EFFECT OF SYNTHESIS TEMPERATURE ON THE GROWTH OF MULTIWALLED CARBON NANOTUBES FROM ZEAMAYS OIL AS EVIDENCED BY STRUCTURAL, RAMAN AND XRD ANALYSES

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ABSTRACT
Tubular structure and well dense multiwalled carbon nanotubes were formulated using Chemical vapor deposition techniques. In this experiment, multilayered carbon nanotubes were synthesized in the range of 450-750 °C using the catalytic decomposition of Zea mays oil over Fe and Mo supported on silica catalysts in a CVD reactor. The CNT production yield increased with increased temperature. The as-grown CNT products were characterized by Scanning electron microscopy, High resolution transmission electron spectroscopy, Raman spectroscopy, and X-ray diffraction. The purified CNT products composed of perfect graphene layers. The experimental results showed that multiwalled CNT properties were highly dependent on synthesis temperature changes. The optimum temperature of higher crystallinity and highest yield was observed at 650°C.

Keywords: Carbon nanotubes; CVD; Zeamays oil.

INTRODUCTION
Carbon nanotubes discovered by Sumio Iijima in 1991, have attracted much attention from the research community owing to their superior physical and chemical properties, such as high tenacity, high electron conductivity, superior surface property, excellent field emission property, metal and semiconductor properties. These properties of CNTs render them to have potential applications in the areas of electronic, energy storage, nanocomposites, and medical field. CNTs can be produced by different techniques; among them most widely used ones are arc discharge, laser ablation, and chemical vapor deposition methods. CVD method is relatively simple, economical, and easy to scale up. CVD has been widely used, owing to its potential to produce large amount of CNTs of high purity and the ease of controlling reaction conditions to produce the desired type of carbon nanostructures. As the CNT researchers, it is advisable to choose a hydrocarbon precursor from unconventional, new botanical hydrocarbon based CNT. It is found that fossil-based CNT production technology would not be sustainable due to unstable supply of oil resources. Our effort is mainly focused on identifying and using regenerative, environmentally clean and cheap natural products for synthesis of CNTs. One such a natural hydrocarbon product is Zea mays oil. Additionally, the catalyst is the key factor for CNT growth in CVD reactor. Transition metals such as Fe and Co supported catalysts and hydrocarbons such as methane, ethane, and acetylene were used in CCVD synthesis of CNTs. Silica supports has been investigated to determine the effect of the support on the size of metal nanoparticles and the diameter and structural characteristics of CNT products. However, the catalytic activity of the catalysts, the optimal parameter setting and thermodynamic behavior of CNT growth are complicated and yet to be realized. Combination of Fe and Co catalysts lead to formation of SWNTs with good quality and quantity. In this work, we tried to synthesis CNTs by catalytic decomposition of Zea mays oil, an eco friendly natural...
carbon precursor, over silica impregnated with Fe and Mo catalyst by chemical vapor deposition method. However the Multiwalled CNT from *Zea mays* oil by using CVD has not yet been reported.

**EXPERIMENTAL**

**Preparation of mixture of catalysts**

The preparation of Fe/Mo supported on silica was conducted using wet impregnation method. Fe/Mo catalyst supported on silica (SiO$_2$) particles (Fe: Mo: SiO$_2$ =1:0.4:4) were prepared as follows. Metal salts (Merck) i.e. Fe(NO$_3$)$_3$.6H$_2$O and (NH$_4$)Mo$_7$O$_{24}$.4H$_2$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 hours, removed from the furnace and ground in an agate mortar. The fine powders were then calcined for 1 hour at 450°C and then re-ground before loading into the reactor.

**Fabrication 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, *Zea mays* 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, 100ml per minute nitrogen gas flow and 0.5ml per minute precursor flow.

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$_2$O$_2$ was added to form oxidative slurry that continued to be heated and stirred for 30 minutes. The addition of HCl, H$_2$O$_2$, 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.

**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 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.

**RESULTS AND DISCUSSION**

In this experimental condition, generates new idea of alternative strategy to synthesize high-dense and tubular shape of nanotubes. The correspondence synthesis temperature changes with the characteristics of the CNT were observed. By increasing the synthesis temperature, the geometry and size of nanotubes
were affected in CNT nucleation-growth process. To examine the microstructure of CNT, HRTEM micrographs on the walls of CNTs that are grown on Fe/Mo catalysts, are illustrated in Figure 1.

Analyzing SEM results we find the average diameters of the CNTs grown on catalyst surface. At lower temperature (450°C), we got mostly amorphous carbon with low yield of MWNTs.

![Fig.-1a, b and c: SEM images of MWNTs grown at different Temperatures.](image)

This indicates that at lower temperature the catalyst activity is not enough for effective catalytic decomposition of *Zea mays* oil and thus little products were formed. Study of SEM images of the CNTs grown on catalyst surface at 450°C reveals that no clear growth of CNT formation was occurred even though we sent *Zea mays* oil at this temperature. No CNT growth at temperatures and lower than 550°C. The temperature at 650°C can be declared as a critical synthesis temperature due to the hydrocarbon source decomposes at this temperature. For the CNTs grown at 650°C in Figure 1b, we obtained carbon nanotubes with average diameter of 25nm and they were found to be longer. Yield of the Multiwalled carbon nanotube at this temperature was found to be 53%. The temperature is at 750°C and we observed low yield of MWNTs of larger diameter with amorphous carbon. Reaction temperature at 750°C and above deposition of carbon black on the inner side of the quartz tube has been visually observed. Formation of amorphous carbon and low yield of MWNTs may be attributed to the partial decomposition of the carbon precursor at higher temperatures. The diameter of MWNTs increases with increase in temperature due to the agglomeration of the catalyst particles. (Fig.-1c)
The Transmission electron microscopy was used to measure the dimensions and size of the resulting nanotubes. The sheets of graphite are orderly arranged in concentric cylinders i.e., the tubular structure of nanotubes, is clearly seen in the TEM images in agreement with XRD pattern. It can be observed from Figure-2 in which the nanotubes, formed are of Multiwalled type, and most graphene layers grow perpendicularly to the growth axis of the tubes. The HRTEM images in Figure-2b suggest that as-grown nanotube with an average outer diameter of about 30nm whereas their length is very difficult to measure, varying roughly between several and ten micrometers. As-grown carbon nanotubes on Fe/Mo catalyst supported on silica at 750°C in Figure-2c, we find that this type of nanotube exhibits a larger diameter. Both SEM and HRTEM results provided us with the growth mechanism of carbon nanotubes. The growth mechanism of carbon fibers was first predicted by Baker et al who assumed that this growth mechanism constituted the dissociation of hydrocarbon gases by the catalyst material, and then carbon atoms would diffuse into the catalyst nanoparticles, following which they would saturate, precipitate, and end up with carbon nanotubes while cooling the system down to room temperature. According to our results, we observed that the catalyst nanoparticles are at the tip of the carbon nanotubes, and so-called tip growth mechanism, of which results were very compatible with the literature. A XRD measurement was carried out using Cu K radiation to examine the structure of the CNTs and the resulting 2θ scan is shown in Figure-3. The peak at 2θ = 26.164° 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.
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 Figure-4. 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 sp² and sp³ amorphous carbon. In CNTs, this band is activated from the first-order scattering process of sp² carbons by the presence of in-plane substitutional heteroatoms, vacancies, grain boundaries, or other defects, and by finite-size effects. All of these characteristics lower the crystal symmetry of the quasi-infinite lattice. When observed in MWNTs the D band has been generally viewed as a defect in the tubes. The quality of a sample has often been evaluated using the D/G band intensities. G-band occurs at 1585.39 cm⁻¹ and D-band appears at 1350.18 cm⁻¹. For high-quality samples without defects and amorphous carbon, the I_D/I_G ratio is often less than 2 %. The I_D/I_G ratios were calculated to estimate the variation of CNT crystallinity with Fe/Mo catalyst. I_D/I_G ratio was found to be 0.86. This reveals that the trend of CNT crystallinity varies with synthesis temperature. Our results indicated that the best crystallinity was shown by CNT grown on Fe/Mo catalyst at synthesis temperature of 650 °C. There was no lower frequency radial breathing mode peaks detected for all samples which indicate no single-walled CNT was produced.
CONCLUSION
Multiwalled carbon nanotubes were obtained by chemical vapor deposition of Zeamays oil an unconventional natural precursor, as a carbon source on Fe/Mo supported on silica catalyst. Based on the result, the formation of MWCNT has been optimized at 650 °C synthesis temperature which is in good agreement with SEM, HRTEM, Raman and XRD analyses. The experiment has succeeded with the lowest I_D/I_G ratio of about 0.86 at 650 °C. The highest yield of 53% was obtained at the same temperature. As a result, synthesis temperatures were strongly affected by the growth of MWCNT.

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