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Growth and Structural Studies of Carbon nanotubes from Unconventional Natural Precursor by Spray Pyrolysis Approach

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Abstract
The discovery of Carbon Nanotubes has created new era in the field of nanotechnology, Spectacular properties of these nanostructured materials, stimulating scientists to peep into this tine tube tie featured carbon Nanotubes in large quantities. Chemical vapor deposition is the most popular method of producing carbon Nanotubes and its of low-cost and highly useful technique for mass production of carbon nanotubes. *Oryza sativa* oil a botanical hydrocarbon, has been found to be effective precursor for the synthesis of multi-walled carbon nanotubes (MWCNTs) by spray Pyrolysis over well dispersed Fe/Mo catalyst supported on silica at 750 °C under Nitrogen atmosphere. As-grown MWCNTs were characterized by SEM, HRTEM and Raman Spectroscopic.

Keywords: Plant derived hydrocarbon, Carbon nanotubes, SEM, HRTEM, Raman spectroscopic analysis & XRD analysis.

1. Introduction

Carbon nanotubes (CNTs) were promising materials since its discovery by Sumio Iijima in fullerenes soot [1, 2]. They have attracted great interest owing to their unique Physio-Chemical properties and mechanical properties [3]. CNT has shown great potential for applications in the various field such as Bio sensors [4], Field electron emission [5], Nanocomposite [6], Energy storage [7], Purification [8], Artificial implants [9], Tissue engineering [10], Bio-medical applications [11]. From the application point of view it is highly desirable to synthesize well-graphitized nanotubes at low cost. In general carbon nanotubes are mainly synthesized by Arc Discharge [12], Laser Ablation [13] and Chemical Vapor Deposition (CVD) [14]. Among all, CVD is the most economical method and is easily scalable for mass production of CNT. Considering the environmental effects and decreasing fossil fuels such as petroleum product source, since these precursors are depleting in several decades time Moreover, the cost of these petroleum based products is expected increase in the near future. Therefore, it is inevitable to look for alternative eco-friendly carbon precursors. Recently, there have been a few reports on the synthesis of CNTs from plant derived carbon precursors such as Camphor [15], Turpentine oil [16], Eucalyptus oil [17], Palm oil[18], Neem oil [19], Coconut oil [20], Pine oil [21], Olive oil [22], Jactropha curcas oil [23], Cymbopogen flexuosus oil [24], Madhuca longifolia [25], Brassica Juncea [26], Helianthus annuus oil [27] and Glycine max oil [28].

In this article, we report the synthesis of MWCNTs by Catalytic decomposition of *Oryza sativa* oil (Vaporizing temperature around 257 ºC), an eco friendly natural Carbon precursor, over silica impregnation Fe-Mo Catalyst by Spray Pyrolysis method

2. Experimental Method

The Natural plant derived precursor *Oryza sativa* oil is renewable, Cheap, inexpensive and in near future have no chance of Shortage. Composition of Fatty Acids in *Oryza sativa* presented in Table 1. The schematic diagram of spray pyrolysis set-up was shown in Fig.1 (a) and (b).

Table 1: Percentage Composition in *Oryza sativa* (Rice Bran) oil

% of Fatty Acids	% Composition	Formula	Structure
Linoleic (C18:2)	34.4	$C_{18}H_{32}O_2$	CH_3-$(CH_2)_4$-CH=CH-CH_2-CH=CH-$(CH_2)_7$-COOH
Linolenic (C18:3)	2.2	$C_{18}H_{30}O_2$	CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-$(CH_2)_7$-COOH
Myristic (C14:0)	0.6	$C_{14}H_{28}O_2$	CH_3-$(CH_2)_{12}$-COOH
Oleic (C18:1)	38.4	$C_{18}H_{34}O_2$	CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$-COOH
Palmitic (C16:0)	21.5	$C_{16}H_{32}O_2$	CH_3-$(CH_2)_{14}$-COOH
Stearic (C18:0)	2.9	$C_{18}H_{36}O_2$	CH_3-$(CH_2)_{16}$-COOH

2.1. Preparation of mixture of catalysts

The preparation of Fe/Mo supported on silica was conducted using wet impregnation method. Fe/Mo catalyst supported on silica (SiO_2) particles (Fe:Mo:SiO_2 =1:0.4:4) were prepared as follows [29]. Metal salts (Merck) i.e. $Fe(NO_3)_3.6H_2O$ and $Co(NO_3)_3.3H_2O$ were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merck). The solvent was then evaporated and the resultant cake heated to 90-100 °C for 3 hours, removed from the furnace and ground in an agate mortar. The fine powders were then calcined for 1 hour at 450 °C and then re-ground before loading into the reactor.

2.2. Synthesis and purification of carbon nanotubes

The catalyst was placed on the quartz boat. The boat was placed in the heating furnace. The carrier gas nitrogen (100 mL/min) was flushed out before switch on the reaction furnace to remove air and create nitrogen atmosphere. The temperature was raised from room temperature up to the desired growing temperature. Subsequently, *Oryza sativa 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 lasted for 30 minutes at a temperature of 750 °C. The reactor was then allowed to cool to room temperature with nitrogen gas flowing. The carbon product on the silica support was then weighed to determine the carbon yield of the spray pyrolysis. We define carbon yield here as the functional mass increase (m1-m0)/m0, where m1 and m0 are respectively, the final mass of the catalyst support with carbon deposit and the initial mass of the catalyst support. Of course, not all the carbon mass is in the form of MWCNTs. Nevertheless, the amount of amorphous carbon detected in electron microscope images was small and our practical definition of the relative yield is believed to provide a reasonable assessment of MWCNTs production in these experiments. The yield does not change appreciably as time progressed beyond 45 minutes. The amount of CNTs produced is proportional to the amount of catalyst used. So, the optimum condition for the synthesis of high yield of relatively pure MWCNTs of narrow size 20-40 nm were established as reaction temperature around 750 °C, 80 mg of catalyst substrate, 45 minutes reaction time, 100 mL per minute nitrogen gas flow and 0.5mL per minute precursor flow.

The as-grown MWCNTs were purified by the following procedure. 40 mg of raw 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_2O_2 was added to form oxidative slurry that continued to be heated and stirred for 30 minutes. The addition of HCl, H_2O_2, subsequent heating and stirring was repeated three more times, each time allowing the heated oxidative slurry to stir for 30 minutes. Phase separation was allowed to proceed followed by filtering the carbon phase and washing with 1N HCl and distilled water. The collected sample was dried at 120 °C in air for 2 hours.

2.3. CNT characterization

The crystalline structure of as grown CNT samples was characterized by Raman Spectroscopy. Raman spectra of samples were performed by JASCO NRS-1500W, green laser with excitation wavelength 532 nm. X-ray diffraction (XRD) with Cu-K radiation using an automated X-ray diffractometer (Shimazu Lab XRD-6000). As grown carbon samples surface morphology was examined using scanning electron microscope (SEM, Hitachi S-4700) and high-resolution transmission electron microscope (HRTEM, JEOL-3010). For HRTEM studies, the samples were prepared by sonication of products in isopropanol and few drops of resultant suspension was put onto holey carbon grid and dried.

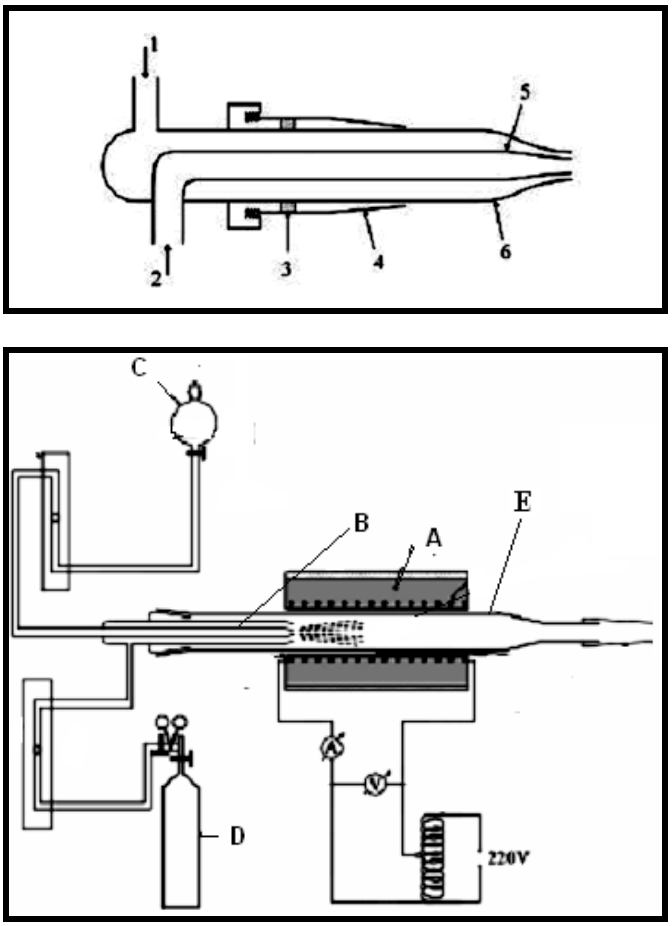

Figure 1 (a): The schematic diagram of spray pyrolysis set-up. (A) Heating source, (B) Spray nozzle, (C) Carbon feed stock inlet, (D) Nitrogen gas and (E) Quartz tube.
(b): Schematic diagram of the Sprayer 1. Gas inlet; 2. Solution inlet; 3. Tightening; 4. Polished glass-to-glass connection; 5, 6-Inner and outer pyrex tube.

3. Results and discussions

Fig. 2a and 2b show the scanning electron microscopy image of the as-grown nanostructures over Fe-Mo bimetallic catalyst, impregnated in silica at 750 °C under the flow of nitrogen by CVD assisted spray pyrolysis method. SEM image clearly reveals that MWCNTs grew nicely on the surface of the silica particles. In Fig. 3a and 3b we have presented the high resolution HRTEM images of MWCNTs, grown over Fe-Mo bimetallic catalyst impregnated on silica support at 750 °C with a flow rate of methyl ester of *Oryza*

sativa oil at 0.5 mL per minute. Fig. 3a and 3b shows that, the nanotubes have a periodic compartment like structure with small variation in internal diameter. The diameters of the nanotubes were in the range of 15-20 nm (Fig. 2b).

Raman spectroscopy was employed to characterize the crystalline nature of the synthesized MWCNTs as show in Fig. 4. Typical Raman spectra of MWCNTs indicating two characteristic peaks. The G band peak at 1573 cm^{-1} corresponds to in plane oscillation of carbon atoms in the graphene wall of MWCNTs and high degree lower D-band peak at 1357 cm^{-1} represents the degree of defects or dangling bonds. On the other hand, band at 2697 cm^{-1} known as the G' band and attributed to the overtone of the D-band. G'-band originates from thicker multi-layered nature of carbon nanotube G-peak is assigned to E_2g mode of graphite lattice and D-peak corresponds to an A_1g mode due to the structural defects of the graphite crystal [30, 31]. The intensity ratio of G and D peaks (I_G/I_D) is used to characterize the degree of graphitization carbon materials, i.e., ratio of I_G/I_D of the as-grown MWCNTs is 1.52. This higher value of I_G/I_D ratio shows good graphitization of the nanotube and also may be due to the relatively lower defect such as amorphous carbon. The XRD results confirm the graphitic nature of the MWCNTs peak at 26^o (C 002) and the presence of the Fe catalyst peak at 44^o (Fe 011) [32].

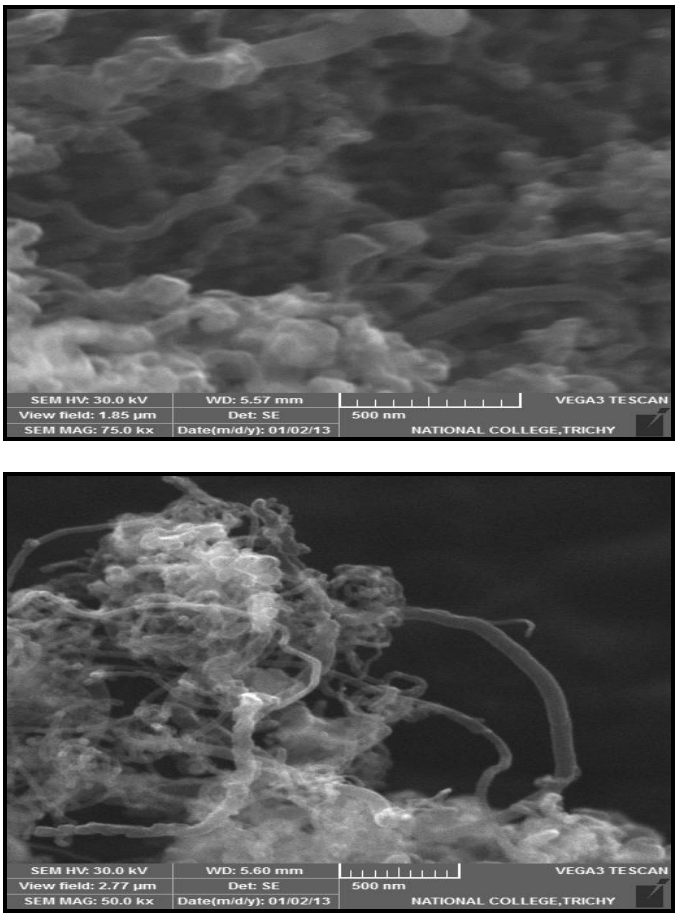

Fig. 2 a & b: SEM micrographs of as grown MWCNTs at 750 °C

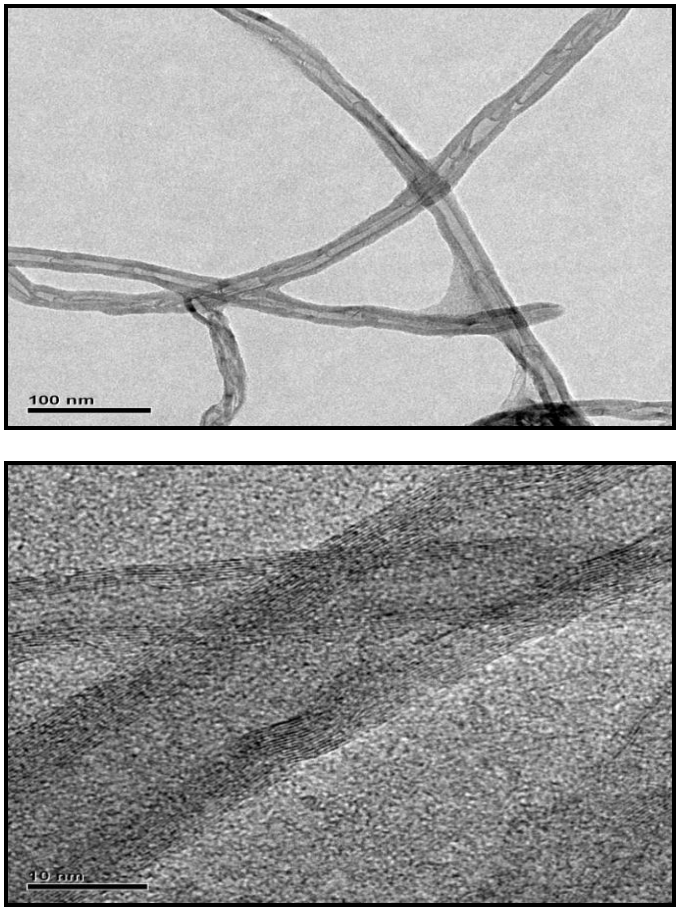

Fig. 3 a & b: HRTEM micrographs of as grown MWCNTs at 750 °C

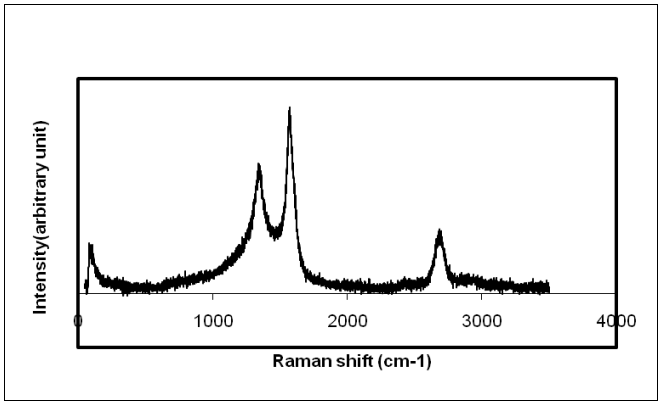

Figure 4: Raman spectroscopic analysis of as grown MWCNTs at 750 °C.

Table 2. Raman peak position, G & D intensity and I_G/I_D ratios for plant derived precursors

Plant derived source	RBM peak	D-Peak	G-peak	D'-peak	I_G / I_D Ratio
Methyl ester of *Oryza sativa* (rice bran oil)	No peak	1357	1573	2697	1.52

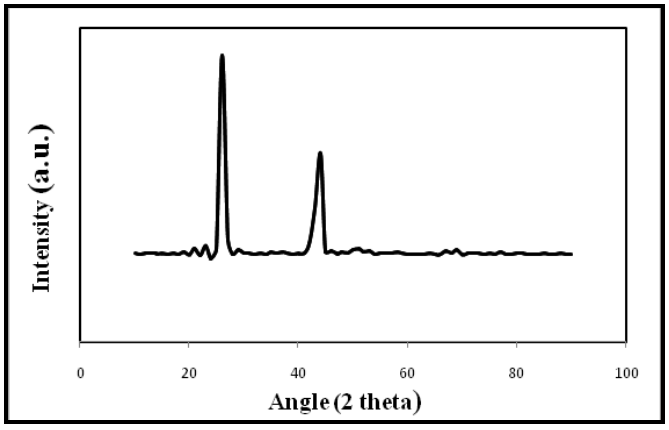

Figure 5: XRD analysis of as grown MWCNTs at 750 ° C

3.1. Growth Mechanism of MWCNTs

The mechanism of CNT nucleation and growth is one of the challenging and complex topics in current scientific research. It is well established, that during CNT nucleation and growth, the following consecutive steps were taken place.

1. Decomposition of carbon sources
2. Diffusion of carbon species through the catalyst Nanoparticles
3. Precipitation of the carbon species in the form of Multi layered 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 most accepted growth model suggests bulk diffusion of carbon species into the metal particles. The third step is the precipitation of the carbon in the form of CNTs from the saturated catalyst particle. Based on experimental results, a possible growth mechanism of MWCNTs was proposed. It is known from the fact that catalytic centers on catalyst particle act as nucleation site for the growth of MWCNTs. [33]

4. Conclusion

Multiwalled carbon nanotubes were obtained by chemical vapor deposition of *Oryza sativa* oil an unconventional natural precursor, as a carbon source. Based on result, the formation of MWCNTs has been optimized at 750 ºC synthesis temperature which is in good agreement with SEM, HRTEM and Raman spectroscopic analysis. The experiment has succeeded in minimizing diameter distribution of nanotubes in the range from 0.5 to 2.5 nm and lowest I_D/I_G ratio of about 0.86. The highest yield of 73% was obtained at the same temperature. As a result, synthesis temperatures were strongly affected by the growth of MWCNTs.

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