Parametric Evaluation of Multiwalled Carbon Nanotubes Synthesised from Used Cooking Oil by Catalyst Assisted Spray Pyrolysis Method

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ABSTRACT

The market for carbon nanotubes (CNTs) is augmented due to their assorted commercial applications and the annual number of CNT related journal publications and issued patents continue to grow. Due to their extraordinary mechanical, electrical and optical properties, CNTs have stimulated extensive research since their discovery by Sumio Iijima in the early 1990s as already reported in the year 1952 by Radushkevich and Lukyanovich. The present work aspire to explore a natural renewable green precursor for the synthesis of Multiwalled carbon nanotubes (MWCNTs) using waste cooking oil at different temperature ranging from 550°C to 750°C with interval of 100 °C on Fe-Mo supported on alumina under N2 atmosphere. The characterization of the as-grown carbon nanomaterials were analyzed by Scanning electron microscopy (SEM), High resolution transmission electron microscopy (HRTEM), XRD and Raman spectroscopic analysis. We confirmed that the yield and diameter of as-grown MWNTs were not same at all temperatures. The crystalline perfection of CNTs increases first as the temperature increases from 550°C to 650°C and then decreases as the temperature increases from 650°C to 750°C. Our results indicated that the synthesis temperature could affect the degree of graphitization of CNTs.

Keywords: *Carbon nanotubes; Spray-pyrolysis; HRTEM; SEM, XRD analysis, Raman spectroscopic analysis, Used Cooking Oil*

1. INTRODUCTION

Synthesis of carbon nanotube (CNT) have attracted the great attention of number of research groups, since discovered in 1991 **[1]** CNTs are now considered to be a top class subject in academic researches as well as in various industrial due to their outstanding electrical and mechanical properties **[2]**. Numerous applications have been developed by using CNTs such as field emission devices **[3]**, transistors **[4]**, sensors **[5]**, energy storage **[6]**, logic circuits **[7]**, catalyst support **[8]**, biomedical applications **[9]**. Various synthetic methods such as arc discharge **[10]**, laser vaporization **[11]**, chemical vapor deposition (CVD) **[12]**, solvothermal **[13]**,

hydrothermal **[14]**, electrolysis **[15]**, ball milling **[16]** have been developed for the production of CNTs. Recently, the synthesis of CNTs using Spray pyrolysis method has attracted much attentions because of many advantages such as high purity, high yield, controlled growth and spray pyrolysis method involves vaporization and pyrolysis of carbon source occur simultaneously **[17]**.Mostly petroleum products are used as precursors for synthesizing CNTs using CVD method apart from these volatile petroleum based hydrocarbons, carbon nanotubes have been synthesized from polymers, metallocenes and domestic fuels such as kerosene and liquefied petroleum gas **[18]**. According to the principles of green chemistry, the feed stock of any industrial process must be a renewable natural resource. Hence, it is the time's prime demand to explore renewable natural materials for CNTs synthesis. Recently there have been a few reports on synthesis of Multi-walled carbon nanotubes (MWNTs) and vertically aligned ones by thermal decomposition of turpentine, camphor and eucalyptus oil **[19-21]**. Our research groups have also succeeded in growing MWNT from Eco-friendly green bio-hydrocarbons such as Pine oil, *Jactropha curcas* oil, *Cymbopogen flexuosus* oil, *Madhuca longifolia* oil, *Brassica Juncea* oil, *Oryza sativa* oil, *Glycine Max* oil, *Zingiber Officinale* and *Moringa oleifera* oil **[22-30]**.

In this work, we report synthesis of MWNTs from plant derived hydrocarbon used cooking oil having vaporizing temperature around 325°C by catalytic decomposition carbon precursor over alumina impregnated with Fe and Mo catalyst. Unlike any fossil or petroleum product, there is no fear of its being depleted as it is a regenerative source and can be obtained easily by cultivating as much quantity as required.

2.EXPERIMENTAL

2.1 Preparation of mixture of catalysts

The alumina supported Fe/Mo catalyst was prepared by the metal ion impregnation method $Fe(SO_4)_3$ (0.3 g Alrich, technical grade) and $(NH_3)_2MoO_4$ (0.04 g with 99.95% purity) were dissolved in approximately 50 ml of de-ionized water and approximately 2 g of a alumina was added to the solution giving a Fe:Mo:Al_2O_3 ratio 1:0.2:15. The water was removed by rotary evaporation and the solid dried at 100 °C the resulting powder was grinded thoroughly using a mortar and pestle. The fine powders were then calcined for 1hour at 450 °C and then re-grinded 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 **[31]**.

2.2 Fabrication and purification of nanotubes

The catalyst was positioned on the centre of the quartz boat and the heating furnace was placed with boat. 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 to the desired growing temperature. consequently, used cooking oil was introduced into the quartz tube through spray nozzle and the flow was maintained at the rate of 0.5 mL/min. The reaction time lasted for 45 minutes for each deposition at different temperatures from 550°C to 750°C with 100°C. The reactor was then allowed to cool to room temperature with nitrogen gas flowing. The yield does not change substantially 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 MWNTs of narrow size 15-45 nm were projected as reaction temperature around 650 °C, 80 mg of catalyst substrate, 45 minutes reaction time, 100 mL per minute nitrogen gas flow and 0.5 mL per minute precursor flow.

The as-grown MWNTs 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. **[32]**

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 field-emission scanning electron microscope (FE-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.

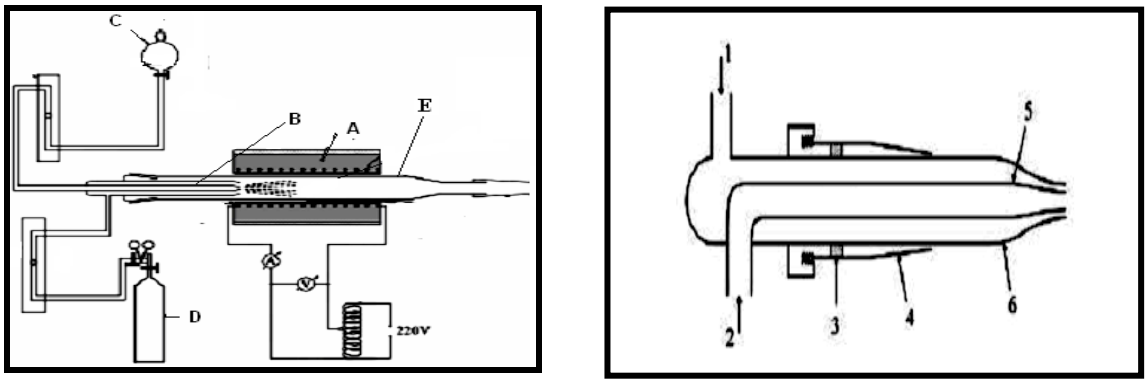


Fig. 1 (a): The schematic diagram of Spray Pyrolysis set-up. (a) Heating source, (b) Spray nozzle, (c) Carbon feed stock inlet, (d) Nitrogen gas, (e) Quartz tube
(b) Schematic diagram of the Sprayer 1. Gas inlet; 2. Solution inlet; 3. Tightening; 4. Polished glass-to-glass connection; 5, 6-Inner and outer pyrex tube.

3. RESULTS AND DISCUSSION

3.1 Effect of Temperature on the Growth of MWNTs

Fig. 2 and 3 illustrate the SEM and HRTEM images of the MWNTs synthesized at different temperatures ranging from 550 to 750 ^oC with 100 ^oC intervals over Fe-Mo catalysts

supported on alumina using waste cooking oil as precursor at a flow rate of 20 mL per hour under N_2 atmosphere. The diameter of MWNTs was in the range of 34-82 nm. As the temperature increases the crystallization perfection of the graphitic walls of MWNTs also increases. This study further confirms that low yield of carbon deposit was produced at 550 °C attributed to poor activation of catalysts. The carbon deposit yield increases to maximum at 650 °C due to almost equal rate of catalytic decomposition of precursor. A decrease in carbon deposit yield observed at 750 °C possibly due to high rate of pyrolysis followed by encapsulation of catalysts**.**

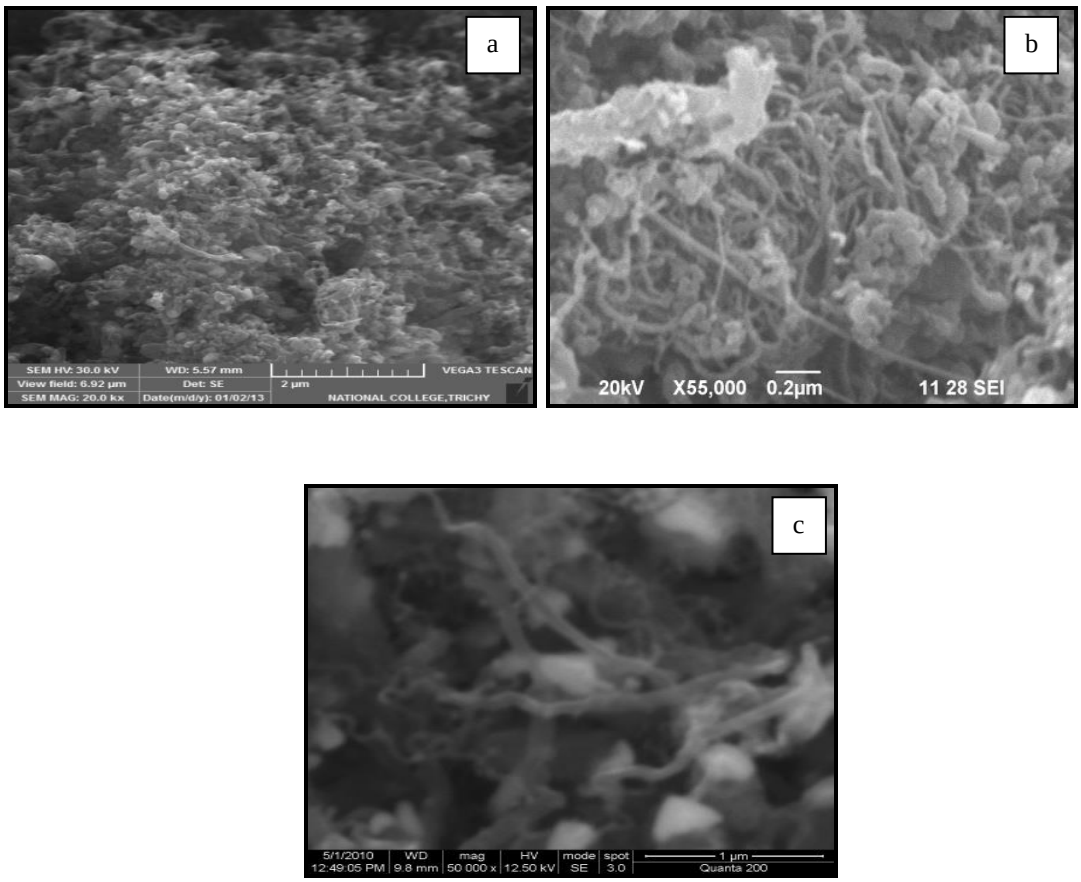
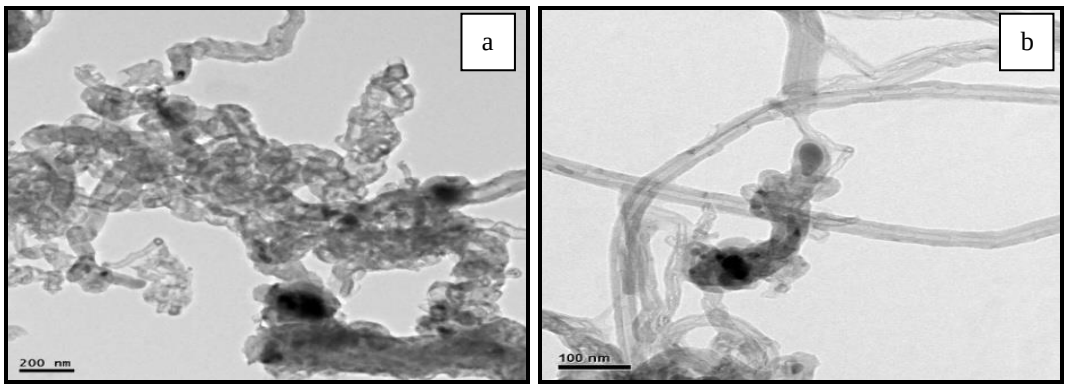


Fig. 2a, b & c: SEM images of MWNTs grown at different Temperatures.



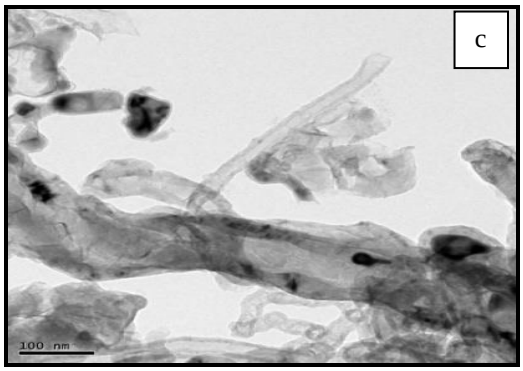


Fig. 3a, b & c: HRTEM images of MWNTs grown at different Temperatures.

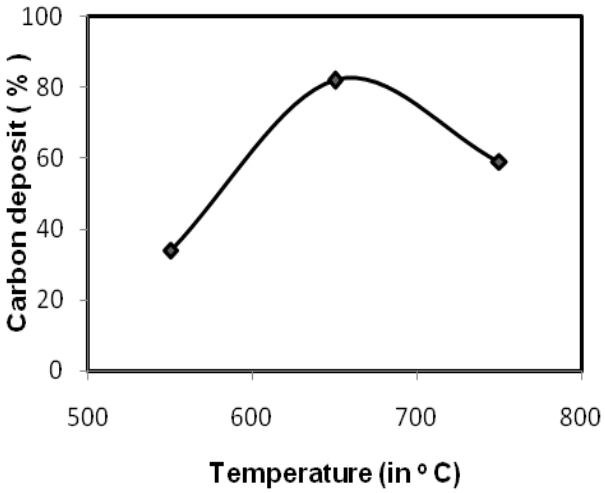


Fig. 4 Variation of Carbon deposit with reaction temperature

3.2 Raman Spectroscopy Analysis of MWNTs

Figure 5 shows the Raman spectrum obtained for the MWNTs grown at 650°C. The two main typical graphite bands are present in the Raman spectrum of MWCNTs bundles: the band at 1580 cm^{-1} (G band) assigned to the in-plane vibration of the C–C bond (G band) and the band at 1342 cm^{-1} (D band)
activated by the presence of disorder in carbon systems. The Raman spectrum also exhibits a band at 2683 cm^{-1} called the G' band and attributed to the overtone of the D band **[33]** confirms presence of MWNTs. The observed I_G/I_D ratio value was about 1.17 further confirms the well crystallization of graphene layers of MWNTs synthesized using the chosen precursor at 650 °C under N_2 atmosphere. No lower frequency RBM peaks in Raman spectrum of the samples synthesized in this work show the absence of SWNTs

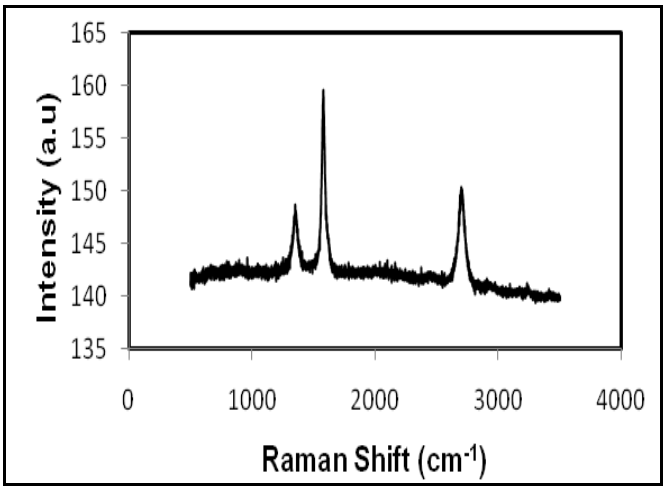


Fig. 5 Raman Spectrum of grown MWNTs at 650°c

3.3 XRD Analysis of MWNTs

A XRD measurement was carried out using Cu Kα radiation (λ=1.54060Å) to examine the structure of the MWNTs was recorded with 2-theta (2θ) between 10º to 80º. Fig. 6 shows the XRD diffraction pattern of as-synthesized MWCNTs having two peaks at 26º and 44º. At synthesis temperature of about 650ºC appearance of characteristic peak of graphite at 26° shows the presence of MWNTs in the sample **[34].** The interlayer spacing of 0.337nm, similar to that of graphite (0.334nm), shows orderly stacking in the MWNTs. The peak at 44° with layer distance of 0.203nm corresponds to d(101**)** **[35].**

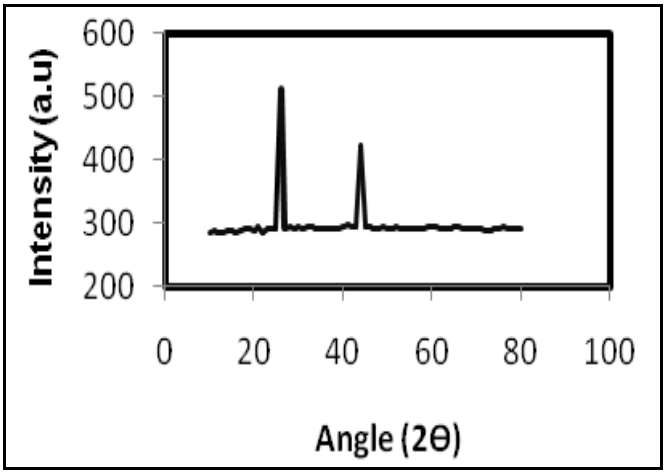


Fig. 6 XRD spectrum of grown MWCNTs at 650°C

4 CONCLUSIONS

The MWNTs were profitably synthesized by using spray pyrolysis method. We scrutinized the effect of temperature on the quality of the grown MWNTs. We established that the yield and diameter of as-grown MWNTs were not same at all temperatures. The crystalline perfection and yield of MWNTs increases first as the temperature increases from 550°C to 650°C and then decreases as the temperature increases from 650°C to 750°C. Our results also reported that the synthesis temperature could affect the degree of graphitization of CNTs. At 650 ºC this process yields better outcome.

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