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Carbon Nanotubes from Plant Derived Hydrocarbon - An Efficient Renewable Precursor

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Abstract

The present work aspire to explore cost effective a natural renewable Eco-friendly green precursor for the synthesis of Multi-walled carbon nanotubes (MWCNTs) using methyl ester of Moringa oleifera oil over Fe-Co impregnated Alumina support at 650 °C under N_2 atmosphere. The characterization of the as-grown carbon materials were analyzed by Scanning electron microscopy (SEM), High resolution transmission electron microscopy (HRTEM), XRD and Raman spectroscopic analysis. The bimetallic catalyst of Co and Fe supported on alumina gel particles improves the quality and uniformity in diameters of CNTs. The diameters of as-synthesized nanotubes are in the range of 19 nm to 22 nm

Keywords: *Carbon nanotubes; Moringa oleifera oil; Raman & XRD spectroscopic analysis; Spray-pyrolysis; SEM.*

1. INTRODUCTION

Carbon nanotubes (CNTs) are now well into their teenage years. Earlier on, theoretical predictions and various experimental evidence showed that CNTs possess chemical and physical properties that surpass those of many other nanosized materials. This has activated intense research into CNTs world wide. The vital publication of Iijima (Iijima, 1991) made carbon nanotubes (CNTs) one of the key component in nanoscience and technology. as the numerous new applications are being proposed, so is the rapid rise in demand for its large production. This is due season to explore new environment friendly natural renewable precursors.

In general, CNTs are synthesized by arc discharge, laser ablation, and CVD or spray Pyrolysis. Among these methods CVD or spray pyrolysis method is regarded as a promising method to synthesize carbon nanotubes (CNTs) because of its benefits to achieve a high yield of CNT_S and can be easily scaled up for the production of CNTs at a relatively low cost (Karthikeyan *et al.* 2008). Several papers have been published and describe a simple routine for synthesizing low-cost CNT arrays in large scale from petroleum-based precursors such as benzene, xylene and hexane (Sadeghian *et al.* 2009). These carbon precursors are related to fossil fuels and there may be a crisis for these precursors in the near future. There are few reports on the synthesis of CNTs from plant based precursors such as camphor (Kumar *et al.* 2003), 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.* 2008), and reports from plant derived methyl esters *Oryza sativa oil* (Kalaiselvan *et al.* 2015; 2016), *Cymbopogen flexuosus* oil (Mageswari *et al.* 2014), *Helianthus annuus* oil (Angulakshmi *et al.* 2012; 2013), *Glycine Max* Oil (Angulakshmi *et al.* 2013), *Madhuca Longifolia* Oil (Kalaiselvan *et al.* 2013 ; 2014) and *Brassica Juncea* Oil (Kalaiselvan *et al.* 2014 ; 2016). The advantages of the plant derived carbon precursor are that it is a renewable biomaterial, and abundantly available and owing to these two factors, it has a huge potential to be used as the carbon source for the synthesis of CNTs, and therefore, the resulting product can be commercialized at a lower cost (Kalaiselvan *et al.* 2014).

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2. EXPERIMENTAL METHODS

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

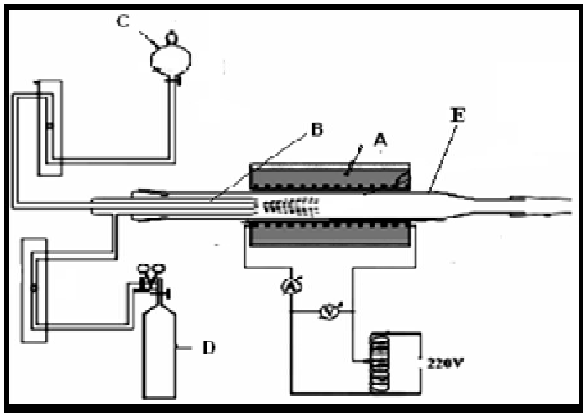


Fig. 1: The schematic diagram of spray pyrolysis set-up. (A) Heating source, (B) Spray nozzle, (C) Carbon feed stock inlet, (D) Nitrogen gas, (E) Quartz tube.

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.

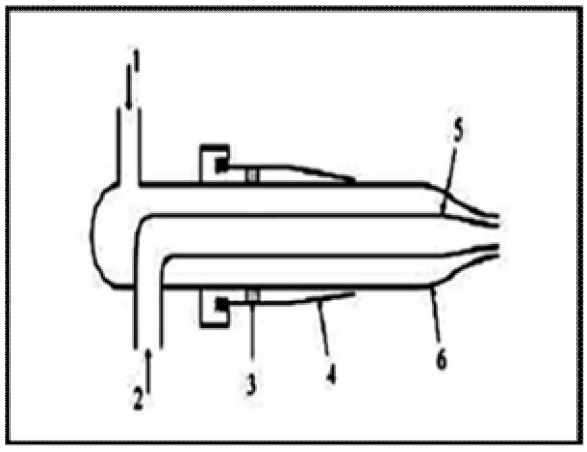


Fig. 2: Schematic diagram of the Sprayer 1. Gas inlet; 2. Solution inlet; 3. Tightening; 4. Polished glass-to-glass connection; 5, 6-Inner and outer pyrex tube.

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 *Moringa oleifera* 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 also the role of the support for the reaction products which appear pyrolytic decomposition of the starting materials (methyl ester of *Moringa oleifera* oil) over Fe-Co impregnated Alumina support. The used electrical furnace is able to assure a uniform temperature up to 650 °C.

2.1 Preparation of bi-metallic catalyst nanoparticles

The bimetallic catalyst of cobalt and iron supported on silica gel particles were used as catalyst for CNTs growth by spray pyrolysis. The mixture of $Co(NO_3)_3$. $3H_2O$ and $Fe(NO_3)_3$. $6H_2O$ were heated at 90 ^oC to liquefy the Co and Fe nitrates. One-third weight of alumina gel with respect to the total weight of metal nitrates were added into liquefied mixture of Co and Fe nitrates and stirred well for 30 min. The well stirred mixture of catalyst was cooled down to room temperature and kept in oven for drying at 60 ^oC for 24 hour. (Afre *et al.* 2006**]** The complete dried catalyst ground into fine particles in an agate mortar. The fine powder were then calcined for 1 hour at 450 °C and then re-ground before loading into the reactor.

2.2 Synthesis and purification of 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, *Moringa oleifera* 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 45 minutes for each deposition at different temperatures from 550-750 °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 $(m_1-m_0)/m_0$, where m_1 and m_0 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 MWNTs. 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 MWNTs 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 MWNTs of narrow size 20-40nm were established as reaction temperature around 650 °C, 80mg of catalyst substrate, 45 minutes reaction time, 100 ml per minute nitrogen gas flow and 0.5ml per minute precursor flow. The as-grown MWNTs were purified by the following procedure. 50 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 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.

3. RESULTS & DISCUSSION

Fig. 3a and 3b show the scanning electron microscopy image of the as-grown nanostructures over Fe-Co bimetallic catalyst, impregnated in silica at 750 °C under the flow of nitrogen by CVD assisted spray pyrolysis method. SEM image clearly reveals that MWNTs grew nicely on the surface of the silica particles.

In Fig. 4a and 4b we have presented the high resolution HRTEM images of MWNTs, grown over Fe-Co bimetallic catalyst impregnated on silica support at 650 °C with a flow rate of methyl ester of *Moringa oleifera* oil at 0.5 ml per minute. Fig. 4a & 4b shows that, The catalyst particles observed at the tip of the carbon nanotubes (Fig. 4a). The inner diameters of the nanotubes were in the range of 14-18nm and the outer diameters of the grown nanotubes found in the range of 42-50nm. The wall and inner core clearly visible (Fig. 4b).

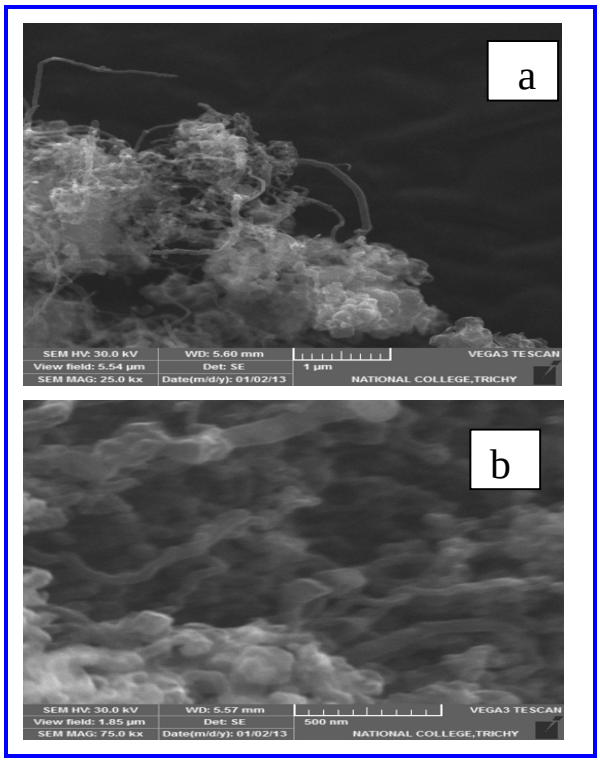


Fig. 3a & 3b : SEM images of MWNTs grown Fe-Co supported on alumina at 650 °C

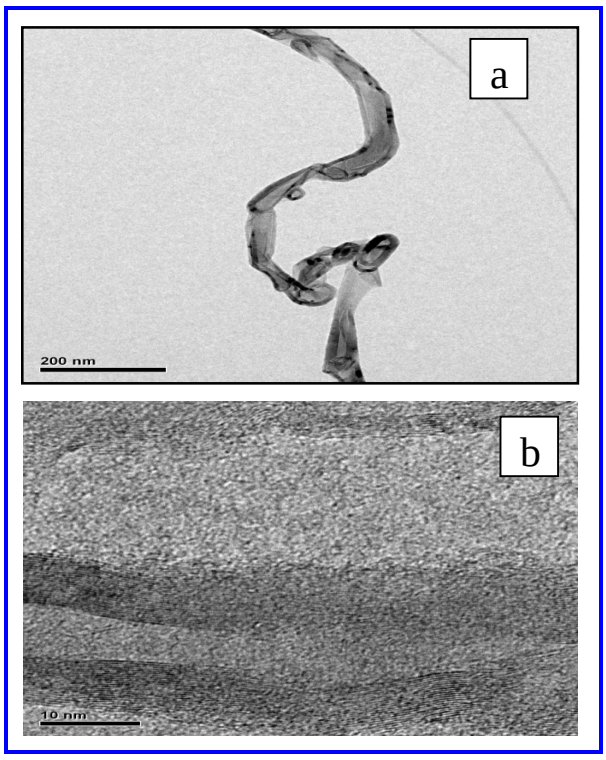


Fig. 4a &4 b : HRTEM images of MWNTs grown Fe-Co supported on alumina at 650 °C

3.1 Raman Spectroscopy

The Raman technique is used in qualitative and quantitative analysis of carbon nanotubes. The grown CNT were then characterized by Raman spectroscopy as shown in Fig.5. The G band is a tangential shear mode of carbon atoms that corresponds to the stretching mode in the graphite plane. The D band is present in all carbon allotropes, including sp^2 and sp^3 amorphous carbon. The results of Raman spectroscopy of MWNTs grown on the catalyst surface at 650 °C, indicating two characteristic peaks at 1334.21 cm^{-1} and 1582.84 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. The D bands are associated with the disorder or defective planar graphite structure. The D peaks at 1334 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. For high-quality samples without defects and amorphous carbon, the I_D/I_G ratio is often less than 2 % (Kumar *et al.* 2005 ; Andrews *et al.* 2006). I_D/I_G ratio was found to be 0.84 indicates lower defects which is in good agreement with theoretical evidence. There was no lower frequency radial breathing mode peaks detected in as-grown nanotubes which indicate no single-walled CNT was produced.

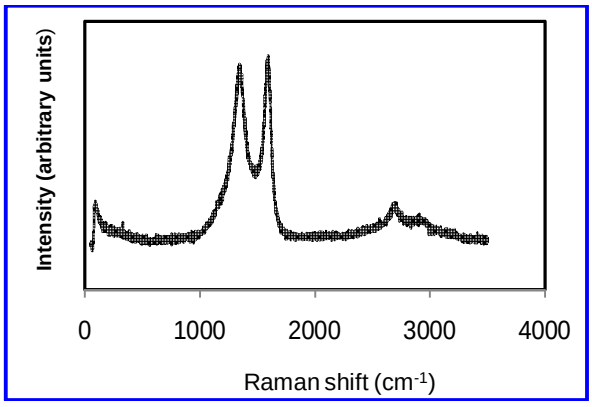


Fig. 5 : Raman Spectrum of grown MWCNTs at 650°C

3.2 XRD analysis

XRD measurement was carried out using Cu K radiation to examine the structure of the CNTs and the resulting 2 theta scan Fig. 6 shows that the MWNTs crystal structure was studied by X-Ray Diffraction method. The intense peaks at 26° and 44° can be as indexed (002) and (101) reflections of hexagonal graphite. The peak at 2 theta = 26° corresponds to the graphite, which is attributed here to the graphitic structure of CNTs. Appearance of characteristic peak of graphite shows the presence of Multiwalled carbon nanotubes in the sample (Cao *et al.* 2001).

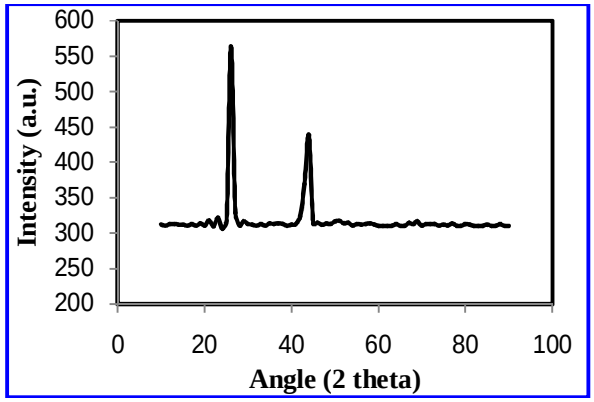


Fig. 6: XRD spectrum of grown MWCNTs at 650 °C

4. CONCLUSION

Multiwalled carbon nanotubes were obtained by chemical vapor deposition of *Moringa oleifera* oil an renewable natural precursor, as a carbon source. Based on result, the formation of MWCNT has been optimized at 650°C synthesis temperature which is in good agreement with SEM, HRTEM, XRD & Raman spectroscopic analysis. The experiment has succeeded in minimizing I_D/I_G ratio of about 0.84. The highest yield of 61% was obtained at the same temperature.

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