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Simplified Synthesis of Multi-Walled Carbon Nanotubes from a Botanical Hydrocarbon: *Rosmarinus Officinail*s Oil

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Abstract

Rosmarinus officinails Oil, a botanical hydrocarbon has been found to be an effective precursor for the synthesis of multi-walled carbon nanotubes. Multi-walled carbon nanotubes were prepared by catalytic decomposition of Rosmarinus officinails oil over well dispersed Fe-Co catalyst impregnated silica support with 20 mL/hr feed rate of carbon source at 650 ˚C by spray pyrolysis method. The as grown multi-walled carbon nanotubes were characterized by FESEM, HRTEM, XRD and Raman spectroscopy. Raman spectroscopy reveals that as-grown nanotubes are well graphitized. The HRTEM images reveal that the tip growth mechanisms of MWNTs with diameter range of 30-40 nm were found. We conclude that the Rosmarinus officinails oil has been found to be valuable precursor for the synthesis of low cost and high quality of MWNTs for large scale production.

Keywords: *Multi-walled Carbon Nanotubes; Rosmarinus officinails; Spray Pyrolysis.*

1. INTRODUCTION

Nanotechnology is the creation of functional materials, devices and systems through control of matter on the nanometer scale and the exploitation of novel phenomena and properties of matter (physical, chemical, biological, electrical etc.) at that length. Carbon nanotubes (CNT) have attracted growing interest owing to their unique physico-chemical and mechanical properties and many potential applications. In general, CNTs are synthesized by arc discharge (Journet *et al.* 1998), laser ablation (Guo *et al.* 1995), chemical vapor deposition (CVD) (Cassell *et al.* 1999) and spray pyrolysis (Kamalakaran *et al.* 2000). Among these methods chemical vapor deposition (CVD) has attracted more and more attention. The main reason is the capability of the method to both produce a relatively large amount of high purity CNTs and also gain better control of synthesis parameters (Thostenson *et al.* 2001; Chen *et al.* 2006). In addition, CVD is the only method that allows self-assembly process and the synthesis of patterned arrays or electrodes (Downard *et al.* 2008; Hsiou *et al.* 2004). The catalytic CVD process involves the use of catalyst particles, usually as either a powder or thin film on appropriate substrates. Several studies have already shown relationship between the catalyst particles size and the diameter of grown CNTs (Choi *et al.* 2000; Wei *et al.* 2001). Transition metals are generally used as catalyst owing to their catalytic decomposition of carbon source, ability to form carbides and possibility for carbon to diffuse through and over the metals extremely rapidly (Fonesseca *et al.* 1996). Since it is catalyst that initiates the nucleation of

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carbon nanotube (CNT); it is imperative that the size of metal to be used as catalyst should be in nanoscale.

Most of the carbon materials have been synthesized from precursors based on the petroleum products (Maheshwar Sharon *et al.* 1998). Considering the environmental effects and decreasing petroleum product sources, efforts are now directed to away from them and swich over to reproducible natural carbon sources such as camphor (Maheshwar Sharon *et al.* 1994) and turpentine oil (Afre *et al.* 2005) etc. as they are good source of hydrocarbons.

In the present paper we report our attempt to synthesize multi-walled carbon nanotubes by catalytic decomposition of *Rosmarinus officinails* oil (an eco-friendly natural carbon precursor) using three different transition elements supported on silica in nitrogen atmosphere. In search of identifying un conventional oil rich in hydrocarbon, to produce carbon nano materials after screening many oils we found *Rosmarinus officinails* oil to be a suitable precursor.

2. MATERIALS & METHODS

2.1 Synthesize of Multi-walled Carbon Nanotubes

A mono metallic catalyst Fe (Fe: SiO2), Bimetallic catalyst Fe/Co (Fe: Co: SiO_2 1:0.6:4) and tri-metallic catalyst Fe/Co/Mo (Fe: Co: Mo: SiO_2) supported on silica was prepared as per the following reference (Mhlanga *et al.* 2009). Appropriate quantities of metal salts (Merk) Fe $(NO_3)_3.6H_2O$, Co $(NO_3)_3 3H_2O$ and $(NH_4)_6$ $Mo_7O_{24}.4H_2O$ were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merk). The solvent was then evaporated and the resultant cake was heated between 90 and 100 °C for 3hrs. Further it was removed from the furnace and grounded into fine powder. The fine powders were then calcined for 1 hr at 450 °C and then reground before loading into the reactor. The catalyst was placed in the quartz boat that was inserted into the center of the quartz tube placed in the heating furnace. The carrier gas Nitrogen was flushed out before switching on to the reaction furnace to remove air and create nitrogen atmosphere. The temperature was raised from room temperature up to the desired growing temperature. Subsequently, *Rosmarinus officinails* oil was introduced into the quartz tube through spray nozzle and the flow was maintained using saline tube at the rate of 0.5 mL/min. The deposition time was last for 30 mins for each deposition at different temperatures from 550 °C to 750 °C. Nitrogen flow was maintained until the furnace was cooled to room temperature. The MWNTs were synthesized at different temperatures ranging from 550 °C to 750 °C. The as-grown MWNTs had been characterized through SEM, HRTEM, XRD and Raman Spectral studies.

3. RESULTS & DISCUSSION

3.1 Effect of catalyst on the growth of MWNTs

Catalyst is the main part for carbon nanotube nucleation; its size seems to be the determining factor for the formation of SWNTs or MWNTs and its diameter. The peculiarity of these transition metals to catalyse CNT formation is mostly linked to their catalytic activity for the decomposition of carbon compounds, there ability to form carbides and the possibility for carbon to diffuse through and over the metals extremely rapidly. Our preliminary experiments carried with Co and Fe impregnated with silica gel shows that, the Co catalyst grown CNTs having good graphitization compare to Fe catalyst grown CNTs. We observed here that both Co and Fe give high yield of CNT as at 650 °C. Hence, the combination of these two catalysts improved quality and quantity of CNTs. Fonseca et al. observed that Fe is more active than Co but the quality of resulting CNTs, in terms of graphitization and structure, is less good with iron Fonseca *et al.* 1996). Combination of these two (Co and Fe) catalyst leads to the formation of SWNTs with different support materials (Okazaki *et al.* 2003; Maruyama *et al.* 2002). In this study we have not found any trace of SWNTs in our samples at higher temperatures, the reason behind this is not yet understood well. In the case of trimetallic catalyst the synergistic effect of Mo was very evident. Mo was required to enhance the activity of oxide catalyst and

even distribution of metal particles on substrate. The variation in concentration of the catalyst varies the quantity of CNTs growth. At higher temperatures (550 °C, 650 °C and 750 °C) the catalyst gets agglomerated results in the formation of thicker tubes. This catalyst agglomeration happens due to the surface melting states of nano-sized particles compare to there bulk amount. Our experiments using bimetallic catalyst give better yield compare than trimetallic catalyst; the further studies were carried out using bimetallic catalyst.

3.2 SEM and HRTEM analysis

Spray pyrolysis of the *Rosmarinus officinails* oil solution at various temperature leads to a large amount of carbon soot-like deposition along the total heating zone (~ 15 cm) inside the quartz tube Fig.1. Micro structural investigations of as-grown samples were carried out using SEM and HRTEM techniques.



Fig. 1: The snap shot of CNTs grown over catalyst support kept in a quartz boat

Fig.2 illustrates the SEM images of the CNTs samples grown at different temperatures and flow rates. There is no growth of CNTs at 550 °C at the precursor flow rate of 10 mL/hr over silica supported Fe, Co, catalyst. Because this temperature is not sufficient to pyrolyse the carbon source. On the other hand, the precursor flow rate of 20 mL/hr at 650 °C CNTs have smooth surface and nearly uniform diameter and have similar morphology. When the experimental conditions was 750 °C with 30mL/hr of carbon feed stock, the MWNTs were formed with a size of around 40-60 nm with low yield.

The diameter of nanotubes increased with increasing temperature suggesting an increased mobility of the Fe particles on the quartz tube, leading to larger Fe clusters. Fig.3 (a), 3(b) & 3(c) shows the HRTEM images of CNTs grown at various temperatures and flow rates. The HRTEM images clearly show the amorphous carbon covered on the walls of CNTs which has been shown in Fig.3(a). There is no clear growth of CNTs at 550 °C with flow rate of 10mL/hr. It can be noticed that amorphous carbon and metal particles are nearly absent. When the growth temperature of 650 °C with precursor flow rate of 20 mL/hr which confirms that the images fig.3(b) have a tubular structure with 30-40 nm i.e., they are multiwalled carbon nanotubes (MWNTs). The tip growth of MWNTs has been observed to be generally covered by catalyst particles Fig.3(b). This is suggestive of the fact that tip growth mechanism is responsible for the formation of the MWNTs in present case.

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 (Leonhardt *et al.* 2006), while a weak contact favors tip- growth mechanism, a strong interaction promotes base growth (Bower *et al.* 2000). These catalyst particles have lifted off the support and elongated due to the flow nature and stress induced by the carbon surrounding the catalyst. The growth temperature increased at 750 °C with the precursor flow rate of 30 mL/hr, diameter of MWNTs was increased.

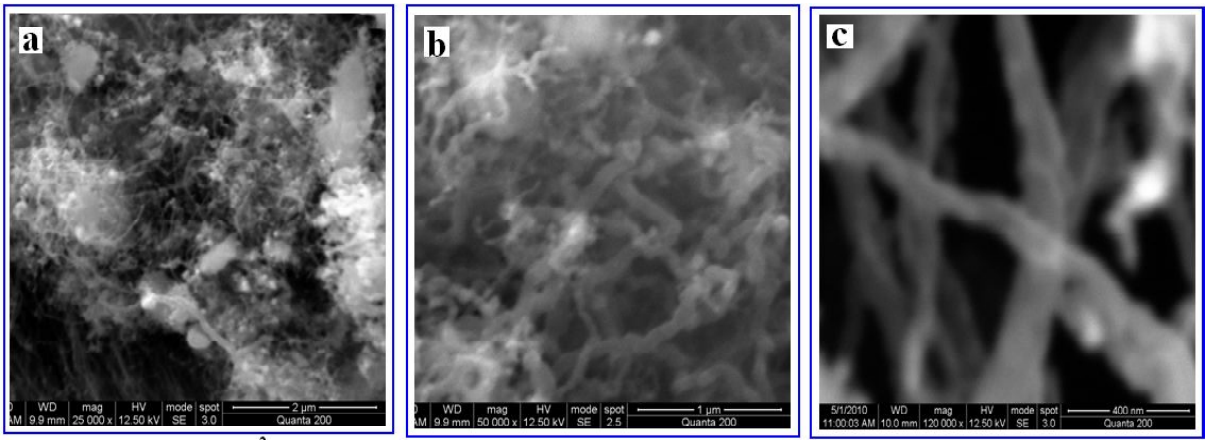


Fig. 2: SEM images of MWNTs grown on Fe, Mo catalyst supported on silica at various temperature ranging from 550 °C (a), 650 °C (b), and 750 °C (c).

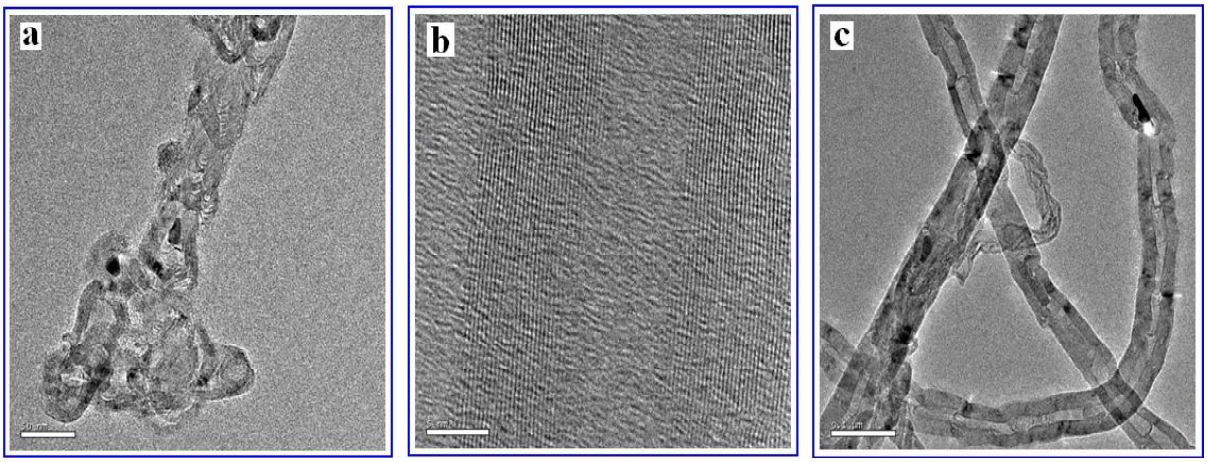


Fig. 3: HRTEM images of MWNTs grown on Fe, Mo catalyst supported on silica at various temperature ranging from 550 °C (a), 650 °C (b), and 750 °C (c).

3.3 Raman spectroscopy studies of MWNTs

Raman spectroscopy is an important tool for studying CNTs samples, which provides information about the structure and the presence of disorder in the sample. Raman spectra of as-grown CNTs were taken by an Ar ion laser of wave length 514nm. Fig.4 shows the representative Raman spectra of a CNTs sample as grown at 650 °C. In the Raman-shift range 500-2500 cm^{-1}, two peaks are observed at 1358 and 1589 cm^{-1} corresponding to D and G bands, respectively. The G band corresponds to the tangential stretching (E_2g) mode of highly oriented pyrolytic graphite and suggests the CNTs are composed of crystalline graphitic carbon. The higher intensity of the G band peak indicates the higher degree of graphitization/ crystallinity. This is in agreement with our HRTEM observations. On the other hand, the D band at 1342 cm^{-1} originates from

disorder in the Sp^2-hybridised carbon and indicates lattice distortions in the curved grapheme sheets, tube ends etc.

The intensity ratio of D and G peaks (ID/IG) is used to characterize the purity of CNTs. Generally, lower ID/IG value indicates a higher degree of graphitization (Singh *et al.* 2003; Li *et al.* 1997). The ID/IG value of as –grown CNTs is ~0.345. This value reveals a higher degree of graphitization when compared to those values reports for CNTs grown by thermal decomposition of acetylene, etc (e.g. ID/IG~0.85-1.3) Sveningsson *et al.* 2001) and spray pyrolysis of natural precursors (e.g. turpentine, eucalyptus oil and camphor) (ID/IG~0.85-1.3) (Ghosh *et al.* 2008; Kumar *et al.* 2003).

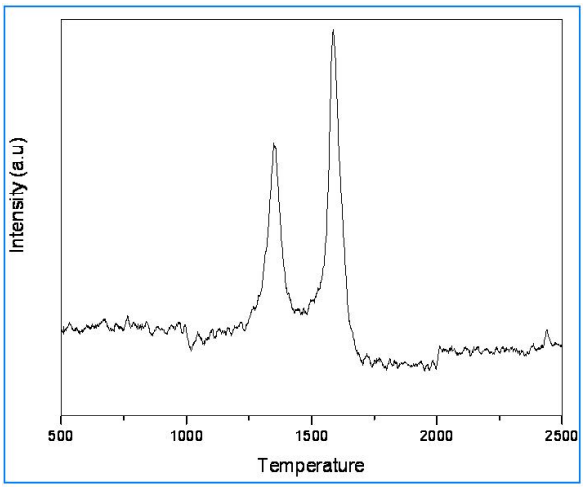


Fig. 4: Typical Raman Spectrum of the MWNTs grown at 650 °C

Fig. 5 shows the typical XRD pattern of CNTs grown at 650 °C. The peaks are indexed to be the (00.2) and (10.1) reflections of hexagonal graphite. The presence of the (00.2) peak in the XRD spectra of CNTs indicates the concentric cylindrical nature of the graphene sheet (d00.2=0.342nm) nested together and the nanotubes are multi-walled in nature. The interlayer spacing (d00.2=0.342nm) found by XRD is consistent with that obtained d00.2~0.342nm) from HRTEM and is characteristic of CNTs. The purity of as-grown CNTs is better than that obtained by CVD using conventional hydrocarbon (Mayne *et al.* 2001).

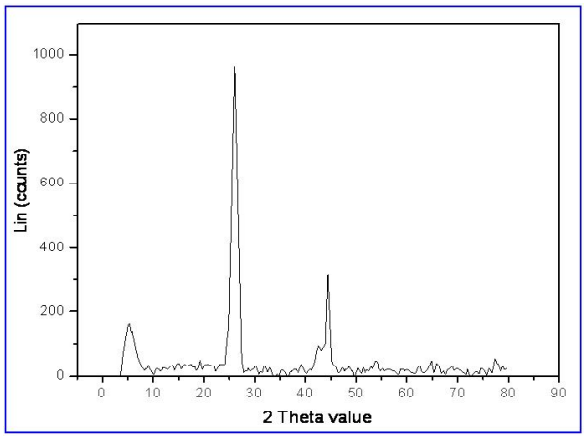


Fig. 5: XRD patterns of MWNTs grown at 650 °C

4.CONCLUSION

The synthesis of multi-walled carbon nanotubes from *Rosmarinus officinails* oil an eco friendly natural precursor using various catalysts supported on silica was demonstrated. The optimum reaction conditions for synthesis of MWNTs were 650 °C and the precursor flow rate of 20mL/hr. The tip growth mechanism of multi-walled carbon nanotubes was discussed. The studies in this work demonstrate that the carbon materials are potential precursor for the CNTs production under suitable experimental conditions. It is clear that specific carbon nanostructures can be synthesized by suitably altering the experimental parameters.

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