

## ENTANGLED MULTI-WALLED CARBON NANOTUBES FROM *CITRUS LIMONUM* OIL

S. Mageswari<sup>1</sup>, P. S. Syed Shabudeen<sup>2</sup> and S. Karthikeyan<sup>3\*</sup>

<sup>1</sup>Department of Chemistry, Vivekanandha College of Engineering for Women,  
Tiruchengode, TN, India.

<sup>2</sup>Department of Chemistry, Kumaraguru College of Technology, Coimbatore, TN, India.

<sup>3</sup>Department of Chemistry, Chikkanna Government Arts College, Tirupur, TN, India

\*E-mail: [skmush@rediffmail.com](mailto:skmush@rediffmail.com)

### ABSTRACT

Multi-walled carbon nanotubes have been synthesized by simple method of spray pyrolysis using *Citrus limonum* oil on Fe/Mo catalyst supported on silica and their characteristics were investigated. *Citrus limonum* oil: a plant based precursor was used as a carbon source. Multi-walled carbon nanotubes were synthesized using *Citrus Limonum* oil at different temperatures ranging from 550 °C to 750 °C. The characteristics of MWNTs markedly changes such as crystallinity, diameter, etc., confirmed by scanning electron microscope (SEM), high resolution transmission electron microscope (HRTEM), X-ray diffraction analysis (XRD) and Raman spectral studies. The HRTEM and Raman spectroscopic studies confirmed the evolution of MWNTs with the outer diameter between 20 and 40 nm. The bimetallic catalyst of Mo and Fe supported on silica as supporting materials to produce quality, quantity and uniformity of MWNTs.

**Keywords:** Spray pyrolysis; Multi-walled carbon nanotubes; Bimetallic Catalyst

©2014 RASĀYAN. All rights reserved

### INTRODUCTION

Carbon nanotubes (CNTs) are an interesting class of nanostructures which have been extensively studied since their discovery in 1991<sup>1</sup>. Because of outstanding electrical, thermal and mechanical properties, CNTs have potentials for applications in nanoelectronics, sensors, field emission and as reinforcing agents in composite materials<sup>2,3</sup>. The CNTs have been synthesized by various of techniques, but some more prominent ones are arc discharge, laser vapourization spray pyrolysis and chemical vapour deposition (CVD)<sup>4-7</sup> method. Among these methods spray pyrolysis is also promising method for synthesizing CNTs. This method is a sister method of CVD. In the spray pyrolysis method pyrolysis of the carbon precursor and deposition occur in one step, while in CVD it takes two steps. In the CVD method carbon precursor vaporizes at lower temperature in the first furnace and pyrolysis at higher temperature in the second furnace under the flow of carrier gas. Recently the spray pyrolysis method has attracted attention due to the possibility of producing carbon nanotubes on a commercial scale<sup>8</sup>. Till date, several precursors such as carbon monoxide<sup>9</sup>, methane<sup>10</sup>, acetylene<sup>11</sup>, benzene<sup>12</sup>, xylene<sup>13</sup>, etc. have been used as a carbon feedstock to synthesize CNTs. These carbon sources are related to fossil fuels which may not be sufficiently available in near future. However, comparatively less number of studies has been made regarding the synthesis of CNTs from natural precursors. Some natural precursor used in earlier studies corresponds to eucalyptus oil, turpentine oil<sup>14-16</sup>, Pine oil<sup>17</sup>, *Helianthus annuus* oil<sup>18</sup> *Jatropha curcas* oil<sup>19</sup>, *Glycine max* oil<sup>20</sup>, and *Cymbopogen flexuosus* oil<sup>21</sup>. *Citrus limonum* oil, being a natural precursor which is renewable and cheap, has the potential to be the green alternative for industrial scale production of MWNTs. A detailed study of the growth of nanostructured carbons from *citrus limonum* oil has not to the best of our knowledge, been published.

In this paper, we attempt to synthesis MWNTS from *Citrus limonum* oil by spray pyrolysis method using Fe/Mo bimetallic catalyst supported on silica under nitrogen atmosphere at different temperature viz., 550 °C, 650 °C and 750 °C.

## EXPERIMENTAL

### Synthesis of multi-walled carbon nanotubes

A silica supported Fe-Mo catalyst (Fe: Mo: SiO<sub>2</sub> = 1:0.1:4) was prepared by wet impregnation method<sup>22</sup>. Appropriate quantities of metal salts (Merck) i.e. Fe (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O 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 h, removed from the furnace and ground in an agate mortar. The fine powders were then calcined for 1 h at 450 °C and then re-ground 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 100 mL/min into the quartz tube to remove any oxygen from the quartz tube. The temperature was raised from room temperature to the desired growth temperature. Subsequently, *Citrus limonum* oil was introduced into the quartz tube through a spray nozzle and the flow was maintained at the rate of 0.5 mL/min. The deposition was conducted for 30 min for each process at different temperatures from 550 °C to 750 °C. Spray pyrolysis was carried out for 45 minutes and thereafter the 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) and Raman spectroscopy (JASCO NRS-1500W, green laser with excitation wavelength 532 nm).

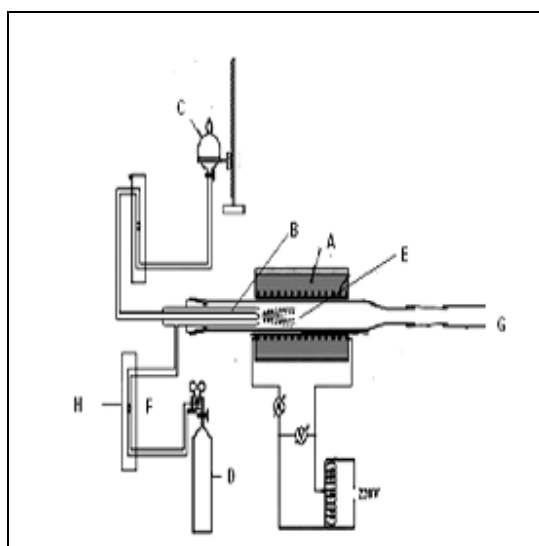


Fig.-1: Schematic diagram of the home-made spray-pyrolysis set-up.

A - furnace, B - spray nozzle, C - separating funnel containing carbon feed stock, D - nitrogen gas cylinder, E - quartz boat containing catalysts with supporting material, F - rubber tube, G - outlet, H - flow meter.

## RESULTS AND DISCUSSION

The as grownup MWNTs were principally entangled like spaghetti as shown in SEM pictures Figure 2. The Figure 2a shows at lower temperatures (550 °C), the MWNTs yield is low as a result of at these temperatures carbon supply decomposed fraction semiconductor diode in formation of amorphous carbon. Figure 2b illustrates a pleasant growth of MWNTs with diameter of 20-40 nm was discovered at 650 °C. Figure 2c revealed low populations of MWNTs with increasing the diameter were observed at 750 °C. The increasing diameter may be due to agglomeration of catalyst particles at this temperatures SEM observations reveals that in our experimental conditions, carbon nanotubes can not be grown at either low ( 550 °C) or high (750 °C) temperatures and smaller diameter and high yield carbon nanotubes are formed at 650 °C.

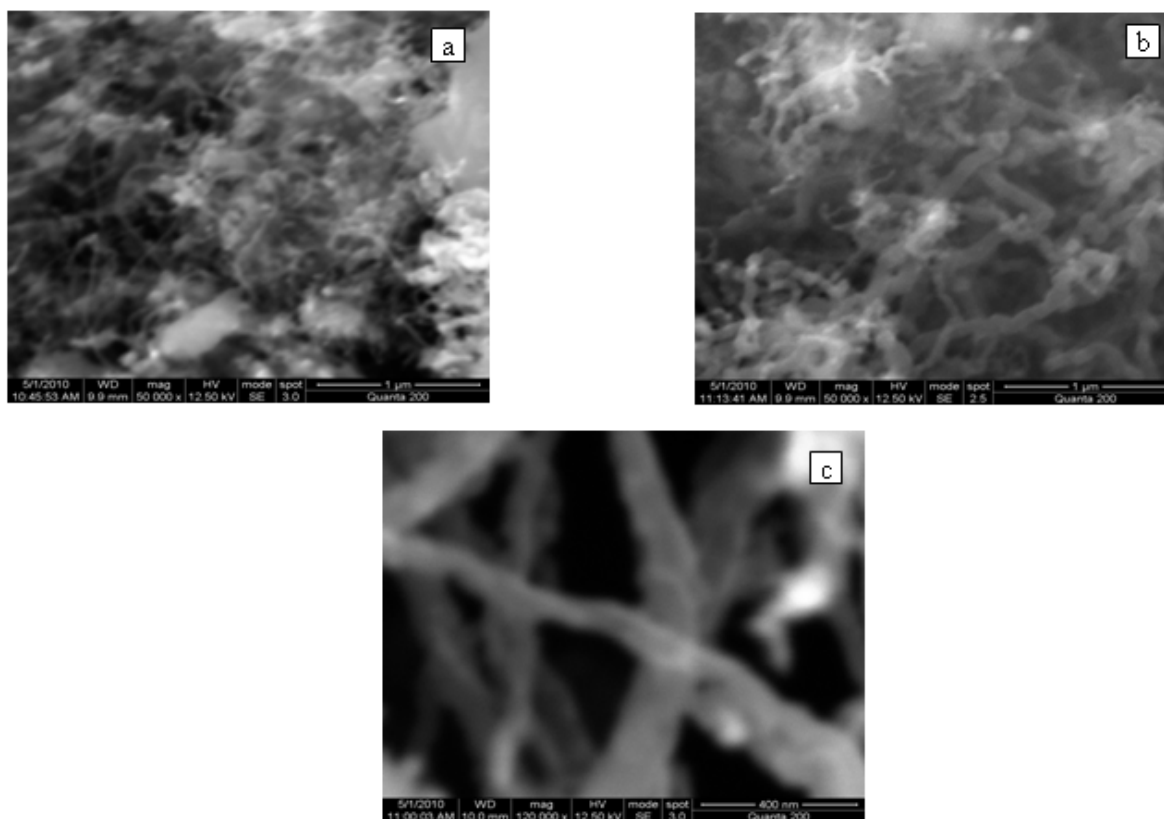


Fig. -2: SEM images of MWNTs grown on Fe-Mo catalyst supported on silica at various temperatures ranging from 550 °C (a), 650 °C (b), and 750 °C (c).

The morphologies of the carbonaceous deposit obtained were characterized by HRTEM. Figure 3a shows there is no clear growth of MWNTs at 550 °C because these temperatures are not sufficient to activate the catalyst for pyrolysis of carbon source. Figure 3b demonstrate a high resolution TEM images clearly shows well-graphitized layers of a typical MWNTs grown from spray pyrolysis of *Citrus limonum* oil at 650 °C. At 650 °C selectivity towards MWNTs close to 100% is reached. In the best optimized condition, amorphous carbon or metal particles are rarely seen in our samples, which are usually observed in catalytically grown MWNTs. Figure 3c shows a higher temperature apparently favors the growth of nanotubes with a bigger diameter due to agglomeration of catalyst particles. This finding agrees with experimental results from several authors<sup>17-23</sup>.

The results of Raman spectroscopy analysis in Figure 4 represent the MWNTs grown on the catalyst surface at 650 °C, indicating two characteristic peaks at 1348  $\text{cm}^{-1}$  and 1578  $\text{cm}^{-1}$  which correspond to D and G bands, respectively. The G bands are related to stretching vibration in the basal plane of graphite crystal, which have been normalized to the same intensity. The D bands are associated with the disorder or defective planar graphite structure. The D peaks at 1346  $\text{cm}^{-1}$  can be attributed to the defects in the curved graphene sheets. Therefore, the Raman spectrum provides definite evidence that the MWNTs have graphitic structure. The similar result was observed in W.Z. Li et al<sup>24</sup>.

Figure-5 shows that the MWNTs crystal structure was studied by X-Ray Diffraction method. The peaks are indexed as the (002) and (101) reflections of hexagonal graphite. Intense peaks are found at 26.35° and 44.44° can be indexed to the (002) and (101) planes, respectively.

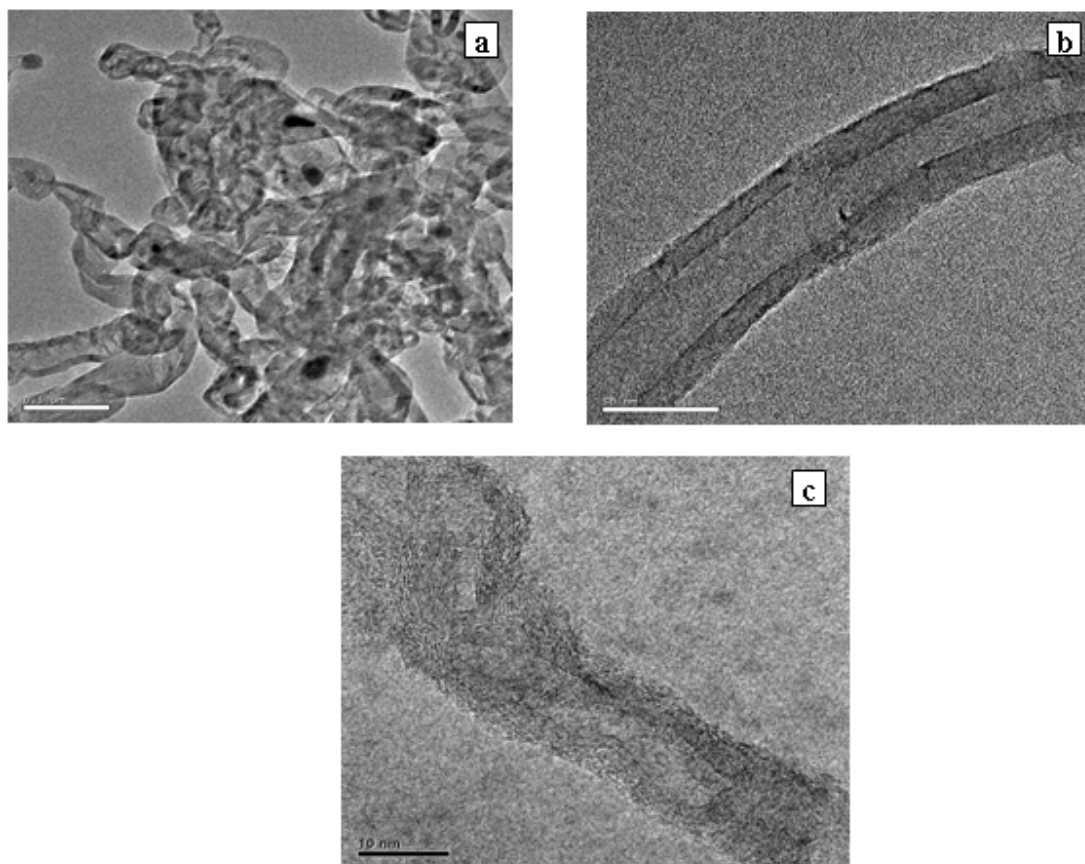


Fig. - 3: HRTEM images of MWNTs grown on Fe-Mo catalyst supported on silica at various temperatures ranging from 550 °C (a), 650 °C (b) and 750 °C (c)

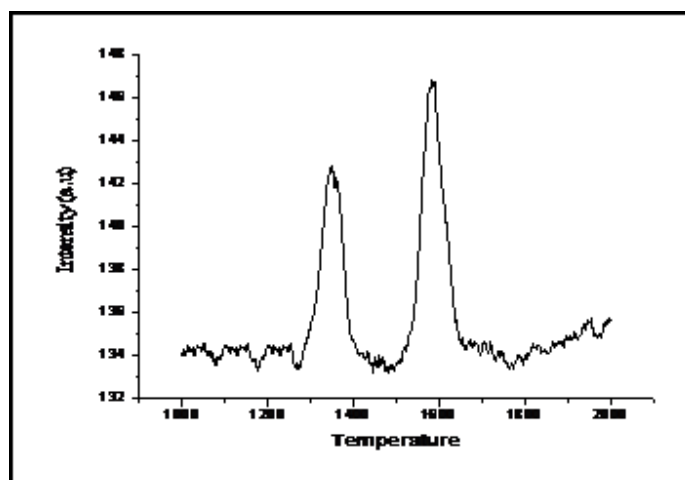


Fig. -4: Typical Raman Spectrum of the MWNTs grown at 650 °C

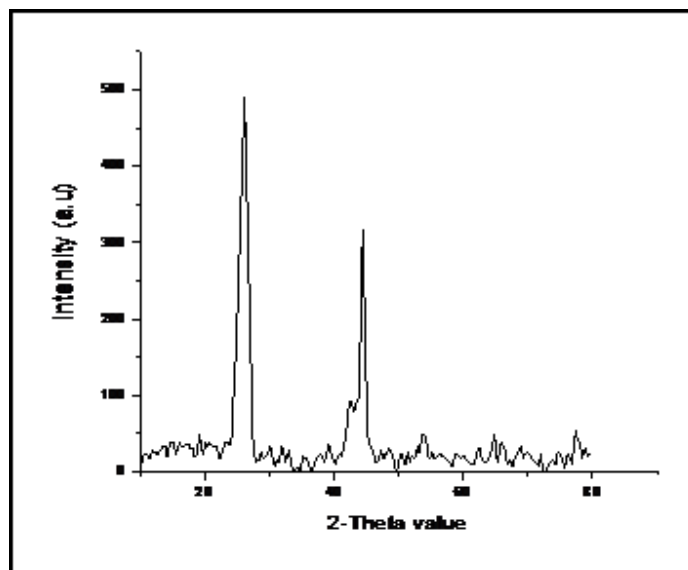


Fig. – 5: XRD patterns of MWNTs grown at 650 °C

### CONCLUSION

Multi-walled carbon nanotubes are nicely grown at all temperature from 550 to 750 °C. Here, we have optimized the growth MWNTs from *citrus limonum* oil by spray pyrolysis method at 650 °C using silica supported Fe/Mo catalyst under N<sub>2</sub> atmosphere. The maximum MWNTs yield found here is 40% at 650 °C. HRTEM images clearly show the nanotubes diameter variation with increase in reaction temperature. Raman spectroscopy reveals that as grown multi-walled carbon nanotubes are well graphitized. Formation of bimetallic catalyst of Fe and Mo probably assists in homogeneous dispersion of metal particles on the support material, resulting in the formation of higher quantities of carbon nanotubes.

### REFERENCES

1. S. Iijima, *Nature*, **354**, 56 (1991).
2. S. Khan, K. N. Tripathi, M. Aggarwal, K. Tripathi, M. Husain, and Z. H. Khan, *J. Exp. Nanosci.* **2**, 215 (2007).
3. M. Paradise and T. Goswami, *Mater. Des.*, **28**, 1477 (2007).
4. T.W. Ebbesen and P. M. Ajayan, *Nature*, **358**, 220 (1992).
5. A. Thess, R. Lec, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. Hee, S.G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria and D. Tomanek, *Science*, **273**, 483(1996).
6. R. Sen, A. Govindraj and C. N. R. Rao, *Chem. Phys. Lett.*, **267**, 276 (1997).
7. A. S. Afolabi, A. S. Abdhulkareem and S. E. Iyuke, *J. Exp. Nanosci.*, **2**, 269 (2007).
8. S. R. C. Vivekchand, L. M. Cele, F. L. Deepak, A. R. Raju and A. Govindaraj, *Chem. Phys. Lett.*, **386**, 313 (2004).
9. H. Dai, A. G. Rinzler, P. Nikolaev, A. Thess, D. T. Colbert and R. E. Smalley, *Chem. Phys. Lett.*, **260**, 471 (1996).
10. J. F. Colomer, C. Stephan, S. Lefrant, G. Van Tendeloo, I. Willems, Z. Konya, A. Fonseca, C. Laurent and J. B. Nagy, *Chem. Phys. Lett.*, **317**, 83 (2000).
11. W. Z. Li, S. Xie, L. X. Qian, B. H. Chang, B. S. Zau and W. Y. Zhau, *Science*, **274**, 1701 (1996).
12. R. Kamalakaran, M. Terrones, T. Seeger, P. Kohler-Redlich, M. Ruhle, Y. A. Kim, T. Hayashi and M. Endo, *Appl. Phys. Lett.*, **77**, 3385 (2000).
13. B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang and G. Ramanath, *Nature*, **416**, 495 (2002).
14. P. Ghose, R. A. Afre, T. Soga and T. Jimbo, *Mater. Lett.*, **61**, 3786 (2007).

15. K. Aswathi, R. Kumar, R. S. Tiwari and O. N. Srivastava, *J. Exp. Nanosci.*, **5**, 498 (2010).
16. G. Alonso-Nunez, J. Lara-Romero, F. Paraguay-Delgado, M. Sanchez-Castaneda and S. Jimenez-Sandoval, *J. Exp. Nanosci.*, **5**, 52 (2010).
17. S. Karthikeyan and P. Mahalingam, *Inter. J. Nanotechnol. Appl.*, **4**, 189 (2010).
18. S. Karthikeyan and V. S. Angulakshmi, *J. Environ. Nanotechnol.*, **1**, 40 (2012).
19. S. Karthikeyan and P. Mahalingam, *Inter. J. green Nanotechnol. Phys. Chem.*, **2**, 39 (2010).
20. S. Karthikeyan, V. S. Angulakshmi, C. Sathishkumar and M. Karthik, *J. Environ. Nanotechnol.*, **2**, 101 (2013).
21. S. Mageswari and S. Karthikeyan, *J. Environ. Nanotechnol.*, **1**, 28 (2012).
22. S. D. Mhlanga, C. M. Karthick, C. Robin, J. W. Michael and J.C.S. Neil, *Afr. J. Chem.*, **62**, 67 (2009).
23. R. A. Afre, T. Soga, T. Jimbo, M. Kumar, A. Ando and M. Sharon, *Chem. Phys. Lett.*, **414**, 610 (2005).
24. W. Z. Li, H. Zhang and C. Y. Wang, *Appl. Phys. Lett.*, **70**, 2684 (1997).

[RJC-1159/2014]