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SYNTHESIS AND RAMAN CHARACTERIZATION OF MULTIWALLED CARBON NANOTUBES BY CATALYTIC CHEMICAL VAPOUR DEPOSITION

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ABSTRACT

Catalytic chemical vapour deposition (CCVD) was used to synthesize CNTs, on silica substrate using xylene as carbon precursor and ferrocene as catalyst source. The carbon nanotubes are multiwall nanotubes which have been found to grow in bundles with CNTs within the bundles growing in one direction in a zig zag manner. The inner diameter of the tubes is found to decrease with total (outer) diameter of the CNTs. These CNTs have been characterized using SEM, XRD, TEM and Raman spectroscopy. The results obtained from these techniques have been interrelated.

Key words*: carbon nanotubes, microstructure, raman microscopy, chemical vapour deposition*

INTRODUCTION

Carbon Nanotubes were first discovered in cathode deposits obtained in arc evaporation of graphite in 1991 by Iijima [1]. The techniques widely used for the synthesis of CNTs are arc discharge, laser ablation and catalytic chemical vapour deposition of certain hydrocarbons. Among these methods, catalytic chemical vapour deposition technique (CCVD) is considered more suitable in terms of purity, control of tube size and large scale production. CCVD synthesis of CNTs is carried out by the pyrolysis of hydrocarbons over nanoparticles of a catalyst such as iron, cobalt or other transition metals dispersed over a support [2-5] or finely dispersed in the reactor, floatation technique. The presence of catalyst nanoparticles are essential for the formation of nanotubes and to control the diameter of nanotubes to some extent [6]. Not only the tube diameter, but even the microstructure of the tubes is controlled by the type of precursor, catalytic particle and the processing conditions. Different authors have used different techniques. In the present work, multiwall CNTs have been synthesized by CCVD technique using pyrolysis of Xylene as carbon source and iron particles as catalyst on silica powder substrate and subsequent characterization by SEM, TEM, X-ray Diffractometer and Raman Microscope.

MATERIALS AND METHODS

Multiwalled carbon nanotubes were synthesized by floating catalyst chemical vapour deposition method. The pyrolysis setup used for the synthesis of MWNTs is shown schematically in Fig. 1. The quartz boat containing the catalyst support, silica powder, was placed at the pyrolysis zone of the horizontal tube reactor. The temperature of the pyrolysis zone was monitored using a programmable temperature controller CHINO KP1000. The reactor was connected to a gas delivery system, mass flow controller NISHKO μCS3000. Mixture of Ar and H_2 of the desired composition was introduced at controlled rate. The furnace was heated to a temperature of 800^{o}C. On attainment of the desired reaction temperature, the liquid hydrocarbon, xylene, containing 1 wt% of ferrocene was injected in the reactor along with Ar containing 10% H_2. After the reaction, the furnace was allowed to cool to room temperature under inert atmosphere. The growth and structure of the CNTs were studied using SEM, TEM, X-ray Diffractometer and Raman Microscope.

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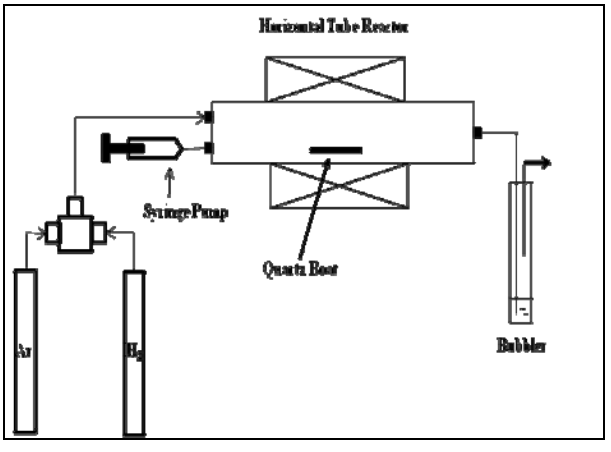


Fig. 1 Chemical Vapour Deposition Setup

Since the synthesized CNTs may contain large amount of impurities such as amorphous carbon, metal and silica particles, purification was carried out using acid cleaning method, by treating the CNTs with 50% HF solution for 20 hours for the removal of Silica particles, subsequently the CNTs were treated with 1N HCl solution for 20 hrs followed by washing with distilled water [7-13]. The washed CNTs were dried at 100^{o}C to remove moisture.

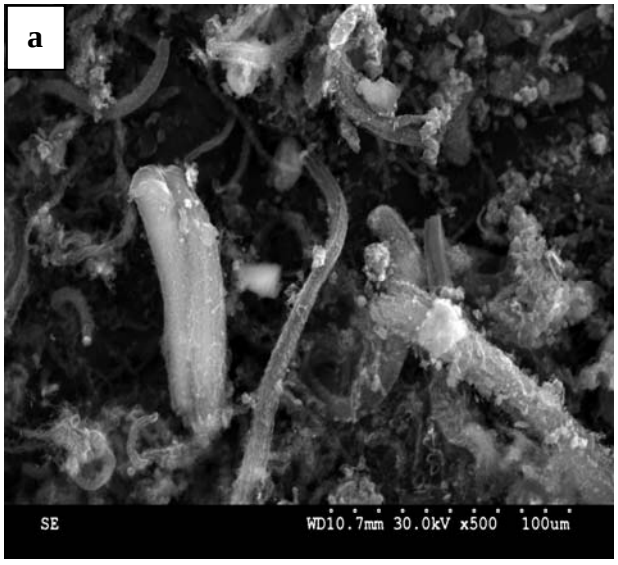
The percentage carbon yield was determined by the change in weight. The CNTs were observed under SEM HITACHI S-3000N operated at 30 kV to study the growth of the CNTs, morphology as well as the microstructure. TEM Philips, Technai-20 operated at 200kV was used to examine the tubular nature of the CNTs and impurities, if present. Raman spectra were taken with Renishaw inVia Raman microscope using Argon ion laser at 514nm excitation.

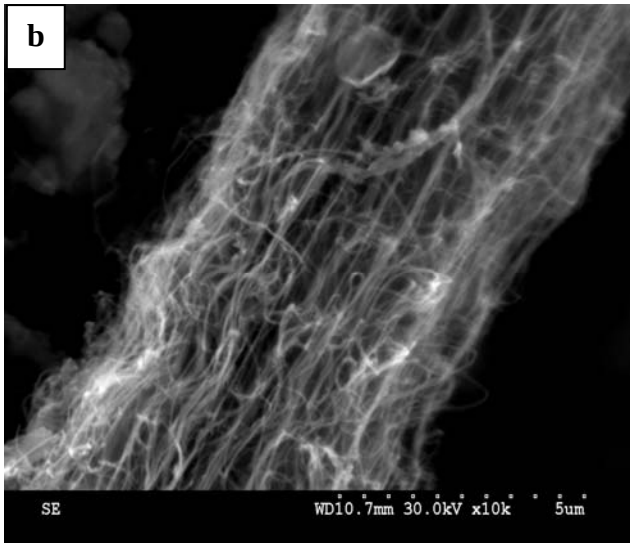
RESULTS AND DISCUSSION

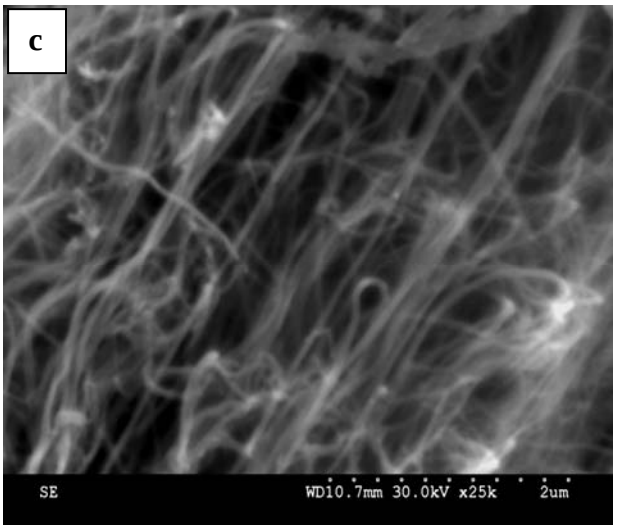
Fig. 2 shows the SEM micrographs of the CNTs. As seen from Fig. 2 (a) carbon nanotubes are grown in bundles. Along with nanotube bundles, growth of carbon particles can also be seen in Fig. 2 (a) The bundles are oriented in different directions. This is because the preferred crystal directions of the catalysts required for growth of CNTs are oriented in

different directions. In catalyst floatation technique, it is difficult to have all the crystal planes oriented in one particular direction. Fig. 2 (b) shows that even within a nanotube bundles, the individual nanotubes are not perfectly aligned. These, though grow in one direction, posses wavy nature of growth. This is also evident from Fig. 2 (c) and 2 (d) which show that some of the tubes coil back. This is due to interruption of the growth by flowing gases as well as Van der Waal forces between the growing tubes.

Fig. 3 shows TEM micrographs of the purified CNTs. TEM micrographs reveal that the CNTs are multiwall nanotubes, with outer diameter ranging from 13- 20 nm. The wall thickness ranges from 2-5 nm. No tube exhibit catalyst embedded in the tubes. This shows that the acid leaching technique removes all the metallic impurities from the nanotubes. Another characteristic TEM observation is that the inner diameter of the tube decreases with increase in outer diameter. This suggests that the outer walls are formed first and with time and concentration, the inner walls start growing.







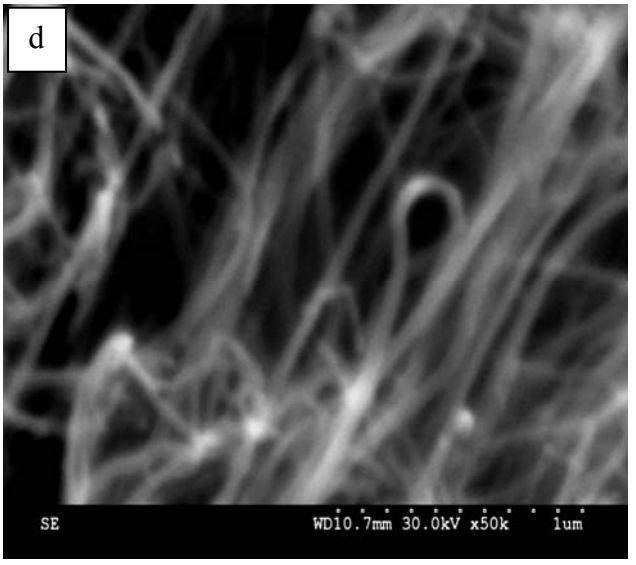


Fig. 2 (a - d): SEM micrographs show the dense growth of the CNTs

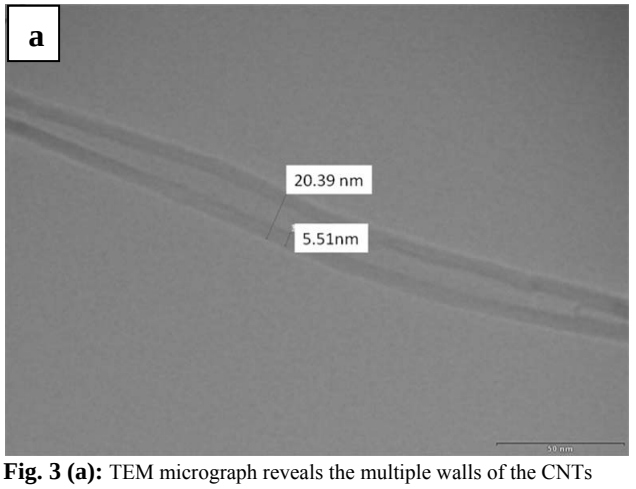
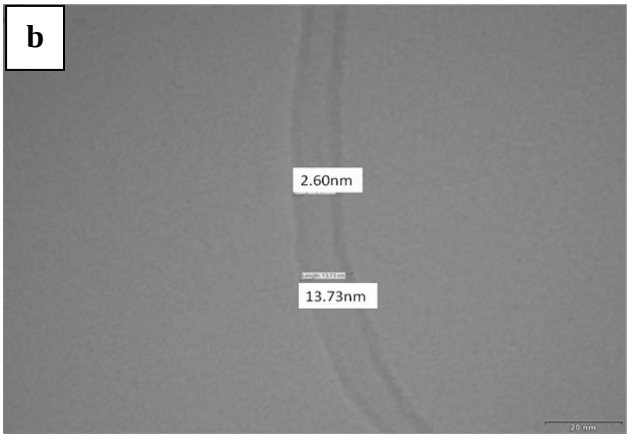


Fig. 3 (a): TEM micrograph reveals the multiple walls of the CNTs



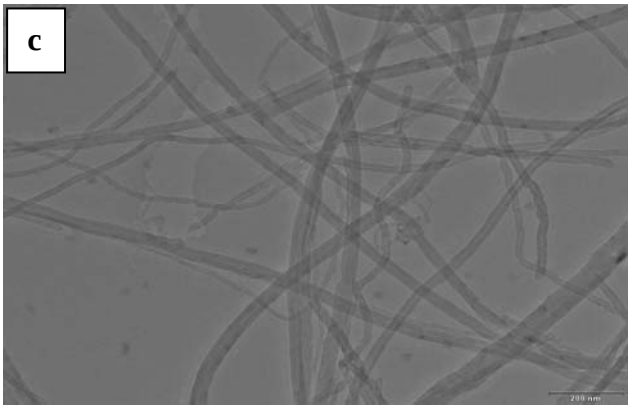


Fig. 3 (b, c): TEM micrographs reveal the multiple walls of the CNTs

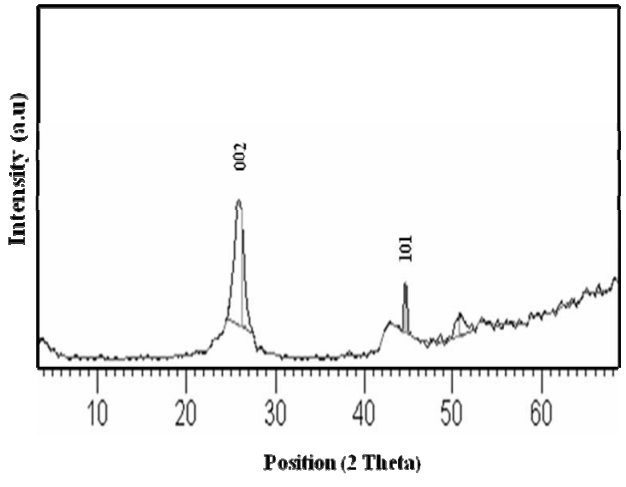


Fig. 4: X-Ray diffractogram of the CNTs.

Fig. 4 shows XRD of CNTs. As evident from the Fig. CNTs related peaks are detected at $2\theta=26.25^{o}$ and 44.63^{o} which represent graphite (002) and (101) peaks respectively.

Micro-Raman Spectroscopy is a powerful technique for learning the graphitic structure of the CNTs. The Raman spectra of carbon based materials mainly exhibit two main first order peaks assigned to G (graphitic) band and D (disordered carbon) bands. Fig. 5 shows Raman spectra of CNTs.

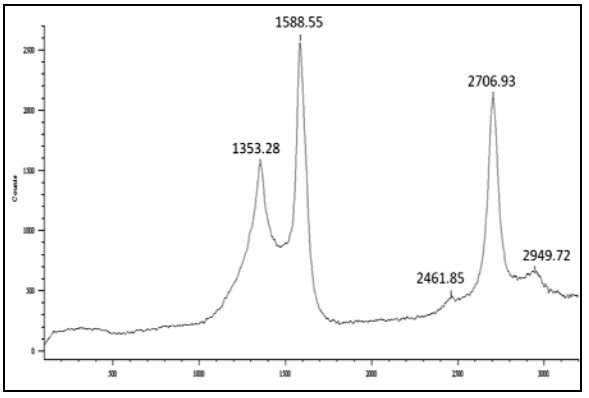


Fig. 5: Raman spectra of MWNTs

It shows D-band at 1353.28 cm^{-1}, due to scattering from a defect which breaks the symmetry of the graphene sheet. Raman band at 1588.5 cm^{-1} is due to the G-band in CNTs basically due to the vibrational mode corresponding to the movement in the opposite directions of the two neighboring carbon atoms in a graphite sheet. The G-band is closely related to vibration in all sp^2 carbon materials. The Raman spectra of multiwalled CNTs exhibit two peaks corresponding to D-band and G-band of polycrystalline graphitic structures. Ratios of intensities of the D-band to G-band have been used as an indicator of the amount of disorder within the carbonaceous materials and nanotubes in particular. The second order Raman spectra, also consists of a dominant D* line, seen at around 2706.93 cm^{-1}, which is the second order of the D line 1353.28 cm^{-1}. The D* peak is unique for multiwalled carbon nanotubes. Except the strong D* band, two additional weak bands are observed, one at 2949.72 cm^{-1} which is thought to arise from a combination of the Raman modes at 1353.28 cm^{-1} and 1588.55 cm^{-1}, the other weak band appears at 2461cm^{-1} is assigned to $G+A_{2u}$ modes.[14-21].

The I_D/ I_G ratio as calculated from the Raman spectra of the CNTs grown in the present studies is 0.41 which is a mid ordered graphitic structure. The XRD spectra and TEM observations also show that the grown carbon nanotubes are mid ordered graphitic in nature. This shows that the observations made from Raman studies are complimentary to the observations made by TEM studies.

CONCLUSION

The present studies on growth of carbon nanotubes using Xylene as carbon sources and Ferrocene as floating catalyst show that the carbon nanotube bundles get oriented in different directions corresponding to the orientation of the crystal planes of the catalyst. Further, the characterization techniques, TEM, XRD and Raman spectra are complementary characterization techniques and hence Raman spectra can be conveniently used to study the microstructure of CNTs.

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