

Effect of irradiation on doped multiwalled carbon nanotubes for biological applications

P. KUMARESAN

Nano Science Research Centre, Department of Physics, Thiru.A.Govindasamy Government Arts College, Tindivanam-604 002, Tamil Nadu, India

Ion irradiation and the inevitable damage it creates has long been a topic of great interest in the field of medicine. Irradiation of MWNTs with diameters of about 10 nm by 3 keV Ar ions followed by X-ray photoelectron spectroscopy and TEM probing demonstrated that the bombardment resulted in the appearance of carbon dangling bonds, which can be understood in terms of single and multi atom vacancies[2]. A gradual amorphization of the carbon network was reported, and for maximum irradiation doses used (more than 10^{19} ions/cm²) MWNTs with originally hollow cores transformed to nano-rods composed of amorphous carbon, but the irradiation did not change the sp² hybridization of carbon to sp³ hybridization. In particular, the effect of selecting a particular ion during irradiation, determines the mobility of the material. The critical bottlenecks in drug discovery may be overcome by using arrays of CNT sensors [3] and current information technology solutions for identification of genes and genetic materials for drug discovery and development. This investigation will be carried out to study the effect of swift heavy ion irradiation on the surface morphology of f-MWCNTs.

(Received January 6, 2011; accepted February 17, 2011)

Keywords: MWCNTs, CVD, TEM, Functionalized CNTs, Drug release efficiency

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, significant progress has been achieved for both understanding the fundamental properties and exploring possible biological applications [4]. The amorphization of MWCNTs by 3 keV Ar ions with a much lower irradiation dose of $4 - 10^{16}$ ions/cm² was also reported. Spatially localized Ar ion irradiation (with doses up to 10^{16} ions/cm²) of individual MWCNTs deposited on SiO₂ substrates was used to create a defective region which worked as a potential tunnel barrier for electrons in the MWCNT. The impact of low-dose (10^{12} ions/cm²) ion irradiation on bundles of MWCNTs was experimentally studied.

The bundles were irradiated with an 500-eV Ar ion beam followed by transport measurements. Inorganic hollow MWCNTs have attracted great interest in nanomedicine because of the generic transporting ability of porous material and a wide range of functionality that arises from their unique optical, electrical, and physical properties [5]. In this paper, we describe recent developments of hollow and porous inorganic nanomaterials in nanomedicine, especially for drug delivery [6].

The CVD technique produces high quality MWNTs and MWNTs do not need a catalyst for growth, while SWCNTs can only be grown in the presence of a catalyst. MWNTs can be obtained by controlling the pressure of inert gas in the discharge chamber and the arcing current. In the case of MWCNT growth by the CVD method [7], the by-products are polyhedron-shaped multi layered graphitic particles. They applied a potential of 18 V and a

helium pressure of 500 torr. Analysis by transmission electron microscopy (TEM) revealed that the nanotubes consisted of two or more carbon shells.

In the CVD method, CNTs are synthesized by taking hydrocarbons (the commonly used sources are methane, ethylene, and acetylene) and using an energy source, such as electron beam or resistive heating, to impart energy to them. The energy source breaks the molecule into reactive radical species in the temperature range of 550°–750°C. These reactive species then diffuse down to the substrate, which is heated and coated in a catalyst (usually a first-row transition metal such as Ni, Fe, or, Co), where it remains bonded. As a result, the CNTs are formed. Synthesized microtubules of up to 50 μm length of CNTs by catalytic decomposition of acetylene over iron particles at 700° C. Iron nanoparticles (embedded in mesoporous silica) as catalyst for large-scale synthesis of aligned CNTs [8]. The tubes were 50 μm long and well graphitized. They used acetylene as the hydrocarbon and cobalt as the catalyst at a temperature of 700°C. MWCNTs prepared by this process had an average diameter of 20–30 nm and consisted of 26 layers.

Mechanically, CNTs are currently the strongest known fibers. Determination of their strength and toughness is very important for applications. They are quite stiff and exceptionally strong because the carbon-carbon bond observed in graphite is one of the strongest in nature. Elastic properties of CNTs can be obtained from experiment by assuming them structural members. They estimated the Young's modulus of isolated CNTs by measuring the amplitude of their intrinsic thermal vibrations in the TEM [9].

2. Results and discussion

2.1 Characterization Studies

2.1.1 X-ray Studies

The X-ray diffraction patterns of f-MWNTs are similar to the MWNTs. This indicates that the crystallinity and morphology of the MWNTs are preserved during the functionalization of CNTs with potassium permanganate using PTC. Fig. 1 shows the XRD pattern of the MWNTs, in which the (002) peak emerges at around 26° , corresponding to an inter-planar spacing of 0.341 nm, which is little greater than that of f-CNTs of about 0.334 nm. It is confirmed that the graphite-like structure in purified MWNTs. Functionalized MWNTs still have the same cylinder wall structure as raw MWNTs and the inter-planar spacing of functionalized samples remains the same.

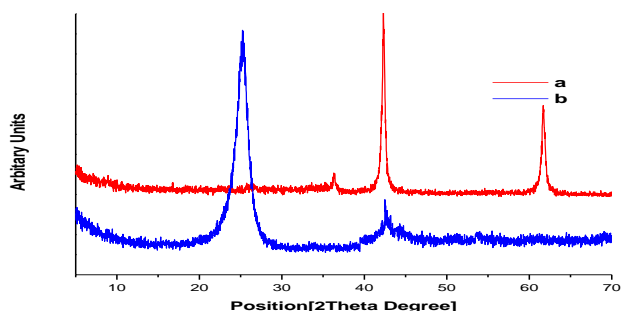


Fig. 1. X-ray diffraction patterns (a) f-MWNTs (b) MWNTs

2.1.2 FT-IR analysis

The oxidation results of MWCNTs were determined by the Fourier Transform Infrared Spectroscopy (FT-IR). After the oxidation of f-MWCNTs three new peaks appeared on FT-IR spectrum of f-CNTs (fig. 2). It shows a very broad and intense absorption peak at 3370 cm^{-1} due to intermolecular H-bonded O-H stretch. The small and less intense peak at 1623 cm^{-1} is associated with the absorption frequency of the olefinic double bond in conjugation with carbonyl group. The peak at 1384 cm^{-1} is due to O-H bending deformation in -COOH groups.

The more intense and very sharp peak seen at 2362 cm^{-1} was due to non terminal C=C stretching present MWCNT framework. This peak is completely disappeared in the FT-IR spectrum of purified MWCNTs. Therefore, it proves that the C=C groups in MWCNTs are disappeared and they are readily bonded with carboxylic acid (-COOH) groups and hydroxyl (-OH) groups. Thus the generation of -OH and -COOH groups on MWCNTs due to purification was confirmed.

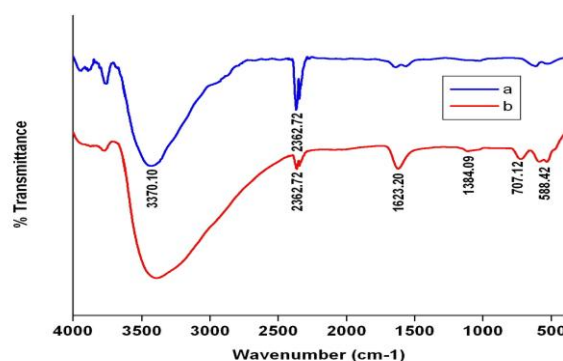


Fig. 2. FT-IR spectroscopy of a) raw and b) Functionalized MWCNTs

2.1.3 TEM analysis

The TEM images of as-synthesized MWCNTs are displayed in Fig. 3, indicate the graphene layers which constitute the wall of the nanotubes were straight and little defects. It is worth noting that the MWCNTs produced by the catalytic decomposition of acetylene at the Fe-Mo/MgO catalyst surface diffuse rapidly and finally assemble into an ordered structure, localized near the catalyst surface [10]. The initiation of a graphitization process is increased by the Fe sub-particles are present in catalysts [11]. It is possible to see lots of regular shapes and the regions of high-density tangles nanotubes.

The MWCNTs are often decorated with agglomeration of nanoparticles. It should also be noted that less amorphous carbon was found on the outer surface of the CNTs. TEM micrographs of MWCNTs after the required purification process and functionalized by KMnO_4 using PTC were presented in Fig.3. The Fe-Mo/MgO catalyst retains the crystallinity and shapes of MW CNTs after purification with acids. Moreover, no amorphous carbon was observed on these nanotubes. It is also clear from the images that the CNT end cap, which is present in the TEM image of CNTs, is not present in the TEM image of f-MWCNTs.

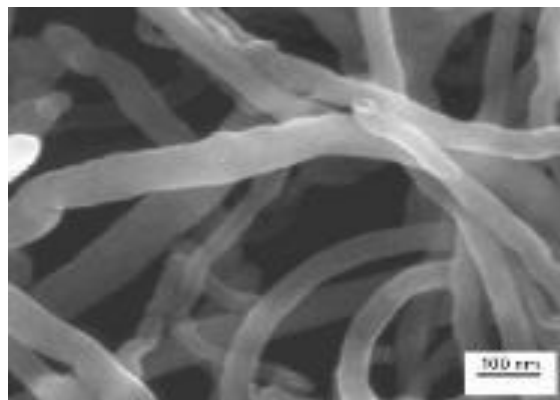


Fig. 3. TEM image of as-synthesized MWCNTs

Ion irradiation offers a unique way to investigate defect structures of MWCNTs and their influences on MWCNTs various properties. The amount of defects created in the MWCNTs was correlated with the nuclear and electronic energy loss of ion beams. Ion irradiation introduces a wide range of defects in a controlled manner and is used to tailor material properties. Ion beam irradiation of carbonaceous materials is a powerful technique to obtain non-hydrogenated amorphous carbon (a-C) and new metastable carbon structures. The irradiation-mediated improvements in thermal stability of MWCNTs under a few MeV H and He ions. The predominant methods to deliver drugs are oral and injection, which has limited the progress of drug development. Market forces are also driving the need for new, effective drug delivery Methods. It is estimated that drug delivery will account for 49% of all pharmaceutical sales by 2011. Meanwhile, upcoming patent expirations are driving pharmaceutical companies to reformulate their products. New drug delivery methods may enable pharmaceutical companies to develop new formulations of off patent and soon-to-be off patent drugs.

3. Conclusion

A highly effective drug delivery system based on functionalized SWCNTs has been developed that overcomes the limitations of other carbon nanotube-based systems. A highly effective drug delivery system based on functionalized SWCNTs has been developed that overcomes the limitations of other carbon nanotube-based systems. In addition, irradiation of higher doses of Li⁺ ion damages the lattice effectively and the crystalline quality of the irradiated region. Based on a number of pertinent control experiments it is possible to conclude that the overall nanoscale drug system is more selective and effective than the free drug and it should result in reduced general toxicity and hence reduced side-effects in patients and also allow a lower amount of the drug to be applied. Most drugs have been formulated to accommodate the oral or injection delivery routes, which are not always the most efficient routes for a particular therapy. New biologic

drugs such as proteins and nucleic acids require novel delivery technologies that will minimize side effects and lead to better patient compliance.

Acknowledgements

We gratefully acknowledge financial supports from the University Grants Commission [UGC-Major Research Project, F.No.38-18/2009 (SR)], New Delhi.

References

- [1] A. Bianco, K. Kostarelos, C. D. Partidos, M. Prato, *Chem Communications* **28**, 571 (2005).
- [2] M. Prato, K. A. B. Kostarelos, *Acc Chem Res* **41**, 16 (2008)
- [3] P. Debbage, *Curr Pharm Des* **15**,153 (2009).
- [4] D. J. Pan, J. L. Turner, K. L. Wooley, *Macromolecules* **37**, 7109 (2004).
- [5] D. Cai, C. A. Doughty, T. B. Potocky, F. J. Dufort, Z. Huang, D. Blair, et al. *Nanotechnology* **18**, 365101 (2007).
- [6] Z. Liu, X. Sun, N. Nakayama-Ratchford, H. J. Dai, *ACS Nano* **1**, 50 (2007).
- [7] M. H. Cato, F. D'Annibale, D. M. Mills, F. Cerignoli, M. I. Dawson, E. Bergamaschi, et al. *J Nanosci Nanotechnol* **8**, 2259 (2008).
- [8] N. W. S. Kam, M. O'Connell, J. A. Wisdom, H. J. Dai, *Proc Natl Acad Sci* **102**,11600–5. 2005
- [9] B. Kang, D. C. Yu, S. Q. Chang, D. Chen, Y. D. Dai, Y. T. Ding, *Nanotechnology*; **19**,375103 (2008).
- [10] B. Z. Tang, H. Y. Xu, *Macromolecules*; **32**, 2569 (1999).
- [11] A. Abarrategi, M. C. Gutierrez, C. Moreno-Vicente, M. J. Hortiguera, V. Ramos, J. L. Lopez-Lacomba, et al. *Biomaterials*; **29**, 94 (2008).

*Corresponding author: logeshkumaresan@yahoo.com