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

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

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

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.

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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 (~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 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 of MWCNTs irradiated in ECP were marginally larger than those of pristine MWCNTs and the G band slightly shifted up by ~3 cm⁻¹, indicating the introduction of covalently bound moieties to the nanotube framework wherein the significant amounts of sp² carbons have been converted to sp³ 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 (~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 ~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).
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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.

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