



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

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Received : 09.04.2014 Accepted : 21.05.2014

### Abstract

Bamboo like Carbon Nanotubes with compartments were synthesized using *Brassica Juncea* over Fe-Mo impregnated alumina support at 650 °C reaction temperature 20 ml/hour gas flow rate and at normal pressure under N<sub>2</sub> 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 C<sub>60</sub> 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 ablation (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).

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

(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

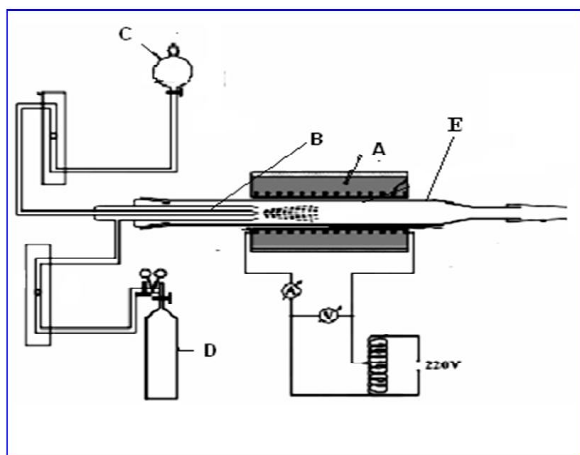


Fig. 1: The schematic diagram of spray pyrolysis set-up. (A) Heating source, (B) Spray nozzle, (C) Carbon feed stock inlet, (D) Nitrogen gas, (E) Quartz tube.

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

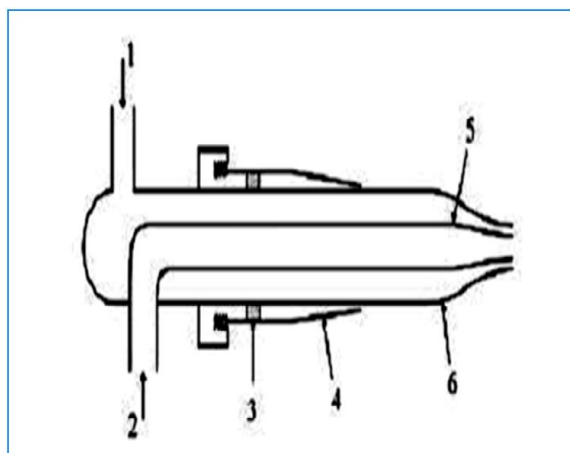


Fig. 2: Schematic diagram of the Sprayer 1. Gas inlet; 2. Solution inlet; 3. Tightening; 4. Polished glass-to-glass connection; 5, 6-Inner and outer pyrex tube.

alumina was added to the solution giving a Fe:Mo:Al<sub>2</sub>O<sub>3</sub> ratio 10:13:13. 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 1 hour 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. 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.

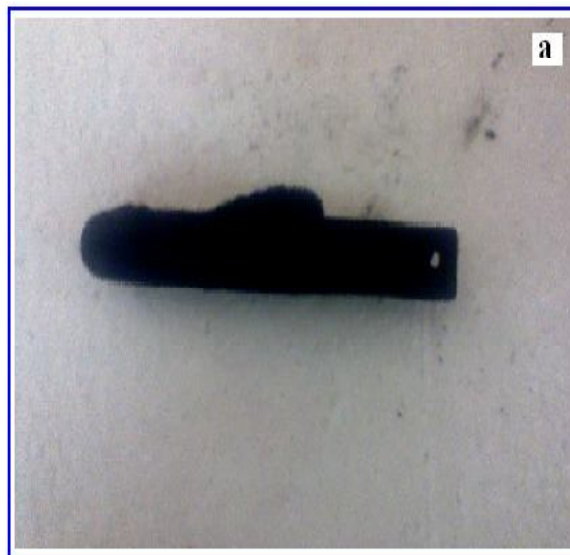


Fig. 3a: A Snapshot of as-grown MWNTs Sample



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

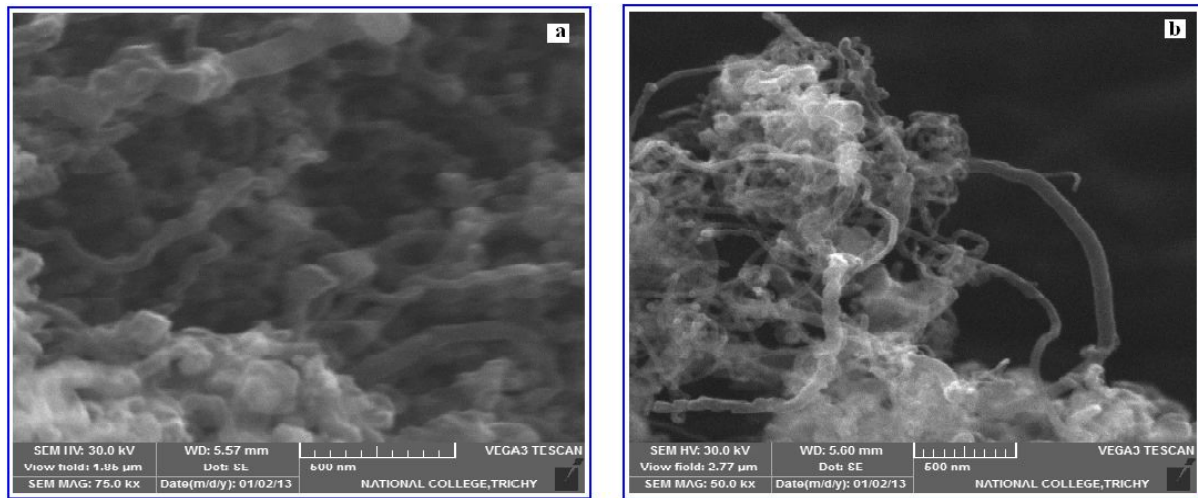


Fig. 4: SEM micrographs of as-grown BS-MWCNTs at 650 °C

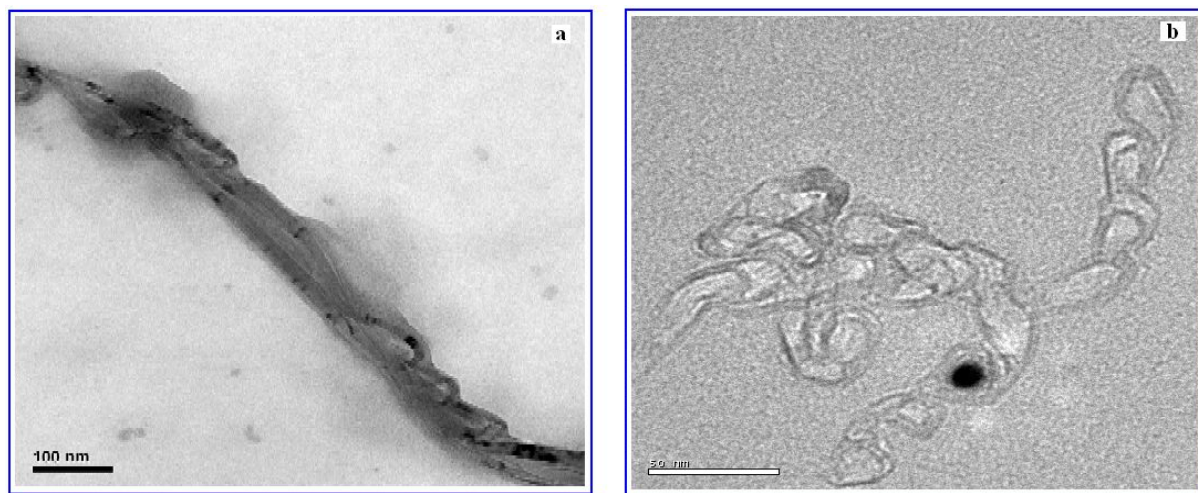


Fig. 5: HRTEM micrographs of as-grown BS-MWCNTs at 650 °C a) a tubular structure with bamboo like structure b) magnified view on BS-MWCNTs.



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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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  $\approx 0.5$ . 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 graphitic structures inside the nanotube (which, as the

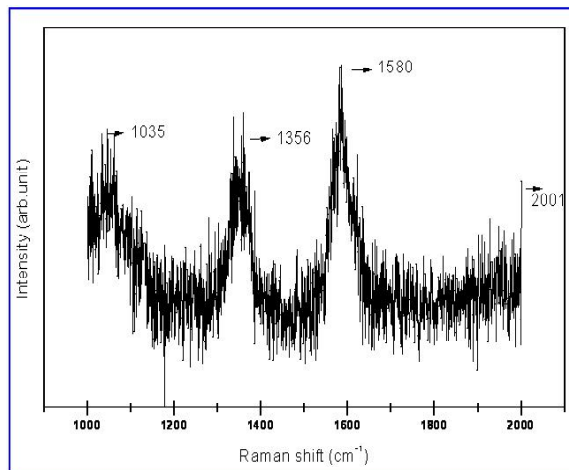


Fig. 6: Raman spectroscopic analysis of as grown BS-MWNTs at 650 °C

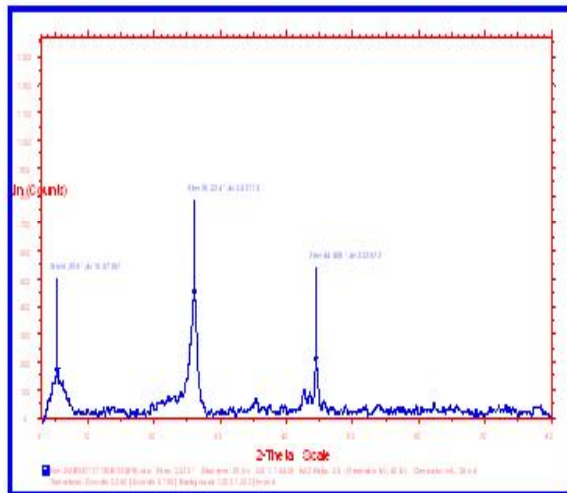
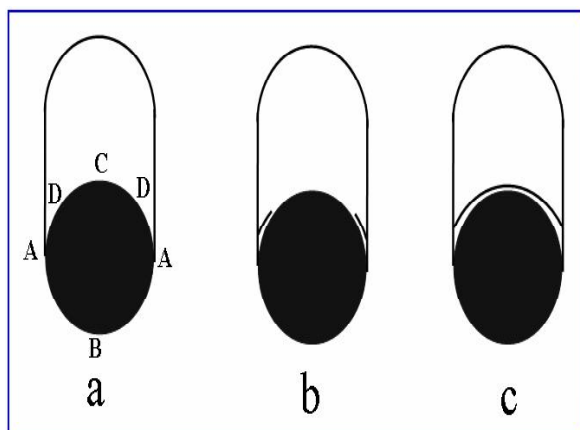


Fig. 7: XRD pattern of as grown BS-MWNTs at 650 °C

name indicates, resemble the structure of the bamboo plant). In fact that BS-MWNTs have been studied extensively 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

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).

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

#### ACKNOWLEDGMENTS

Authors acknowledge the UGC New Delhi for financial support, Institute for Environmental Nanotechnology for technical support and IITM for access to Electron Microscopic analysis.

#### REFERENCES

- Afre, R. A., Soga, T., Jimbo, T., Kumar, M., Ando, A. and Sharon, M., Vertically aligned carbon nanotubes at different temperatures by spray pyrolysis techniques, *Int. J. Mod Phys. B.*, 20(29), 4965(2006).  
doi:10.1142/S0217979206035692
- Afre, R. A., Soga, T., Jimbo, T., Kumar, M., Ando, Y. and Sharon, M., Growth of vertically aligned carbon nanotubes on silicon and quartz substrate by spray pyrolysis of a natural precursor: Turpentine oil, *Chem. Phys. Lett.*, 414, 6–10(2005).  
doi:10.1016/j.cplett.2005.08.040
- Angulakshmi, V. S., Sivakumar, N. and Karthikeyan, S., Response Surface Methodology for optimizing Process Parameters for Synthesis of Carbon Nanotubes, *J. Environ. Nanotechnol.*, 1(1), 40-45(2012).  
doi:10.13074/jent.2012.10.121019

- Angulakshmi, V. S., Rajasekar, K., Sathiskumar, C. and Karthikeyan, S., Growth of vertically aligned carbon nanotubes by spray pyrolysis using green precursor- methyl ester of Helianthus annuus oil, *New Carbon Mater.*, 28, 284-288(2013).  
[doi:10.1016/S1872-5805\(13\)60082-7](https://doi.org/10.1016/S1872-5805(13)60082-7)
- Angulakshmi, V. S., Sathiskumar, C., Karthik, M. and Karthikeyan, S., Synthesis of multi-walled carbon nanotubes from clycine max oil and their potential applications, *J. Environ. Nanotechnol.*, 2, 101-106(2013).  
[doi:10.13074/jent.2013.02.nciset316](https://doi.org/10.13074/jent.2013.02.nciset316)
- Baker, R. T. K., Baker, M. A., Harris, P. S., Feates, F. S. and Waite, R. J., Nucleation and growth of carbon deposits from the nickel catalysed decomposition of acetylene, *J. Catal.*, 26, 51-62(1972).  
[doi:10.1016/0021-9517\(72\)90032-2](https://doi.org/10.1016/0021-9517(72)90032-2)
- Bethune, D. S., Kiang, C. H., Devries, M. S., Gorman, G., Savoy, R., Vazquez, J. and Beyers, R., Cobalt-catalysed growth of carbon nanotubes with single-atomic- layer walls, *Nature.*, 363, 605-607(1993).  
[doi:10.1038/363605a0](https://doi.org/10.1038/363605a0)
- Chernozatonskii, L. A., Gulyaev, Y. V., Kosakovskaja, Z. J., Sinitsyn, N. I., Torgashov, G. V., Zakharchenko, Y. F., Fedorov, E. A. and Valchuk, V. P., Electron field emission from nanofilament carbon films, *Chem. Phys. Lett.*, 233(1-2), 63-68(1995).  
[doi:10.1016/0009-2614\(94\)01418-U](https://doi.org/10.1016/0009-2614(94)01418-U)
- Collins, P. G., Hersam, M., Arnold, M., Martel, R. and Avouris, P., Current saturation and electrical breakdown in multiwalled carbon nanotubes, *Phys. Rev. Lett.*, 86, 3128 (2001).
- Eklund, P., Pradhan, B., Kim, U., Xiong, Q., Fischer, J., Friedman, A., Holloway, B., Jordan, K. and Smith, M., Large-scale production of single-walled carbon nanotubes using ultrafast pulses from a free electron laser, *Nano. Lett.*, 2, 561(2002).  
[doi:10.1021/nl025515y](https://doi.org/10.1021/nl025515y)
- Govindaraj, A. and Rao, C. N. R., Organometallic precursor route to carbon nanotubes, *Pure Appl. Chem.*, 74, 1571(2002).  
[doi:10.1351/pac200274091571](https://doi.org/10.1351/pac200274091571)
- Ghosh, P., Afre, R. A., Soga, T. and Jimbo, T. A simple method of producing single-walled carbon nanotubes from a natural precursor: Eucalyptus oil, *Mater. Lett.*, 61(17), 3768-3770(2007).  
[doi:10.1016/j.matlet.2006.12.030](https://doi.org/10.1016/j.matlet.2006.12.030)
- Iijima, S., Helical microtubules of graphitic carbon, *Nature.*, 354 (6348), 56-58(1991).  
[doi:10.1038/354056a0](https://doi.org/10.1038/354056a0)
- Iijima, S. and Ichihashi, T., Single-shell carbon nanotubes of 1-nm diameter, *Nature.*, 363, 603-605(1993).  
[doi:10.1038/363603a0](https://doi.org/10.1038/363603a0)
- Karthikeyan, S. and Mahalingam, P., Studies of yield and nature of multi-walled carbon nanotubes synthesized by spray pyrolysis of pine Oil at different temperatures, *Int. J. Nanotechnol. Appl.*, 4, 189-197(2010).
- Karthikeyan, S., and Mahalingam, P., Synthesis and characterization of multi-walled carbon nanotubes from biodiesel oil: green nanotechnology route, *Int. J. Green Nanotechnol. Phys. Chem.*, 2, 39-46(2010).  
[doi:10.1080/19430876.2010.532421](https://doi.org/10.1080/19430876.2010.532421)
- Karthikeyan, S., Kalaiselvan, S., Manorangitham, D. and Maragathamani, S., Morphology and structural studies of multi-walled carbon nanotubes by spray pyrolysis using Madhuca Longifolia oil, *J. Environ. Nanotechnol.*, 2, 15-20(2013).  
[doi:10.13074/jent.2013.12.132040](https://doi.org/10.13074/jent.2013.12.132040)
- Krishnan, A., Dujardin, E., Ebbesen, T. W., Yianilos, P. N. and Treacy, M. M. J., Young's modulus of single-walled nanotubes, *Phys. Rev. B: Condens. Matter.*, 58, 14013(1998).  
[doi:10.1103/PhysRevB.58.14013](https://doi.org/10.1103/PhysRevB.58.14013)

- Kumar, M. and Ando, Y., A simple method of producing aligned carbon nanotubes from an unconventional precursor – Camphor, *Chem. Phys. Lett.*, 374, 521-526 (1993).  
[doi:10.1016/S0009-2614\(03\)00742-5](https://doi.org/10.1016/S0009-2614(03)00742-5)
- Kumar, R., Tiwari, R. S. and Srivastava, O.N., Scalable synthesis of aligned carbon nanotubes bundles using green natural precursor: neem oil, *Nanoscale Res. Lett.*, 6, 92-97 (2011).  
[doi:10.1186/1556-276X-6-92L](https://doi.org/10.1186/1556-276X-6-92L)
- Lee, C. J., Lyu, S. C., Kim, H. W., Park, C. Y. and Yang, C. W., Large-scale production of aligned carbon nanotubes by the vapor phase growth method, *Chem. Phys. Lett.*, 359, 109 (2002).  
[doi:10.1016/S0009-2614\(02\)00648-6](https://doi.org/10.1016/S0009-2614(02)00648-6)
- Lee, C. J. and Park, J., Growth model of bamboo-shaped carbon nanotubes by thermal chemical vapor deposition, *Appl. Phys. Lett.*, 77, 3397 (2000).  
[doi:10.1063/1.1320851](https://doi.org/10.1063/1.1320851)
- Li, X., Zhu, H., Ci, L., Xu, C., Mao, Z., Wei, B., Liang, J. and Wu, D., Hydrogen uptake by graphitized multi-walled carbon nanotubes under moderate pressure and at room temperature, *Carbon.*, 39(15), 2077-2079 (2001).  
[doi:10.1016/S0008-6223\(01\)00183-X](https://doi.org/10.1016/S0008-6223(01)00183-X)
- Li, W. Z., Wen, G., Tu, Y. and Ren, Z. F., Controlled growth of carbon nanotubes on graphite foil by chemical vapor deposition, *Chem. Phys. Lett.*, 355(3-4), 141-149 (2001).  
[doi:10.1016/S0009-2614\(01\)00032-X](https://doi.org/10.1016/S0009-2614(01)00032-X)
- Li, W. Z., Wen, J. G., Tu, Y. and Ren, Z. F., Effect of gas pressure on the growth and structure of carbon nanotubes by chemical vapor deposition, *Appl. Phys. A.*, 73(2), 259-264 (2001).  
[doi:10.1007/s003390100916](https://doi.org/10.1007/s003390100916)
- Martel, A. R., Derycke, V., Appenzeller, J., Carbon nanotube transistors and logic Circuits, *Physica B: Condens. Matter.*, 323(1-4), 6-14 (2002).  
[doi:10.1016/S0921-4526\(02\)00870-0](https://doi.org/10.1016/S0921-4526(02)00870-0)
- Matveev, A. T., Golberg, D., Novikov, V. P., Klimkovich, L. L. and Bando, Y., Synthesis of carbon nanotubes below room temperature, *Carbon.*, 39(1), 155-157(2001).  
[doi:10.1016/S0008-6223\(01\)00007-0](https://doi.org/10.1016/S0008-6223(01)00007-0)
- Mahalingam, P., Parasuram, B., Maiyalagan, T. and Sundaram, S., Chemical methods for purification of carbon nanotubes – A Review, *J. Environ. Nanotechnol.*, 1, 53-61(2012).
- Mageswari, S., Jafar Ahamed, A. and Karthikeyan, S., Effect of temperature and flow rate on the yield of multiwalled carbon nanotubes by spray pyrolysis using Cymbopogon Flexsuuous oil, *J. Environ. Nanotechnol.*, 1, 28-31(2012).  
[doi:10.13074/jent.2012.10.121015](https://doi.org/10.13074/jent.2012.10.121015)
- Murakami, Y., Miyauchi, Y., Chiashi, S. and Maruyama, S., Direct synthesis of high-quality single-walled carbon nanotubes on silicon and quartz substrates, *Chem. Phys. Lett.*, 377, 49(2003).
- Oberlin, A., Endo, M. and Koyama, T., Filamentous growth of carbon through benzene decomposition, *J. Cryst. Growth.*, 32, 335–349(1976).  
[doi:10.1016/0022-0248\(76\)90115-9](https://doi.org/10.1016/0022-0248(76)90115-9)
- Paul, S. and Samdarshi, S. K., A green precursor for carbon nanotube synthesis, *New Carbon Mater.*, 26, 85–88(2011).  
[doi:10.1016/S1872-5805\(11\)60068-1](https://doi.org/10.1016/S1872-5805(11)60068-1)
- Pitamber Mahanandia, Jorg, Schneider, J., Martin Engel, Bernd Stühn, Somanahalli, V., Subramanyam and Karunakar Nanda, Studies towards synthesis, evolution and alignment characteristics of dense, millimeter long multiwalled carbon nanotube arrays, *Beilstein J. Nanotechnol.*, 2, 293–301 (2011).  
[doi:10.3762/bjnano.2.34](https://doi.org/10.3762/bjnano.2.34)
- Qian, D. and Dickey, E. C., In-situ transmission electron microscopy studies of polymer - carbon nanotube composite deformation, *J. Microsc. Oxford.*, 204, 39(2001).



- Saito, Y., Nishikubo, K., Kawabata, K. and Matsumoto, T., Carbon nanocapsules and single-layered nanotubes produced with platinum group metals Ru, Rh, Pd, Os, Ir, Pt) by arc discharge, *J. Appl. Phys.*, 80, 3062(1996).  
[doi:10.1063/1.363166](https://doi.org/10.1063/1.363166)
- Suriani, A. B., Azira, A. A., Nik, S. F., Md Nor, R. and Rusop, M., Synthesis of vertically aligned carbon nanotubes using natural palm oil as carbon precursor, *Mater. Lett.*, 63, 2704-2706(2009).  
[doi:10.1109/ISBEIA.2012.6422908](https://doi.org/10.1109/ISBEIA.2012.6422908)
- Yuan, L., Saito, K., Pan, C., Williams, F. and Gordon, A., Nanotubes from methane flames, *Chem. Phys. Lett.*, 340, 237(2001).  
[doi:10.1016/S0009-2614\(01\)00435-3](https://doi.org/10.1016/S0009-2614(01)00435-3)