Research Article

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Effect of Catalyst Composition on the Growth of Multi-walled Carbon Nanotubes from Methyl Esters of *Oryza sativa* Oil

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ABSTRACT

Multi-walled carbon nanotubes on mono-metallic (Fe), bi-metallic (Fe-Co) and tri-metallic (Fe-Co-Mo) catalyst supported on silica were synthesized by spray pyrolysis of Oryza sativa oil at 650 °C for precursor flow rate of 20 mL per hour under N_2 atmosphere. The characterization of the as-grown carbon nanostructure were analyzed by Scanning electron microscopy (SEM), High resolution transmission electron microscopy (HRTEM), XRD and Raman analysis. A high yield with good morphology grown over Fe-Co-Mo tri-metallic catalyst supported on silica at 650 °C is obtained and reported due to combined advantages of catalyst on support material.

Keywords: HRTEM; Multi-walled carbon nanotubes; SEM; Spray pyrolysis; Spectroscopic analysis; XRD analysis.

1. INTRODUCTION

Materials with novel properties are an integral part of modern society. Without these materials many technologies could not be developed. Carbon nanotubes (CNTs) are one such material with novel properties that can improve modern technology. CNTs consist of a rolled graphene sheet with diameters of nanometer size and length up to several micrometers (high aspect ratio of up to 132,000,000:1). Ever Since, Carbon Nanotubes discovered by Iijima in 1991, this advanced carbonaceous nanomaterials have attracted a great deal of interest from various scientific communities by virtue of exceptional electrical **(**Curan *et al.* 1998), mechanical properties and thermal properties (Rodney *et al.* 1995**)**. According to the number of rolled-up graphene sheets CNTs are classified as Single walled CNTs, Double Walled CNTs and Multi Walled CNTs. Various high temperature synthesis methods have been developed for CNTs such as electric arc discharge **(**Ebbesen and Ajayan, 1992), laser ablation **(**Guo *et al.* 1995**)**, chemical vapour deposition (CVD) **(**Kong *et al.* 1998**)**, spray pyrolysis **(**Yang *et al.* 2008**)** and low temperature synthesis route solvothermal **(**Wenzhong Wang *et al.* 2005**)** and hydrothermal **(**Tiana *et al.* 2011**)**. Among these methods, spray pyrolysis method has become an ideal manufacturing route for synthesizing CNTs. It is similar to CVD method with the only difference being the vaporization and pyrolysis of carbon source which occurs simultaneously in spray pyrolysis whereas in CVD method it is of two-step processes.

In the spray pyrolysis synthesis the selection of a metallic catalyst may affect the growth and morphology of the nanotubes. Widely used catalyst materials in carbon nanotubes synthesis are iron cobalt, nickel and molybdenum. Generally, the catalyst metal particles or their mixture are uniformly dispersed on supports. This support plays an important role in influencing the activity of the catalyst. Recently, there have been reports on supports such as alumina, silica, magnesia and zeolites for the synthesis of nanotubes.

Considering the environmental degradation decreasing fossil fuels to the cost of these petroleum based products is expected increase in the near future. Therefore, it is inevitable to look for alternative eco-friendly carbon precursors. Recently, there have been a few reports on the synthesis of CNTs from various plant derived carbon precursors such as Camphor (Kumar and Ando, 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 and Samdarshi, 2011), Pine oil *Jactropha curcas* oil (Karthikeyan and Mahalingam, 2010), Olive oil (Swati Sharma *et al.* 2012), *Cymbopogen flexuosus* oil (Mageswari *et al.* 2014), *Madhuca longifolia* (Karthikeyan *et al.* 2013), *Brassica Juncea (*Kalaiselvan *et al.* 2014; Kalaiselvan *et al.* 2016), *Helianthus annuus* oil (Angulakshmi *et al.* 2013), *Glycine Max* Oil (Angulakshmi *et al.* 2013) and *Oryza sativa* (Kalaiselvan *et al.* 2015).

In this article, we report the effect of catalyst composition on the growth of Multi-walled Carbon nanotubes from methyl esters of *Oryza sativa* oil by Spray pyrolysis method.

2. EXPERIMENTAL

The preparation of Fe, Fe-Co and Fe-Co-Mo supported on silica was conducted using wet impregnation method **(**Cassel *et al.* 1999**)**. 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 a nitrogen atmosphere. The temperature was raised from room temperature up to the desired growing temperature (650 ^{o}C) Subsequently, methyl ester of *Oryza Sativa* 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 all catalyst-support nanoparticls. 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 (m1-m0)/m0, where m1 and m0 are respectively, the final mass of the catalyst support with carbon deposit and the initial mass of the catalyst support. The amount of CNTs produced is proportional to the amount of catalyst used. 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 to heating and stirring was repeated three more times, each time allowing the heated oxidative slurry to stir for 30 min. 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 hrs.

2.1 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.

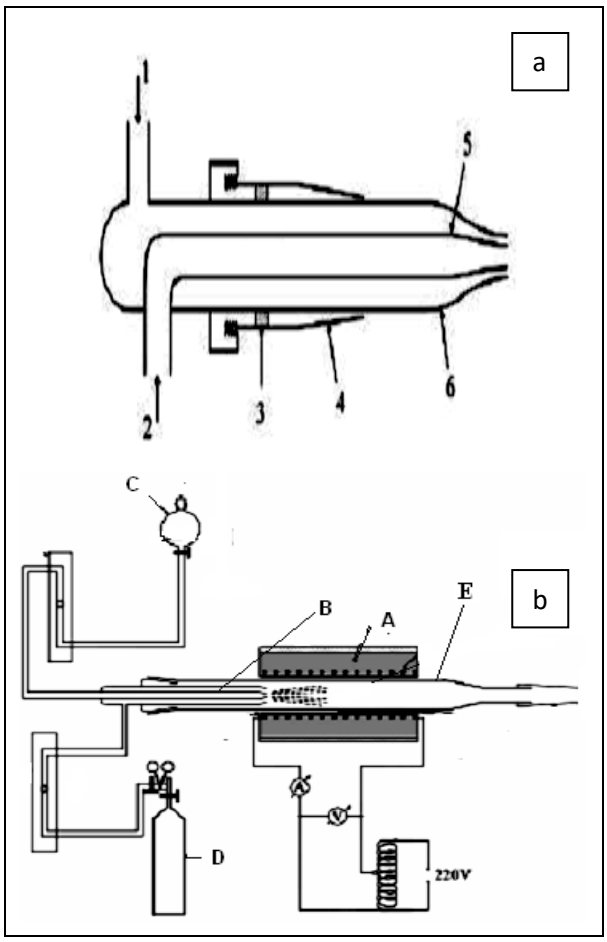

Fig. 1 (a): The schematic diagram of spray pyrolysis set-up. (A) Heating source, (B) Spray nozzle, (C) Carbon feed stock inlet, (D) Nitrogen gas, (E) Quartz tube. (b): Schematic diagram of the Sprayer 1. Gas inlet; 2. Solution inlet; 3. Tightening; 4. Polished glass-to-glass connection; 5, 6- Inner and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

3. RESULTS & DISCUSSION

Fig. 2 (a-c) illustrates the SEM images of the MWCNTs synthesized at different catalyst supported on silica. MWCNTs formed successfully at catalyst. Fig. 2a indicates very less amount of MWNTs with abundant amount of amorphous carbon were grown using *Oryza sativa* oil over Fe catalyst supported on silica at 650 °C by spray pyrolysis method. The fig. 2b. shows that the tubular nature of MWNTs grown over Fe-Co catalyst supported on silica were spiral in shape and covered with a dense outer layer of amorphous carbon and catalyst nanoparticles. The effect of silica supported Fe-Co-Mo catalysts on morphology of MWNTs synthesized from *Oryza sativa* oil at a flow rate of 20 mL per hour at 650 °C was studied. In Fig 2c the typical SEM image of MWNTs synthesized is shown. It is intriguing to note that densely populated good morphology of MWNTs

were grown over Fe-Co-Mo catalyst using *Oryza sativa* oil at 650 °C. The as-grown MWNTs have the diameter in the range of 34-40 nm.

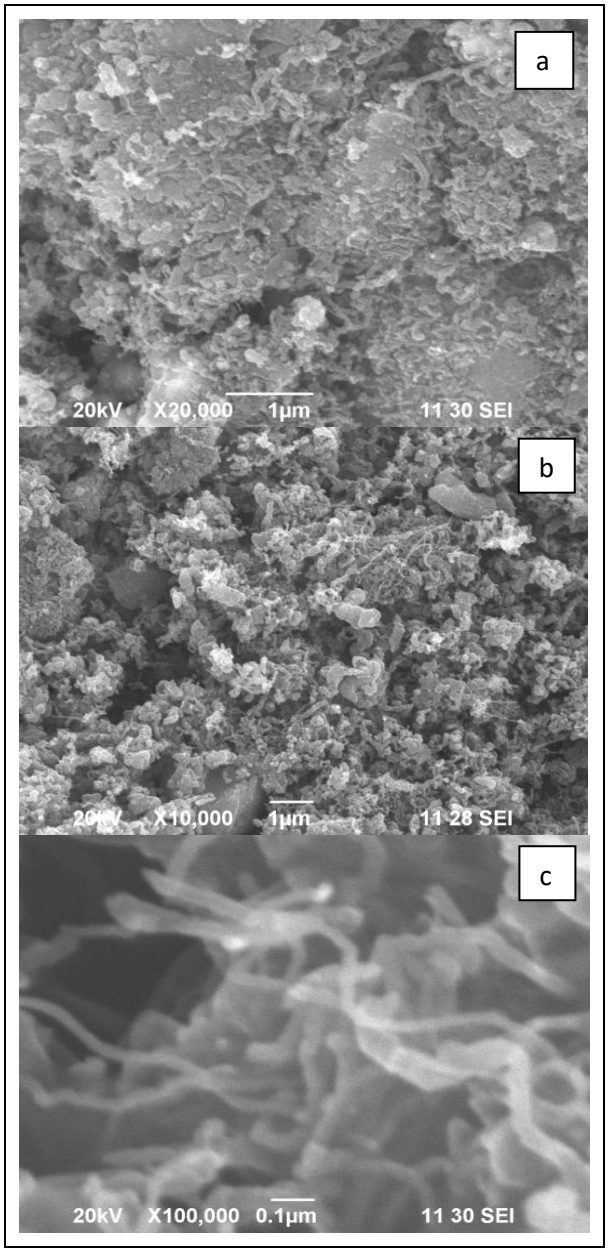

Fig. 2: SEM images of as- grown MWCNTs at different catalyst (a) Fe/Silica (b) Fe-Co/Silica (c) Fe-Co-Mo/Silica

We measured HRTEM images of the as-grown CNTs to investigate growth dependance on the three catalyst fig. 3a-c show HRTEM images of the MWNTs grown on Fe/Silica, Fe-Co/Silica and Fe-Co-Mo/Silica respectively. The good crystalline MWNTs were grown over Fe-Co-Mo supported on silica. Which indicates that tri-metallic combination produces good morphology MWNTs than that of mono and bi metallic combination this may be due to synergistic advantages of high catalytic decomposition over tri-metallic combinations supported on silica and promotional character of molybdenum.

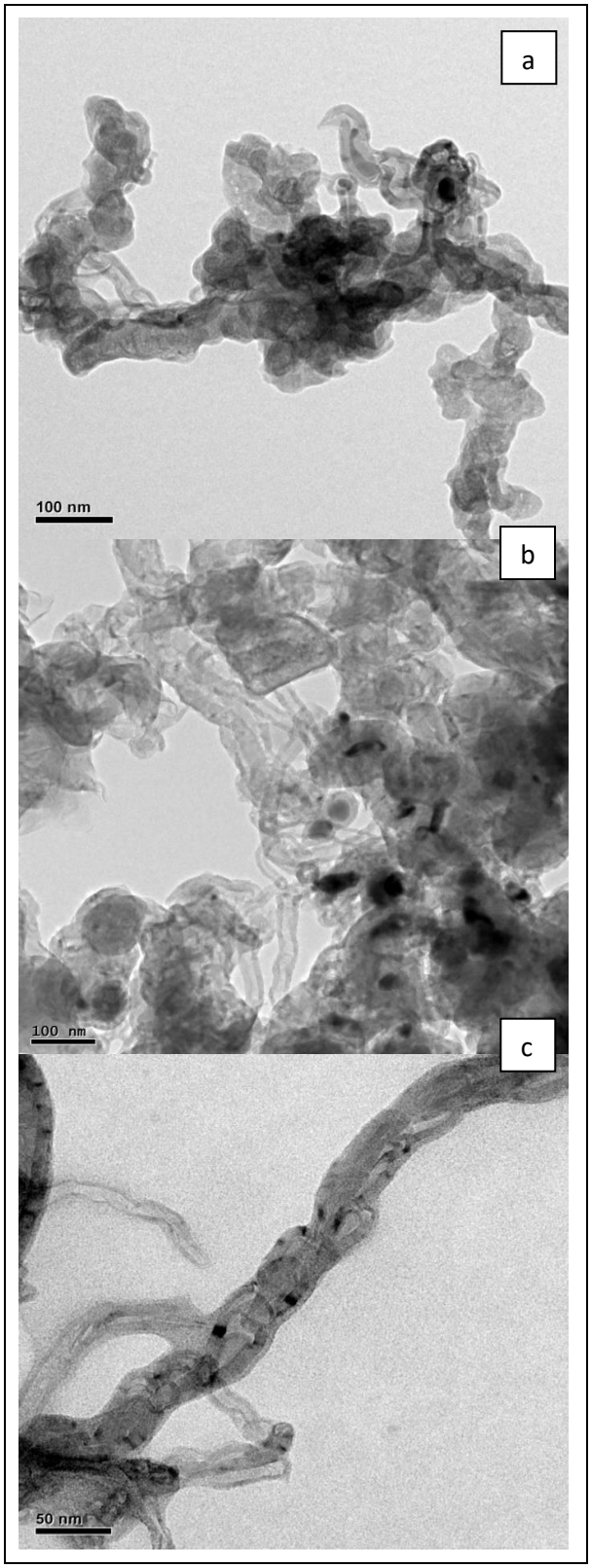

Fig. 3: HRTEM images of as- grown MWCNTs at different catalyst (a) Fe/Silica (b) Fe-Co/Silica (c) Fe-Co-Mo/Silica

We measured HRTEM images of the as-grown CNTs to investigate growth dependance on the three catalyst fig. 3(a-c) show HRTEM images of the MWNTs grown on Fe/Silica, Fe-Co/Silica and Fe-Co-Mo/Silica respectively. The good crystalline MWNTs were grown over Fe-Co-Mo supported on silica. Which indicates that tri-metallic combination produces good morphology MWNTs than that of mono and bi metallic combination this may be due to synergistic advantages of high catalytic decomposition over tri-metallic combinations supported on silica and promotional character of molybdenum.

Fig. 4. shows Raman spectra for the MWNTs grown over Fe/Silica, Fe-Co/Silica and Fe-Co-Mo/Silica respectively. All spectra show mainly three raman peaks at ~1345 cm^{-1} (D peak), at ~1580 (G peak) and at ~2685 (D' peak). The G peak indicates original graphitic features but the D peak has been considered as disorder features of graphitic sheets. The G and D peaks intensity ratio (I_G/I_D) on the raman spectra vary with the ordering of the graphitic structures and may be used to characterize carbonaceous materials. A higher I_G/I_D ratio indicates a higher degree of crystallinity of graphite-like materials (Park *et al.* 2001). In fig. 4 value of I_G/I_D for MWNTs grown on Fe, Fe-Co & Fe-Co-Mo supported on silica is 1.17, 1.53 and 1.94 respectively. It reveals that the degree of crystalline perfection of the MWNTs grown on tri-metallic combination higher than mono and bi-metallic combination which is very consistent with SEM and HRTEM images (Huang *et al.* 2002).

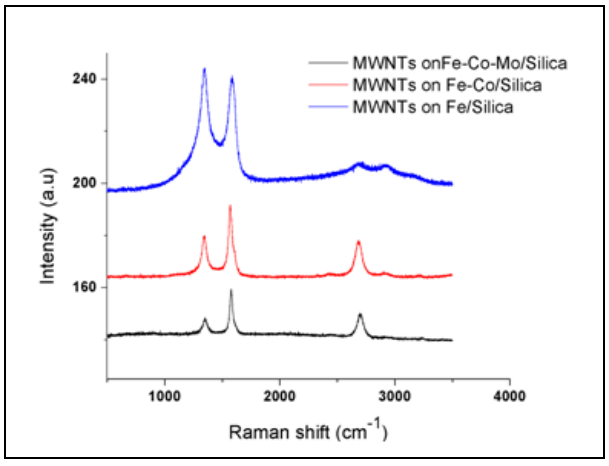

Fig. 4: Raman Spectra of as-synthesized MWCNTs at different catalyst using Spray pyrolysis method

Fig.5 shows XRD diffraction pattern for the MWNTs grown over Fe/Silica, Fe-Co/Silica and Fe-Co-Mo/Silica respectively. The XRD results of MWNTs on different catalysts confirm the graphitic nature of the MWCNTs peak at ~26 º C(002) and the interlayer spacing of 0.339 nm, similar to that of graphite (0.335nm), shows orderly stacking in the MWNTs. The peaks at ~44 º shows the presence of C(101) peak with layer distance of 0.203nm (Chatterjee *et al.* 2003).

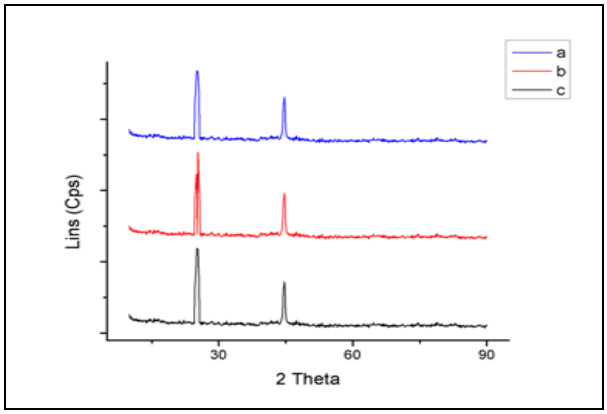

Fig 5: XRD pattern of as-synthesized MWCNTs at different catalyst (a) Fe/Silica (b) Fe-Co/Silica (c) Fe-Co-Mo/Silica

4. CONCLUSIONS

We accomplished the synthesis of MWCNTs by varying catalyst composition using methyl esters of *Oryza sativa* oil at 650 ºC under N_2 atmosphere. The structure and morphology were investigated by SEM, HRTEM, Raman spectroscopy and XRD. It was found that catalyst nanoparticles play important role in synthesis of MWCNTs. Fe supported on silica & Fe-Co supported on silica resulted in low yield and poor crystalline nanotubes. The high yield with good morphology grown over Fe-Co-Mo tri-metallic catalyst supported on silica at 650 °C may be due to synergistic advantages of high catalytic decomposition and promotional character of Molybdenum.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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