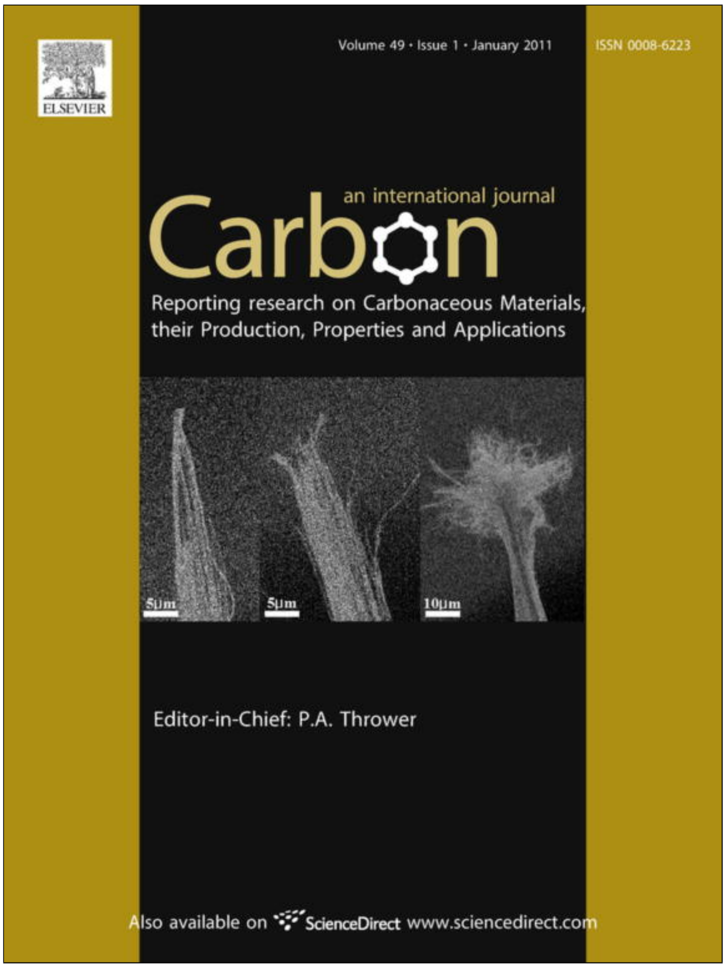
ELSEVIER
Volume 49 • Issue 1 • January 2011
ISSN 0008-6223
an international journal
Carbon
Reporting research on Carbonaceous Materials, their Production, Properties and Applications
5μm
5μm
10μm
Editor-in-Chief: P.A. Thrower
Also available on ScienceDirect www.sciencedirect.com

Structural changes in multi-walled carbon nanotubes caused by γ-ray irradiation

Zhiwei Xu *, *Lei Chen, Liangsen Liu, Xiaoqing Wu, Li Chen*

Key Laboratory of Advanced Braided Composites, Ministry of Education, Tianjin Polytechnic University, Tianjin 300160, China

ARTICLE INFO

Article history:
Received 22 June 2010
Accepted 9 September 2010
Available online 17 September 2010

ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were irradiated by γ-rays in air and epoxy chloropropane (ECP) with an absorbed dose 200 kGy. We found that MWCNTs showed an opposite behavior in structural change when irradiated in the two different media. Gamma-ray irradiation decreased the inter-wall distance of MWCNTs and improved their graphitic order in air, while irradiation in ECP increased the inter-wall distance of MWCNTs and disordered the structure.

Recently, γ-ray irradiation, as a controlled method for modifying the physical and chemical properties of multi-walled carbon nanotubes (MWCNTs), has attracted much attention. It was shown that under γ-ray irradiation the grafting and functionalization of MWCNTs with polymers [1–4] enhanced the solubility of MWCNTs. Another example can be found in the work of Peng et al. [5] where MWCNTs were successfully cut by using γ-ray irradiation with a sensitizer. In addition, Qian et al. [6] improved the hydrogen adsorption capacity of MWCNTs by γ-ray irradiation. These routes to functionalize MWCNTs would shorten and damage the MWCNTs. However, we found that MWCNTs showed an opposite behavior in structural change when they were irradiated in the two different media.

Here we report the structural changes of MWCNTs by γ-ray irradiation in air and epoxy chloropropane (ECP). We used MWCNTs with purity 95% provided by Chengdu Organic Chemicals Co. Ltd., China, without further purification. Typically, 100 mg of MWCNTs and 100 ml of 60% ECP/acetone solution were mixed and sonicated for 30 min. The mixture and pristine MWCNTs were then irradiated in an absorbed dose 200 kGy with 2.0 kGy/h dose rate at room temperature. The MWCNTs irradiated in ECP were washed by acetone and distilled water.

Raman spectra have been recorded by using a Renishaw System 2000 (with microscope) spectrometer with a laser source at 514 nm and a power of 5 mW in Fig. 1. The D ($\sim$1350 cm^{-1}), G (1580 cm^{-1}) and D′ (1600 cm^{-1}) band positions [7] were analyzed by using a mixed Gaussian–Lorentzian curve-fitting procedure. The band positions, the intensity ratio of D to G band (I_D/I_G) and full width at half maximum (FWHM) are presented in Table 1.

As shown in Table 1, the I_D/I_G ratio and FWHM$_G$ of MWCNTs slightly decreased from 0.86 and 49.4 cm^{-1} to 0.79 and 48.9 cm^{-1} after irradiation in air, respectively. The irradiation in air brought about a slight shift to low frequency in the G band, indicative of an increase in the degree of graphitization. These results should be attributed to the defect decrease and graphitic order improvement induced by γ-irradiation in air. However, the I_D/I_G ratio and FWHM$_G$ of MWCNTs irradiated in ECP were marginally larger than those of pristine MWCNTs and the G band slightly shifted up by $\sim$3 cm^{-1}, indicating the introduction of covalently bound moieties to the nanotube framework wherein the significant amounts of sp^2 carbons have been converted to sp^3 hybridization.

Fig. 2a–c displays a series of diffraction spectra for pristine and irradiated MWCNTs. After irradiation in air, the intensity and diffraction angle of (0 0 2) peak (at approximately 26°), which represents the interlayer spacing (d_{002}), went up and a small decrease of inter-wall distance ranging from 3.44 to 3.42 Å ($\sim$6%) is apparent. These results are in good accordance with those of graphite indicated in the literature [8]. However, the peaks related to the inter-wall length, corresponding to indices of graphite (0 0 2) and (0 0 4) (at $\sim$53°), exhibited a shift toward lower angle and the characteristic (0 0 2) peak of MWCNTs became weakened and diffused after irradiation in ECP, indicative of the inter-wall distance increase from 3.44 to 3.47 Å. The decrease in height and sharpness of (1 0 1) and (1 1 0) peaks (at 42° and 78°, respectively) illuminated that the microstructures of MWCNTs were broken

* *Corresponding author:* Fax: +86 22 24528258.
E-mail addresses: xuzhiwei@tjpu.edu.cn (Z. Xu).
0008-6223/$ - see front matter
doi:10.1016/j.carbon.2010.09.023

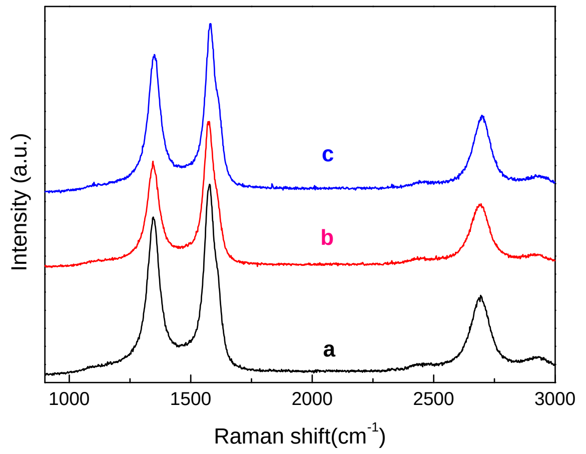

Fig. 1 – Raman spectra of MWCNTs, (a) pristine, (b) irradiated in air, and (c) irradiated in ECP.

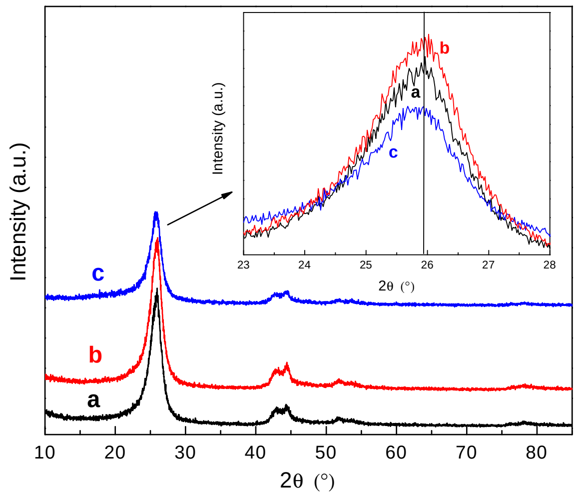

Fig. 2 – X-ray diffraction patterns of MWCNTs, (a) pristine, (b) irradiated in air and (c) irradiated in ECP.

Table 1 – Ratio (I_D/I_G), position (V) and FWHM of different bands in Raman spectra.

	V_D (cm^{-1})	$FWHM_D$ (cm^{-1})	V_G (cm^{-1})	$FWHM_G$ (cm^{-1})	$V_{D'}$ (cm^{-1})	I_D/I_G
Pristine	1346.8	73.7	1572.0	49.4	1604.2	0.86
Irradiated in air	1345.9	71.9	1569.4	48.9	1596.0	0.79
Irradiated in ECP	1350.3	68.8	1575.2	49.7	1605.4	0.94

partially through γ-ray irradiation in ECP, which agree with those reported in literature [1–6].

Gamma irradiation decreased the inter-wall distance of MWCNTs and improved their graphitic order in air, while irradiation in ECP increased the inter-wall distance of MWCNTs and disordered the structure. Also these results are not surprising because it had already been shown that γ-rays caused the improvement in graphitic order of graphite and carbon fibers [8] in air and damaged and shortened the nanotube structure [1–5] in polar liquid. Due to great penetrating power of γ-rays, MWCNTs irradiated in air show a significant rearrangement and the defect concentration can be decreased. As a result, the inter-wall spacing decreases because the defective graphenes typically have large interlayer spacing [9]. Another possible mechanism is that the irradiation can push one carbon atom out of the graphene plane and then a cross-link between neighboring graphene layers is formed [10]. However, besides the above changes, γ-ray irradiation in ECP can shorten tubes [5], and ECP might be strongly bonded to dangling bonds of tubes to form grafting chains [1–4]. The distance of graphene in MWCNTs increases, as the defective structure increases. It is worth expecting that MWCNTs can be employed as 'space radiation shields' at least for short term experiments.

Acknowledgments

The authors acknowledge support from Tianjin Natural Science Foundation (10JCYBJC02300).

REFERENCES

[1] Guo JX, Li YG, Wu SW, Li WX. The effects of gamma-irradiation dose on chemical modification of multi-walled carbon nanotubes. Nanotechnology 2005;16(10):2385–8.

[2] Chen SM, Wu GZ, Liu YD, Long DW. Preparation of poly(acrylic acid) grafted multiwalled carbon nanotubes by a two-step irradiation technique. Macromolecules 2006;39(1):330–4.

[3] Xu HX, Wang XB, Zhang YF, Liu SY. Single-step in situ preparation of polymer-grafted multi-walled carbon nanotube composites under Co-60 gamma-ray irradiation. Chem Mater 2006;18(13):2929–34.

[4] Jovanovic SP, Markovic ZM, Kleut DN, Romcevic NZ, Trajkovic VS, Dramicanin MD, et al. A novel method for the functionalization of gamma-irradiated single wall carbon nanotubes with DNA. Nanotechnology 2009;20(44):4456021–8.

[5] Peng J, Qu XX, Wei GS, Li JQ, Qiao JL. The cutting of MWCNTs using gamma radiation in the presence of dilute sulfuric acid. Carbon 2004;42(12-13):2741–4.

[6] Qian W, Chen JF, Wei LZ, Wu LS, Chen QW. Gamma-ray irradiation-induced improvement of hydrogen adsorption in multi-walled carbon nanotubes. Nano 2009;4(1):7–11.

[7] Cataldo F. A Raman study on radiation-damaged graphite by gamma-rays. Carbon 2000;38(4):634–6.

[8] Xu ZW, Liu LS, Huang YD, Sun Y, Wu XQ, Li JL. Graphitization of polyacrylonitrile carbon fibers and graphite irradiated by gamma rays. Mater Lett 2009;63(21):1814–6.

[9] Yoon M, Howe J, Tibbetts G, Eres G, Zhang ZY. Polygonization and anomalous graphene interlayer spacing of multi-walled carbon nanofibers. Phys Rev B 2007;75(16):165402–6.

[10] Banhart F. Irradiation effects in carbon nanostructures. Rep Prog Phys 1999;62(8):1181–221.