolution transmission electron microscopy (JEOL-3010), Raman spectroscopy (JASCO NRS-1500W) green laser with excitation wavelength 532 nm) and thermo gravimetric analysis (TGA). The as-grown products were subjected to purification process as follows [16]. The sample material was added to 20 ml 1N HCl to form an acidic slurry. This slurry was heated to 60 °C and stirred at 600 rpm. To this heated acidic slurry 20 ml H$_2$O$_2$ was added to form oxidative slurry and stirred for 30 minutes. The sample was filtered and washed with 1N HCl and distilled water. The collected sample was calcined at 400 °C in nitrogen atmosphere for 2 hours. The experiment at optimum reaction conditions were repeated several times to ensure the reproducibility of formation of carbon nanostructures.

1.3. Result and Discussion

Pine oil, Methyl ester of *Jatropha curcas* oil and Methyl ester of *Pongamia pinnata* oil were used for synthesis of carbon nano structures by spray pyrolysis method. These oils were individually sprayed at different rate (10 mL, 20 mL and 30 mL per hour) over silica supported Fe, Co and Mo catalyst at different reaction temperatures (550 °C, 650 °C and 750 °C) to synthesis carbon nanostructures. The as-grown nanostructures were characterized by SEM, TEM, TGA and Raman spectroscopy techniques.

The result shows low yield of carbon nano structures with three types of precursors, Pine oil, Methyl ester of *Jatropha curcas* oil and Methyl ester of *Pongamia pinnata* oil, when sprayed individually at the precursor flow rate of 10mL per hour over silica supported Fe, Co and Mo catalyst at 550 °C. An improved carbon nanostructure formation at 650 °C for the precursor flow rate of 20 mL per hour was observed invariably for the three precursor materials. When the experimental condition was either 750 °C or precursor flow rate of 30 mL per hour, decrease in carbon nanotube yield observed.

Figure 1 illustrates the SEM image of the CNTs samples grown at different temperatures using pine oil as precursor at a flow rate of 20 mL per hour. At 550 °C few CNTs were found to grow because this temperature is not sufficient to pyrolyse the carbon source (Fig. 1a). On the other hand, at 650 °C (Fig. 1b) the formation of CNTs is high because at this temperature the carbon source decomposes effectively. At 750 °C, the quantity of CNTs has decreased and thick nanotubes have been formed (Fig. 1c). Experiments with methyl ester of *Jatropha Curcas* oil as a carbon precursor at different temperatures were conducted and the SEM images of the sample were recorded. The SEM images of sample synthesized at 650 °C revealed the formation of homogeneous and dense distribution of CNTs in a web-like network (Fig. 1e), while very few nanotubes formation at 550 °C (Fig. 1g).

At higher temperature (750 °C) an increase in diameter of the CNTs was observed (Fig. 1f). The morphology of carbon nanotube synthesized at different temperatures using methyl ester of *Pongamia pinnata* oil are recorded using SEM. Few carbon nanostructures were observed at a lower deposition temperature of 550 °C (Fig. 1g). When the temperature was increased to 650 °C chain like carbon nanostructure was dominant (Fig. 1h). At 750 °C, a more uniform distribution of MWNTs was observed with a diameter of around 150 nm (Fig. 1i).
The TEM result shows varied morphologies of carbon nanostructures synthesized at different experimental conditions. All the three precursors used in this study produced mostly amorphous carbon at 550 °C for different flow rate of precursor materials. When the reaction temperature was 650 °C, Pine oil at a flow rate of 20 mL per hour, produced MWNTs of good quality (Fig.2a). The HRTEM result of sample obtained with pine oil as a precursor at a flow rate of 30 mL per hour and reaction temperature of 650 °C, shows (Fig.2b) that the inner and outer diameter of the synthesized MWNTs was about 6.6 and 14 nm and consist of 11 graphene layers with inter layer distance of 0.342 nm. The outer layer of MWNTs were covered with amorphous carbon. Methyl ester of *Jatropha curcas* oil produced well crystalline MWNTs of inner and outer diameter of 3 nm and 9 nm respectively, when the precursor sprayed at a flow rate of 20 mL per hour over silica supported Fe, Co and Mo catalyst at reaction temperature of 650°C (Fig. 2d). However, an increase of precursor flow rate to 30 mL per hour at the same temperature produced largely amorphous carbon and small quantity of metal encapsulated MWNTs of size around 40 nm (Fig. 2c). A metal filled MWNTs of inner and outer diameter of 4 nm and 24 nm respectively was observed when methyl ester
of *Pongamia Pinnata* oil, at a flow rate of 20 mL per hour, was spray pyrolysed at 650 °C over silica supported Fe, Co and Mo catalyst. When flow rate was increased to 30 mL per hour, a short growth of metal encapsulated carbon nanostructures was observed (Fig. 2e). The TEM and TGA studies reveal that the carbon nanostructures are not well graphitized.

The Fig. 2a shows TEM images of sample prepared using Pine oil as carbon source at a flow rate of 20 mL per hour over silica supported Fe, Co and Mo catalyst at a reaction temperature of 650°C. The TEM images indicate that the inner and outer diameter was uniform over entire length of the tube. It is also evident that carbon nanotubes do not contain encapsulated catalyst but amorphous carbon at the outer wall of the tube. The well crystallized graphene layer was confirmed from the $I_G/I_D$ ratio of 2.5 (Fig. 3a). The $I_G/I_D$ ratio increases with increase of precursor flow rate from 10mL per hour to 20 mL per hour, but further increase of precursor flow rate to 30mL per hour results in decrease of $I_G/I_D$ ratio to 0.5 (Fig. 3b). The improved quality can be attributed to increase of precursor concentration in the tube. The higher flow rate of precursor (20 mL per hour) increases precursor concentration in the tube which leads to increase in decomposition of precursor over catalyst. Thus quality carbon nanotubes were formed at a reaction temperature of 650 °C. However, too high a concentration of precursor (30 mL per hour) or a reaction temperature of 750 °C leads to the formation of amorphous product.

**Figure 2.** Representative TEM images of as-grown CNTs under constant reaction temperature of 650 °C for flow rate of precursor: Pine oil (a) 20 mL per hour (b) 30 mL per hour; Methyl ester of *Jatropha curcas* oil (c) 30 mL per hour (d) 20 mL per hour and Methyl ester of *Pongamia pinnata* oil (e) 30 mL per hour (f) 20 mL per hour.
as vapor phase decomposition of precursor is promoted than the decomposition over catalyst. The results are in good accordance with the reports by Afre et al. [17]. They have synthesized MWNTs using turpentine oil as a precursor by spray pyrolysis method in the temperature range of 600 to 800 °C. While Ghosh and co workers [18] reported synthesis of single walled carbon nanotube at a reaction temperature of 850 °C and abundant amount of MWCNTs at lower temperatures using turpentine oil as precursor by CVD method. No lower frequency RBM peaks in Raman spectra of our samples shows the absence of SWNTs.

Figure 3. Typical Raman spectrum (green laser with excitation wavelength 532 nm) of as-grown MWNTs at different flow rate of precursors: Pine oil (a) 20 mL per hour (b) 30 mL per hour; Methyl ester of Jatropha curcas oil (c) 20 mL per hour (d) 30 mL per hour and Methyl ester of Pongamia pinnata oil (e) 20 mL per hour (f) 30 mL per hour.

Thermogravimetric analysis was performed to characterize the thermal behavior of the carbon nanotube synthesized using Pine oil as precursor. The Thermogravimetric graph shows the wt% vs. temperature. Up to a certain period of time there is no weight loss. The oxidation of carbon deposit starts after this point which is indicated by a dip in curve. With increase in temperature the weight loss increases till all the carbon get burnt. The residue is the catalyst and support. The TGA curves gives the temperature corresponds to the maximum mass decrease, which is considered to be a measure of the level of crystallinity of carbon nanotube. The TGA results (Fig.4a,b,c) shows the variation in decomposition temperature for the products synthesized at 650 °C for different flow rate of Pine oil precursor. It was found that the decomposition temperature varied between 568 and 591 °C. The relatively high decomposition temperature of 591 °C for the product synthesized at a reaction temperature of 650 °C for precursor flow rate of 20 mL per hour indicates well crystalline structure formation.

A HRTEM images (Fig. 2d) of sample prepared using Methyl ester of Jatropha curcas oil as carbon precursor at a flow rate of 20 mL per hour over silica supported Fe, Co and Mo catalyst at a reaction temperature of 650°C clearly shows well graphitized layers of a typical MWNTs with uniform inner and outer diameter. The TEM image also reveals that encapsulated catalyst or amorphous carbon is rarely seen in the sample. The image indicates that the MWNTs are composed of around 26 walls and layers grow perpendicular to the growth axis of the tube. An increase of precursor flow rate to 30 mL per hour at the reaction temperature of 650 °C produced largely amorphous carbon and small quantity of metal incorporated MWNTs of size around 40 nm is evident from the TEM images (Fig. 2c). An additional confirmation for high degree graphitization and formation of metal fil-
led MWNTs for sample prepared using the precursor flow rate of 20 mL per hour and 30 mL per hour respectively is shown by Raman spectra (Fig. 3c,d). The G band at 1571 cm\(^{-1}\) was attributed to well crystallized carbon structure, while the D band at 1359 cm\(^{-1}\) was attributed to defects in the structure [19]. The decrease in relative intensity of the G band and D band (I\(_G\)/I\(_D\) ratio) for sample prepared with precursor flow rate of 30 mL per hour indicates more defects in as-grown sample (Fig. 3d). The defects in MWNTs can be attributed to increase of precursor concentration in the tube and encapsulation of catalyst particles. An increase of precursor concentration in the tube leads to increase in decomposition of precursor over catalyst. Above the critical concentration of precursor, rate of decomposition of precursor exceeds rate of diffusion of carbon into the catalyst particle and thus encapsulation of metal particle occurs. The TGA results of MWNTs sample grown using methyl ester of *Jatropha curcas* oil are shown in (Fig.4d,e,f). Higher decomposition temperature and 37% residue observed in the TGA studies for the product synthesized at a reaction temperature of 650 °C for precursor flow rate of 20 mL per hour shows the sample contain around 60% MWNTs with well crystallized structure. A decrease in decomposition temperature and high residue shows defects in structure and metal encapsulation for the sample prepared at 650 °C for the precursor flow rate of 30 mL per hour.

![Figure 4. TGA curves of as-grown CNTs samples at different flow rate of precursors: Pine oil (a) 10 mL per hour (b) 20 mL per hour (c) 30 mL per hour, Methyl ester of *Jatropha curcas* oil (d) 10 mL per hour (e) 20 mL per hour (f) 30 mL per hour, Methyl ester of *Pongamia pinnata* oil, as-grown, (g) 10 mL per hour (h) 20 mL per hour (i) 30 mL per hour and purified (j) 10 mL per hour (k) 20 mL per hour (l) 30 mL per hour.](image)

The TEM images of sample synthesized for 20 mL per hour flow rate of methyl ester of *Pongamia pinnata* oil over silica supported Fe, Co and Mo catalyst at a reaction temperature of 650 °C was shown in Fig. 2f. The average outer diameter of the tube synthesized varied randomly as the reaction temperature was changed. At 550 °C, the diameter of the arborization-like nanostructures were around 65 nm, whilst at 650 °C, the formed MWNTs has inner and outer diameter in the range of 7nm & 33nm. The HRTEM image of the sample synthesized at 650 °C (Fig.2f) indicates the metal particles, seen as a dark spot on the image, were tightly covered by carbon layers with a thickness of a few nanometers. When precursor flow rate was reduced from 30 to 20 mL per hour, due to effective decomposition of precursor and the fluid nature of catalyst particle, the morphology of the product changed from arborization-like nanostructure to magnetic nanoparticle encapsulated in multi-walled carbon nanotubes.
A similar observation was reported by Kang et al. [20]. Also, morphology change from magnetic nanoparticle encapsulated in multi-walled carbon nanotubes to multi-walled carbon nanotubes structure was attributed to the high fluid nature of catalyst at 750 °C. The inner diameter of the carbon structure formed is same as that observed for products synthesized at 650 °C indicates the prevention of agglomeration of catalyst particles by Mo [21].

Amorphous carbon formation in large quantity, at 750 °C or at precursor flow rate of 30mL per hour, may be due to increased thermal decomposition of precursor material. The TGA results are shown in Fig.4g,h,i. It is evident that the weight loss continues to increase rapidly with temperature until reaches a constant value. Residue of the as-grown sample for precursor flow rate of 10 mL, 20 mL and 30 mL per hour at 650 °C was found to be 63.2, 60.9 and 50.5% respectively by weight (Fig.4g,h,i). The TGA results of same samples after purification shows (Fig. 4j,k,l) weight of residue as 3.5, 22.5 and 2.5% mass fraction. The more decline in mass fraction was caused by the acid leaching of catalyst particles that was not encapsulated by carbon. The low residue observed for products synthesized at 550 °C and 750 °C are attributed to low catalytic activity and high thermal decomposition of precursors respectively, which leads to formation of high amorphous carbon and low encapsulated products. The products synthesized at 650 °C shows minimum mass loss in TGA studies, even after purification, is due to better encapsulation of metal particles by carbon layers. The $I_G/I_D$ value of 0.9 (Fig.3e) for samples prepared at 650 °C with flow rate of 20 mL per hour indicates that magnetic nanoparticles encapsulated in carbon nanotubes structure had defects and moderate crystallization of graphene planes [22,23]. This supports the HRTEM results. The increased $I_G/I_D$ value of 1.87 (Fig. 3f) for the same sample, after purification indicates the removal of amorphous carbon and defective structures during purification. The removal of amorphous carbon and defective structures were further supported by higher ignition temperature 610 °C in TGA studies. According to TGA curves, weight of residue for the purified sample decreased to about 13 to 31% mass fraction comparing to unpurified sample due to leaching of metal particle and amorphous carbon removal during purification process. This shows that carbon layers covering the metal particles prevent their dissolution during purification process.

The mechanism of CNT nucleation and growth is one of the challenging and complex topics in current scientific research. Presently, various growth models based on experimental and quantitative studies have been proposed. It is well established, that during CNT nucleation and growth the following consecutive steps were taken place [24].

1. Carbon species formation by decomposition of precursor over the catalyst
2. Diffusion of carbon species through the catalyst particle
3. Precipitation of the carbon in the form of CNTs

The first step involves formation of carbon species by catalytic vapor decomposition of vapors of the precursor material over the catalyst. In the second step the diffusion of carbon species through the catalyst particle takes place. The catalyst surface may exert a diffusion barrier. It is still unclear whether carbon species diffuse on the particle surface [25], on the particle bulk [24] or whether surface and diffusion compete. The most accepted growth
model suggests bulk diffusion of carbon species into the metal particles [26]. The third step is the precipitation of the carbon in the form of CNTs from the saturated catalyst particle.

![Figure 5. TEM images of as-grown CNTs sample synthesized under constant reaction temperature of 650 °C using Methyl ester of Pongamia pinnata oil at a flow rate of 20 mL per hour. (a) indicates the reshaping of catalyst particle (b) metal particle at the tip of tube.](image)

Based on experimental results, a possible growth mechanism of MWNTs was proposed. It is known from the fact that Catalytic centers on catalyst particle act as nucleation site for the growth of MWNTs [22]. The precursor vapor decomposed on surface of the catalyst particle produces carbon. As the reactivity between the catalyst and the carbon exceeds the threshold value, carbon atoms loose their mobility in the solid solution, forming metal carbides [23]. These meta stable Fe and Co carbides decomposed and produce carbon which dissolve in these metal particles. The dissolved carbon diffuses through the metal particle and gets precipitated in the form of crystalline graphene layer. This carburized surface acts as a barrier for further carbon transfer from the gas phase to the bulk of the catalyst since carbon diffusion is slower through metal carbides [27]. The saturated metal carbide have lower melting point and they are fluid like during the growth process [28].

If the rate of precursor decomposition and the rate of diffusion of carbon are equal, then the metal raise through a capillary action and tube growth occurs. The fact that long carbon nanotubes observed have their catalyst particles partially exposed indicates that the direct contact of catalyst surface with carbon precursor is essential for continuous CNT growth (Fig. 5a). This is consistent with the growth mechanism proposed by Rodriguez [29]. In case the decomposition rate exceeds the diffusion rate, more of carbon produced forms a thick carbide layer over the surface of metal which acts as a barrier for further carbon transfer from the gas phase to the bulk of the catalyst. However, the thick carbide layer crystallizes out as graphene layer which encapsulate the metal particle. When a catalyst particle is fully encapsulated by layers of graphene sheets, the carbon supply route is cut and CNT growth stops resulting in short MWCNTs. The catalyst particle undergoes several mechanical reshaping during the tip growth of multi-walled nanotubes [30, 31]. This gives the impression that the catalyst is in liquid state during reaction. The catalyst particle seen inside and at the
The CNTs grow with either a tip growth mode or a base growth mode. Base growth mode is suggested when the catalyst particle remain attached to the support, while tip growth happens when the catalyst particle lifts off the support material. These growth modes depends on the contact forces or adhesion forces between the catalyst particle and support [33], while a weak contact favors tip-growth mechanism, a strong interaction promotes base growth [34]. Catalyst particle seen at tip of CNTs (Fig. 5b) indicate tip growth mode. These catalyst particles have lifted off the support and elongated due to the flow nature and stress induced by the carbon surrounding the catalyst.

2. Part B: Vertically-aligned carbon nanotubes

2.1. Introduction

Aligned carbon nanotubes were first reported by Thess et al. [2]. In the same year the Chinese academy of science reported that a 50 µm thick film of highly aligned nanotubes had successfully grown by chemical vapor deposition (CVD) [35]. Vertically aligned CNTs are quasi-dimensional carbon cylinders that align perpendicular to a substrate [36]. Vertically aligned with high aspect ratios [37] and uniform tube length made it easy spinning into macroscopic fibres [38]. Aligned CNTs are widely used in nano electronics, composite materials as reinforcing agents and self-cleaning applications [39-41]. Aligned CNTs are ideal electrode material for biosensors over entangled CNTs, may be due to its high electrical conductive property [42]. Large CNT arrays have successfully been grown on different substrates, such as mesoporous silica [43], planar silicon substrate [44] and quartz glass plate [45]. Substrate provides a solid foundation for growing aligned CNTs. The substrate must able to inhibit the mobility of the catalyst particles in order to prevent agglomeration. The most commonly used active catalyst for growing CNTs are magnetic elements such as Fe, Co or Ni. Gunjishima et al. [46] used Fe-V bimetallic catalyst for synthesis of aligned DWCNTs. Recently, there have been appreciable attempt of using ferrocene as a catalyst for synthesis of aligned carbon nanotubes [47]. Here we report fabrication of aligned CNTs by spray pyrolysis on silicon wafer using mixture of Pine oil, Methyl ester of *Jatropha curcas* oil and Methyl ester of *Pongamia pinnata* oil with ferrocene.

2.2. Experimental Methods

The syntheses of aligned CNTs were carried out using the spray pyrolysis method. In this spray pyrolysis method, pyrolysis of the carbon precursor with a catalyst take place followed by deposition of aligned CNTs occur on silicon substrate. Pine oil, Methyl ester of *Jatropha curcas* oil and Methyl ester of *Pongamia pinnata* oil were used as carbon source and ferrocene [Fe\(\left(C_5H_5\right)_2\)] (Sigma Aldrich, high purity 98 %) was used as a source of Fe which acts as a catalyst for the growth of CNTs. n type silicon wafer (100) of size (1x1cm\(^2\)) was used as a substrate and kept inside the quartz tube. In a typical experiment, the quartz tube was first flushed with ar-
argon (Ar) gas in order to eliminate air from the quartz tube and then heated to a reaction temperature. The precursor mixture was sprayed into the quartz tube, using Ar gas. The concentration of ferrocene in carbon precursor was ~25 mg/ml. The flow rate of Ar was 200 sccm/min. The experiments were conducted at 650 °C with reaction time of 45 min was maintained for each deposition. After deposition, the furnace was switched off and allowed to cool down to room temperature under Ar gas flow. A uniform black deposition on the silicon substrate was observed. Finely, the substrate containing aligned CNTs was removed from the quartz tube for characterization. The experiments were repeated several times to ensure the reproducibility of the formation of vertically aligned carbon nanotubes.

2.3. Result and Discussion

The morphology of carbon sample grown on silicon substrate using a mixture of Pine oil and ferrocene at 650 °C can be observed in Figure 6a. The image reveals the formation of high abundance of carbon nanotubes which are forest like and vertically-aligned to the substrate surface. The growth of carbon nanotubes seems to be uniform and reaches up to a length of 10µm. Figure 6b shows the SEM image of carbon sample grown on silicon substrate using a mixture of Methyl ester of *Jatropha curcas* oil and ferrocene at 650 °C. The dense, aligned but non-uniform growth of carbon nanotubes was observed. The length of carbon nanotubes grown was found to be varied from 12.5 to 7.5µm. Figure 6c illustrates the SEM image of the carbon nanotubes grown at 650 °C using Methyl ester of *Pongamia pinnata* oil. A thick carbon nanotube with poor structure and alignment was observed.

![Figure 6. Representative SEM images of as-grown vertically-aligned carbon nanotubes at 650 °C using Pine oil (a), Methyl ester of *Jatropha curcas* oil (b) and Methyl ester of *Pongamia pinnata* oil (c).](image-url)

From the experimental results we suggest that the synthesis of aligned CNTs is very sensitive to the carbon precursors used. Ferrocene on thermal decomposition at high temperature forms Fe nano particles on the silicon substrate surface. During the chemical vapor deposition process, the carbon precursor is catalytically decomposed and the carbon fragments formed diffuse into the Fe catalyst. The Fe particles may thus easily become saturated or supersaturated with carbon atoms, and the precipitation of the carbon from the surface of the Fe particle leads to the formation of dense carbon nanotubes [48]. The high surface density of the growing nanotubes serves as an additional advantage for the constituent nanotubes to be “uncoiled”. The Vander waals forces between the tube keep them aligned. Thus, the Fe catalysts can effectively catalyze the growth of highly dense vertically aligned carbon nanotubes on silicon substrate. Further in-
vestigation is going on in our laboratory for a better understanding of the actual growth mechanism of vertically aligned carbon nanotubes.

3. Conclusions, challenges and future prospects

In view of the perspective of green chemistry, we attempt to explore regenerative materials for CNT synthesis with high efficiency. In this research work a well graphitized MWNTs were synthesized from Pine oil and Methyl ester of *Jatropha curcas* oil using silica supported Fe, Co and Mo catalyst by spray pyrolysis method. The optimum reaction conditions for synthesis of MWNTs were 650 °C and precursor flow rate of 20 mL per hour. Spray pyrolysis of Methyl ester of *Pongamia pinnata* oil over silica supported Fe, Co and Mo catalyst results in formation of MWNTs filled with magnetic nanoparticles, which find potential applications in magnetic recording, biomedical and environmental protection. Vertically aligned carbon nanotubes were obtained by spray pyrolysis of Pine oil and Methyl ester of *Jatropha curcas* oil and ferrocene mixture, at 650 °C on silicon substrate under Ar atmosphere. The use of natural precursors gives sensible yield and makes the process natural world friendly as well. A thick carbon nanotube with poor structure and alignment was observed with mixture of Methyl ester of *Pongamia pinnata* oil and ferrocene.

The studies in this work demonstrate that the carbon materials are potential precursor for CNTs production under suitable experimental conditions and comply with green chemistry principles. It is clear that specific carbon nanostructures can be synthesized by suitably altering the experimental parameters. However, it is a challenge to consistently reproduce CNT of same quality and quantity form the precursor of inconsistent composition. Designing of catalyst material and optimization of reaction parameters which is suitable for synthesis of specific morphological CNTs from a renewable natural precursor of inconsistent chemical composition is one of the future prospects in this area of research.

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