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Growth of Bamboo like Carbon Nanotubes from *Brassica Juncea* as Natural Precursor

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Abstract

Bamboo like Carbon Nanotubes with compartments were synthesized using Brassica Juncea over Fe-Mo impregnated alumina support at 650 ^{0}C reaction temperature 20 ml/hour gas flow rate and at normal pressure under N_2 atmosphere. In this experiment we achieved maximum yield of entangled carbon nanotubes from the taken precursor. Morphological and Structural studies have been performed by FESEM, HRTEM and Raman Spectroscopic analysis. We identified the growth of carbon nanotube structures with compartments on the chosen catalytic support material. The diameter of multi-walled carbon nanotubes is found in the range of 60 to 80nm. Tip growth mechanism has been observed from the TEM images. We conclude that the Brassica Juncea material has been found to be valuable precursor for the synthesis of low cost and high quality multi-walled carbon nanotubes for large scale production.

Keywords: *Brassica Juncea; Bamboo CNTs; Spray pyrolysis.*

1. INTRODUCTION

Carbon nanotubes (CNTs) belongs to relatively new class of nanomaterials that have been obviously known for almost last two decades, but their history is a little bit longer. Recently CNTs discovered by Iijima, the first scientist from NEC, Japan described the multiwalled carbon nanotubes (MWNTs) prepared by evaporation method for C60 carbon molecule fabrication in 1991 (Iijima, 1991). In 1993 another two separate works from Iijima and Ichihashi, Bethune *et al.* described the growth process of single walled carbon nanotubes (SWNTs) (Iijima, 1991; Bethune *et al*. 1993). These structures possess desirable mechanical properties (Krishnan *et al.* 1998) interesting electronic behavior, (Collins *et al.* 2001) and unique dimensions (Lee *et al.* 2002). As a result of these properties, nanotubes have potential applications in many fields, including composite reinforcement, (Qian *et al.* 2001) transistors and logic circuits, (Martel *et al.* 2002) field emission sources, (Chernozatonskii *et al.* 1995) and hydrogen storage (Li *et al.* 2001) . The CNTs can be formed by arc discharge (Saito *et al.* 1996) and laser abalation (Eklund *et al.* 2002). Nanotubes can also be formed from the common methods, such as flame synthesis (Yuan *et al.* 2001) and electrochemical synthesis (Matveev *et al.* 2001). The most widely used effective methods for the production of large quantities of CNTs is chemical vapour deposition (CVD) (Govindaraj *et al.* 2002).

There are few studies on the synthesis of CNTs from natural precursors such as camphor

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(Kumar *et al.* 1993), turpentine oil (Afre *et al.* 2005), eucalyptus oil (Ghosh *et al.* 2007), palm oil (Suriani *et al.* 2009), neem oil (Kumar *et al.* 2011), coconut oil (Paul *et al.* 2011), pine oil (Karthikeyan *et al.* 2010), *Jactropha curcas* oil (Karthikeyan *et al.* 2010), *Cymbopogen flexuosus* oil (Mageswari *et al.* 2012), *Helianthus annuus* oil (Angulakshmi *et al.* 2012), *Glycine Max* Oil (Angulakshmi *et al.* 2013), and *Madhuca longifolia* (Karthikeyan *et al.* 2013) are successfully reported.

In this report we have succeeded in growing of carbon nanotubes from plant based carbon source of methyl ester of *Brassica Juncea* oil by spray pyrolysis method. It can be produced from brown Indian mustard seeds (*Brassica juncea*).

2. EXPERIMENTAL METHODS

The scheme of an home-made experimental spray-pyrolysis set-up used in our lab for the synthesis of carbon nanotubes is represented in Fig. 1.

One of the most important components of this experimental set-up is the sprayer (atomizer). The scheme of this sprayer is given in Fig. 2. The sprayer consists of a pyrex nozzle (capillary end of the inner tube) having an inner diameter of 0.75mm, and an outer pyrex tube which has an exit diameter of 2mm. This outer tube directs the carrier gas-flow (N_2) around the nozzle. The inner tube of the sprayer is attached at one end to the solution (methyl ester of *Brassica Juncea* oil) container. The other end of the nozzle is fixed to a quartz tube (reactor) by means of a polished glass-to-glass connection. The quartz tube has an inner diameter of 20 mm and it is placed in a 300 mm long electrical furnace. The quartz tube plays the role of the support for the reaction products which appear pyrolytic decomposition of the starting materials (methyl ester of *Brassica Juncea* oil) over Fe-Mo catalyst impregnated alumina support. The used electrical furnace is able to assure a uniform temperature up to 650 °C.

2.1 Experimental Procedure

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

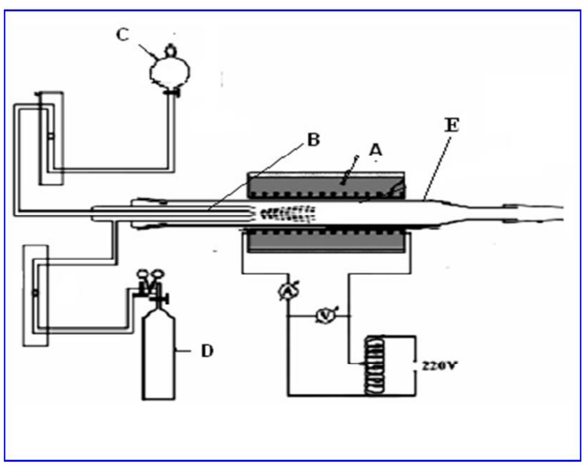

Fig. 1: The schematic diagram of spray pyrolysis set-up. (A)Heating source, (B)Spray nozzle, (C)Carbon feed stock inlet, (D)Nitrogen gas, (E)Quartz tube.

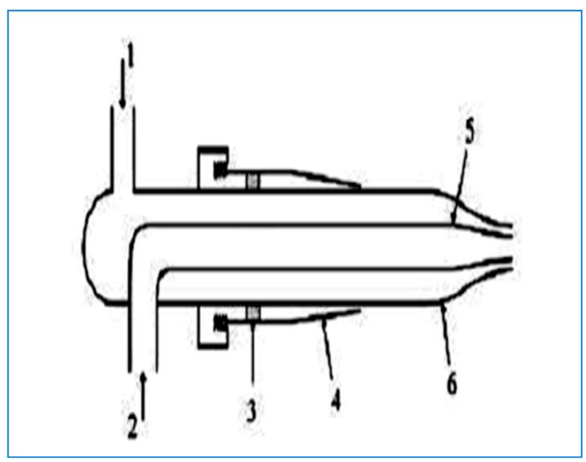

Fig. 2: Schematic diagram of the Sprayer 1. Gas inlet; 2. Solution inlet; 3. Tightening; 4. Polished glass-to-glass connection; 5, 6-Inner and outer pyrex tube.

alumina was added to the solution giving a Fe:Mo:Al_2O_3 ratio 10:13:13. The water was removed by rotary evaporation and the solid dried at 100 °C the resulting powder was grined thoroughly using a mortar and pestle. The fine powders were then calcined for 1hour at 450 °C and then re-grined 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 flow 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, methyl ester of *Brassica Juncea* oil was introduced into the quartz tube through spray nozzle and the flow was maintained at the rate of 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 scanning electron microscopy, (Hitachi SU6600), high resolution transmission electron microscopy (JEOL-3010), Raman spectroscopy (JASCO NRS-1500W, green laser with excitation wavelength 532 nm). The sample material was added to 5% HF solution to form acidic slurry. This slurry was heated to 60 °C and stirred at 600 rpm. The sample was filtered and washed with distilled water. The collected sample was dried at 120 °C in air for 2 hours (Mahalingam *et al.* 2012).

3. RESULTS & DISCUSSION

3.1 SEM and HRTEM observations of CNTs

Fig. 4a and 4b show the field emission scanning electron microscopy image of the as-grown nanostructures over Fe-Mo bimetallic catalyst, impregnated in alumina at 650 °C under the flow of nitrogen by CVD assisted spray pyrolysis method. SEM image clearly reveals that BS-MWNTs grew nicely on the surface of the alumina particles.

Fig. 3a: A Snapshot of as-grown MWNTs Sample

Fig. 3b: Snapshot of setup home-made experime ntal spray-pyrolysis set-up used for the synthesis of BS-carbon nanotubes.

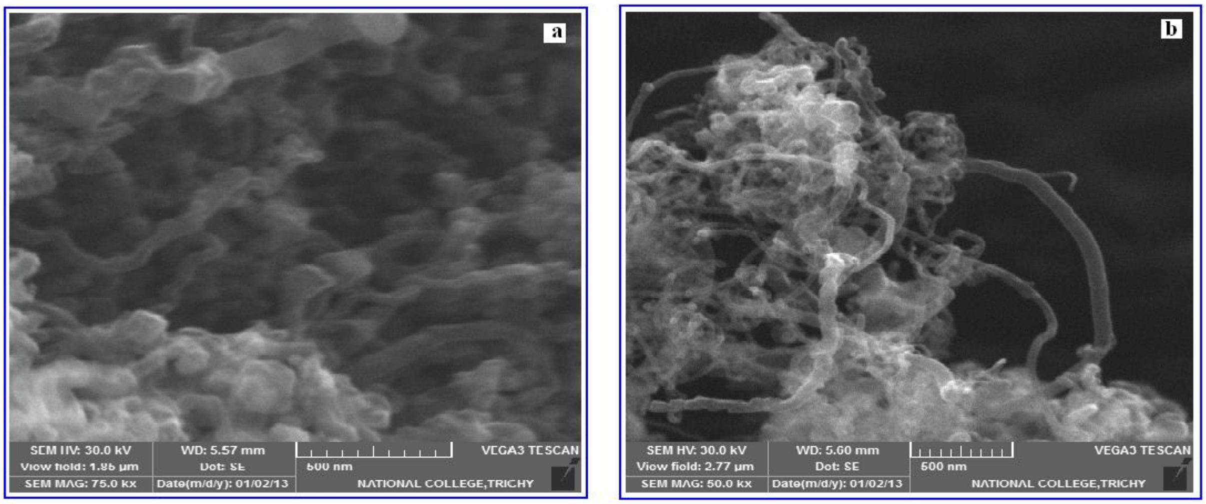

Fig. 4: SEM micrographs of as- grown BS-MWCNTs at 650 °C

Fig. 5: HRTEM micrographs of as grown BS-MWCNTs at 650 °C a) a tubular structure with bamboo like structure b) magnified view on BS-MWCNTs.

In Fig. 5a and 5b we have presented the high resolution HRTEM images of BS-MWNTs, grown over Fe-Mo bimetallic catalyst impregnated on alumina support at 650 °C with a flow rate of methyl ester of *Brassica Juncea* oil at 0.5 ml per minute. Fig. 5a & 5b shows that, the nanotubes have a periodic bamboo-like structure with the inner cavities. The catalyst particles can be observed within the inner cavities (Fig. 5b). The well-developed graphitic layers uniformity of each compartment cavity is not expected as good**.** The diameters of the nanotubes were in the range of 25-30 nm (Fig. 5b).

3. 2. XRD and Raman spectroscopic analysis

Raman spectroscopy was employed to characterize the crystalline nature of the synthesized MWNTs as show in Fig. 6. Typical Raman spectra of Bamboo like MWCNTs indicating two characteristic peaks. The G band peak at 1580 cm^{-1} corresponds to in-plane oscillation of carbon atoms in the graphene wall of Bamboo like MWNTs and high degree lower D-band peak at 1356 cm^{-1} represents the degree of defects or dangling bonds. 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 (Afre *et al.* 2005; Murakami *et al.* 2003). The intensity ratio of D and G peaks (I_D/I_G) is used to characterize the degree of graphitization carbon materials, i.e., smaller ratio of I_D/I_G of the as-grown MWNTs is ≈ 0.5. This value reveals a high degree of graphitization.

The XRD results confirm the graphitic nature of the BS-MWNTs peak at 26 °(C 002) and the presence of the Fe catalyst peak at 44.5 ° (Fe 011) (Pitamber Mahanandia *et al.* 2011).

3.3. Growth Mechanism of BS-MWNTs

In contrast to SWNTs and MWNTs, BS-CNTs have regularly occurring compartment like graphiticstructures inside the nanotube (which, as the name indicates, resemble the structure of the bamboo plant). In fact that BS-MWNTs have been studiedextensively their growth mechanism still poorly understood. The well-known vapour-liquid-solid (VLS) model (Li *et al.* 2001) has been extended to several growth models including base growth model proposed by Lee and Park (Baker *et al.* 1972) and a tip growth model

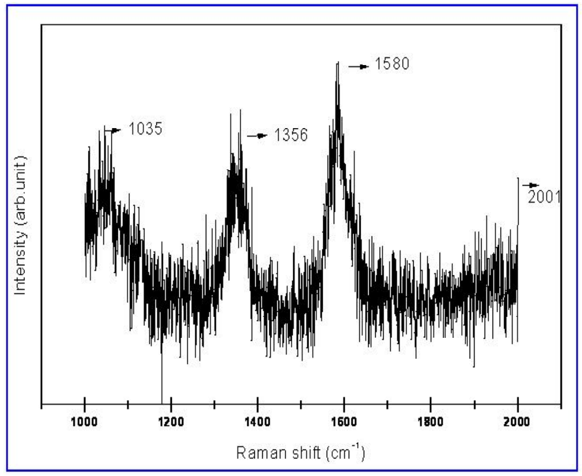

Fig. 6: Raman spectroscopic analysis of as grown BS-MWNTs at 650 °C

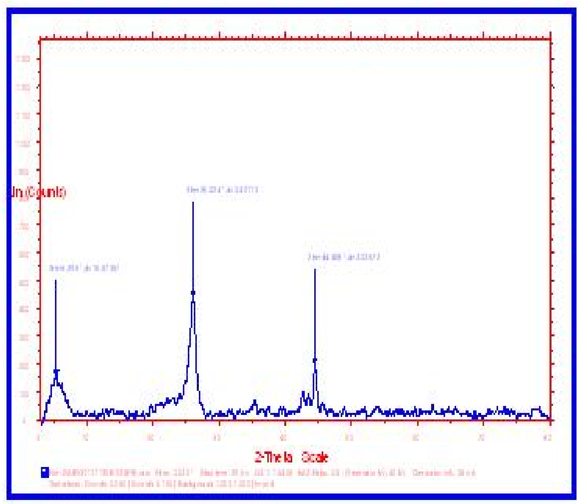

Fig. 7: XRD pattern of as grown BS-MWNTs at 650°C

proposed by Li *et al.* (2001). These models are based on experimental observations and many unresolved issues regarding the atomic level details of the BS-MWNT nucleation process.

The mechanism of carbon nanotube (BS-MWNT) nucleation on catalyst nanoparticles bamboo compartment-like structure inside the outer CNT starts at the junction between the outer wall and the metal particle surface. In this region the precipitated carbon atom is stabilized by the outer wall (compared atoms that precipitate far away from the outer wall). Since precipitation of carbon atoms inside the outer wall can only be achieved by bulk diffusion, formation of BS-MWNTs only occurs at high dissolved carbon concentrations.

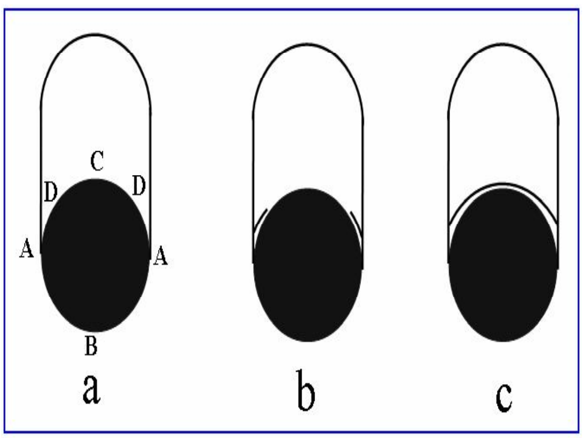

Fig. 8: Growth Model of BS-CNT nucleation

The experimental results which show that BS-MWNTs are formed as carbon concentration were higher than MWNT formation (Li *et al.* 2001).

a) Four region of carbon atoms saturated on nano catalyst and starts precipitation
b) Nucleation of the bamboo compartment-like graphitic structure in metal particle junction
c) Formation of the bamboo compartment

4. CONCLUSION

We have successfully synthesized Bamboo shaped MWNTs with compartments using the catalytic decomposition of *Brassica Juncea* over alumina supported Fe/Mo catalysts. The resulting diameter of the Bamboo shaped MWNTs is around 25-30 nm with lengths up to several microns. Successful growth of BS-MWNTs for both Fe and Mo must be present. SEM, HRTEM, Raman spectroscopy and X-ray diffraction measurements indicates the well graphitized Bamboo shaped MWNTs grown over chosen catalyst nanoparticles.

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