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

L. M. Manocha*, Arpana Basak and S. Manocha

Department of Materials Science, Sardar Patel University, Vallabhbhabh Vidyanagar

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 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 H2 of the desired composition was introduced at controlled rate. The furnace was heated to a temperature of 800°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% H2. 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.

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. 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 2θ=26.25° and 44.63° 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.

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 sp² 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 2461 cm⁻¹ is assigned to G+A₂u 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.

ACKNOWLEDGEMENT

The work was done under UGC Centre for Advanced Studies program. The authors wish to thank UGC for the grant under this program. TEM and XRD studies were done at SICART. Their help is gratefully acknowledged.
REFERENCES

GUIDELINES FOR CONTRIBUTORS


The soft copies of regular (full-length) research papers (not exceeding 15 typed pages), prepared as per the file format shown below may be submitted for publication through e-mail to Prof. T. V. Ramana Rao, Managing Editor (spu.prajna@gmail.com) OR to a Member of the Editorial Board who represents the author’s broad research area with a cc to the Managing Editor latest by August 31, 2011.

Each manuscript must be accompanied by a statement that it has not been published elsewhere and that it has not been submitted simultaneously for publication elsewhere.

Review process: Submitted papers are peer-reviewed by two to three independent reviewers after approval by the Editorial Board. Authors are encouraged to suggest three names of expert reviewers with their e-mail IDs, but selection remains the prerogative of the Editorial Board.

Articles of the following categories are also considered for publication in PRAJNA:

Short Communications are limited to a maximum of two figures and one table. They should present a complete study that is more limited in scope than is found in full-length papers. The items of manuscript preparation listed above apply to Short Communications with the following differences: (1) Abstracts are limited to 100 words; (2) instead of a separate Materials and Methods section, experimental procedures may be incorporated into Figure Legends and Table footnotes; (3) Results and Discussion should be combined into a single section.

Review Articles intended to provide concise in-depth reviews of both established and new areas and summarize recent insights in specific research areas within the scope of PRAJNA are solicited by the Editorial Board from leading researchers. The manuscript of this category should be limited to 5,000 words with an abstract of no more than 250 words, a maximum of 5 tables and figures (total), and up to 50 references. Word count includes only the main body of text (i.e., not tables, figures, abstracts or references).

Commentaries call attention to papers of particular note and are written at the invitation of the Editorial Board.

Perspectives present a viewpoint on an important area of research and are written only at the invitation of the Editorial Board. Perspectives focus on a specific field or subfield within a larger discipline and discuss current advances and future directions. Perspectives are of broad interest for non-specialists and may add personal insight to a field.

Letters are brief comments that contribute to the discussion of a research article published in the last issue of PRAJNA. Letters may not include requests to cite the letter writer's work, accusations of misconduct, or personal comments to an author. Letters are limited to 500 words and no more than five references. Letters must be submitted within 3 months of the publication date of the subject article.

Also announcement of forthcoming Seminars / Conferences / Symposia / Workshops etc. will be considered for publication in PRAJNA.

File format for soft copies:
Texts (should be of Times New Roman with 9 point for Abstract and 11 point for other matter) and Tables, if any, must be saved in *.doc (Word) or *.rtf (rich text) format, graphs in Excel and for illustrations (diagrams, maps, drawings, etc.), the TIF format (300 dpi minimal resolution) is the most appropriate (*.TIF or *.JPEG extension).

Instructions for preparation of manuscripts:
1. The paper should be written in English and neatly typed with double spacing.
2. The title of the paper and the name(s) of the author(s) be in capital letters. The name of the institution be given in small letters below the name(s) of the author(s).
3. The Abstract of the paper, in not more than 150 words, should be provided on a separate page along with 4-6 keywords.
4. The sub-titles, e.g. INTRODUCTION, should be written in capital letters.
5. Displayed formulae, mathematical equations and expressions should be numbered serially. Table should be with a
title in addition to a serial number for it.
6. Photographs / Figures should be original with good contrast so as to be in a form suitable for direct reproduction /
scanning.
7. Footnotes are not normally allowed, except to identify the author for correspondence.
8. All figures must be numbered serially as they appear in the text, and their legends / captions should necessarily be
provided.
9. References should be numbered in brackets [ ] in the order of appearance in the text. All the references in the
bibliographic list must correspond to in-text references and vice versa. Abbreviated periodical titles should follow
standard subject Abstracts. Names which are not listed by any standard subject indexing organizations should be
spelled out in full.
10. All references should be clear and follow the examples below:

   Periodical articles

   Books
   399.

   Chapters from a book

   Thesis or other diplomas
   Dr. R. M. L. Avadh University, Faizabad, India.

   Conference proceedings

   Online documentation
   Information Website: http://plantphys.info/index.html.

Note:
Manuscripts prepared faithfully in accordance with the instructions will accelerate their processing towards
publication; otherwise it would be delayed in view of their expected re-submission.

For and on behalf of Editorial Board, PRAJNA

Prof. T. V. Ramana Rao
Managing Editor, PRAJNA
B R Doshi School of Biosciences,
Satellite Campus, Vadatal Road,
Sardar Patel University,
VALLABH VIDYANAGAR
Gujarat – 388120
Phone: (Lab): 02692-234412 Extn. 111
Mobile: 98254 38147
Fax: 02692-237258 /236475
e-mail: spu.prajna@gmail.com
Website:www.spuvvn.edu

NOTE: This information may be kindly circulated among your colleagues.