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Gamma and neutron irradiation effects on multi-walled carbon nanotubes

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ABSTRACT

In this study, the effects of gamma-ray and neutron radiation on multi-walled carbon nanotubes (MWCNTs) at different doses were investigated. The samples in powder form were exposed to thermal neutrons, fast neutrons, and 10 kGy and 20 kGy doses of gamma-ray radiation. Virgin and irradiated MWCNTs were investigated through structural, optical, morphological, and chemical analysis by Raman spectroscopy, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) to investigate the damage produced by the radiation. The Raman spectroscopy measurements show that the I_D/I_G ratio increased with the irradiation except for the 10 kGy gamma rays. XPS measurements display a higher degree of oxygen incorporation with the neutron irradiation. Detailed analysis of the C1s spectra also shows lower percentages of C═C sp^2 and higher percentages of C−C sp^3 in the MWCNTs irradiated by neutrons. Dark black spots were observed in the MWCNTs by irradiation, which is attributed to the formation of an amorphous structure by TEM measurements. The results show that, overall, the 10 kGy gamma irradiation dose improves the structural quality while the 20 kGy dose gamma rays, fast, and thermal neutrons caused a decrease in the degree of the structural quality of the MWCNTs.

1. Introduction

Because of their excellent thermal properties, low impedance, high tensile strength, ultra-light weight, metallic conductive properties, excellent heat shock resistance, and thermal sublimation below 2200 K, carbon-based materials have been used extensively in radiation-exposed environments such as nuclear reactors and medical, biomedical, and space applications, etc. [1]. Tools and devices made up of carbon nanotubes (CNTs) are widely used in these environments [2–8]. CNTs have been used to make dosimetry devices due to the radiation sensitivity of carbon-based structures [2, 9]. In addition, the interaction of the CNTs with radiation can be used for nano-engineering applications such as formations of molecular junctions between nanotubes and/or nanotube-based quantum dots [10]. CNT-reinforced boron carbide composite has been used in nuclear engineering applications such as neutron absorbers in certain types of fission reactors [11].

It is inevitable that CNTs will be subject to different types of radiation in these environments. Interactions of several different types of radiation with CNTs already have been reported. MWCNTs irradiated with 200 kGy gamma-ray radiation has shown that the degree of graphitization is decreased together with the formation of defects in the carbon lattice [1]. In addition, it has been found that improved surface properties of MWCNTs in the structure at 100 kGy gamma radiation dose [12] eliminates existing defects. In addition to gamma rays, the effects of protons with energy of 170 keV and fluences of $5 \times 10^{14}\,cm^{-2}$ and $5 \times 10^{15}\,cm^{-2}$ irradiation on the MWCNTs have been investigated. For the higher fluence irradiation, some clear changes in the CNTs have been reported such as formation of uneven surfaces, entanglement of nanotubes, and shrinkage of nanotubes in morphology of the MWCNTs. However, in the case of low proton fluence, structural improvement has been observed [13]. Furthermore, electron irradiation on the CNTs has also been examined. It has been determined that the delocalizion of electrons over CNTs increase with increasing irradiation fluence. Damages formation such as amorphization, pits and gaps in the structure of MWCNTs has occurred at 200 keV electron irradiation. The damage formation was attributed displacement and sputtering of atoms in the structures [14].

In technological applications, defect formation and structural modifications may cause some problems in these CNT-based devices, one of which could be the long-term stability of the devices. Knowledge about radiation-beam-induced defect formation and thermal oxidation of CNTs in radiation environments is vital [15, 16]. Therefore, it is quite important to determine the damage mechanisms in the radiation environments [10]. Although electron and proton particle studies have

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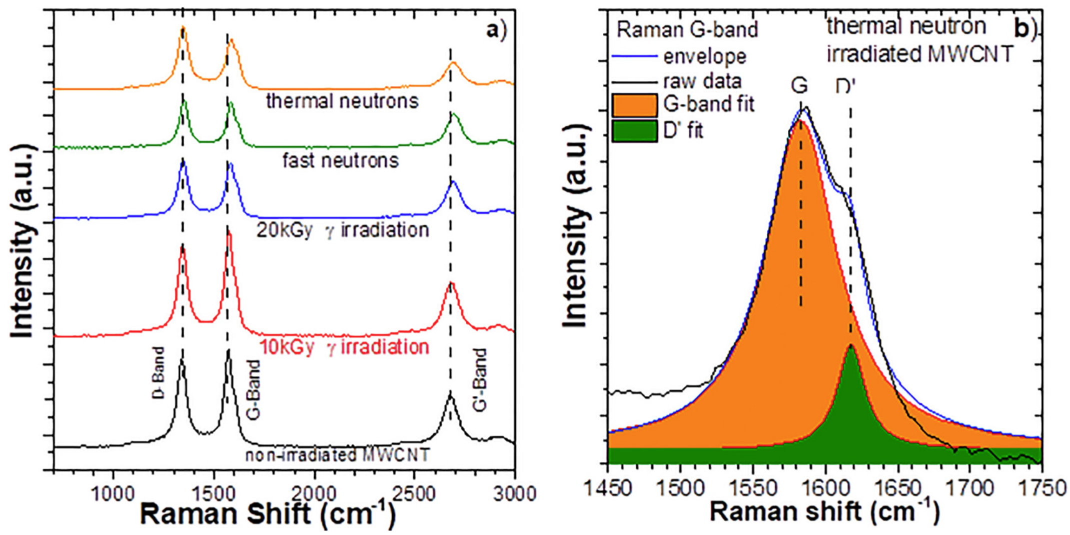

Fig. 1. (a) Raman spectra of the virgin and the MWCNTs irradiated with thermal and fast neutrons and gamma rays with 10 kGy and 20 kGy doses. (b) deconvolution of the G-band region of MWCNT.

been performed on the MWCNTs, neutron particle studies on MWCNTs have not been investigated in detail. In this paper, MWCNTs were irradiated with 10 kGy and 20 kGy gamma doses and fast and thermal neutrons. Irradiated and virgin MWCNTs were analyzed through detailed structural, optical, chemical, and morphological analysis methods to see the irradiation effects on the MWCNTs.

2. Experimental

MWCNTs with diameter of 10–20 nm, length of 10–30 μm, and 99% purity (provided by Grafen Chemical Industries Co., Ltd.) were used in the present study. The samples were irradiated at the Turkish Atomic Energy Authority. All irradiation processes were applied in atmospheric pressure under room-temperature conditions. All samples were in powder form weighing 0.1 g. The uncompressed samples were placed in circular-shaped sample holders of thickness 1.6 mm and diameter 13 mm. The sample holders were then placed in the sample basket. During irradiation, the basket was rotated in the constant source environment in an effort to ensure homogeneous irradiation of the samples. The sample basket dimensions were 220 mm × 250 mm, with a cylindrical container of approximately 10 l in volume. The gamma-ray source was ^{60}Co (Isotop brand, Ob-Servo Sanguis). The 10 kGy and 20 kGy gamma radiation doses were applied on MWCNTs with a dose rate of 1667 Gy/h by adjusting the distance between the samples and the ^{60}Co irradiator. Irradiation was carried out until reaching the desired doses. The ^{241}Am + Be neutron source was used as the fast neutron source. The source consists of ^{241}Am and ^{9}Be atoms blended in the mortar into a steel casing. The source emits 2.2×10^6 neutrons per second. One meter away from the source, neutron doses are 2.2 mrem/h. Fast neutrons from the source do not have a constant energy but their average energy is 4.46 MeV. The flux of the fast neutrons used is $\Phi(0) = 1.7 \times 10^6$ ns^{-1}cm^{-2}. The sample was irradiated with fast neutrons for 6 days (518,400 s), during which time, the sample was exposed to 8.8×10^{11} n·cm^{-2} neutron doses. Another sample was irradiated for the same time with thermal neutrons with the flux of $\Phi(0) = 3.13 \times 10^4$ ns^{-1}cm^{-2}. The total dose exposed was 1.62×10^{10} n·cm^{-2}.

Raman spectroscopy was used to determine the structural qualities of the MWCNT samples. The measurements were performed with a WITec alpha 300 R Micro-Raman spectrometer using a 532 nm wavelength laser. In order to get rid of the heating effects, and thus the annealing effects of the laser used in the Raman measurements, a low power 0.3 mWatt laser was used. The XRD technique was applied on PANalytical/Empryean to measure the structural parameters of the virgin and irradiated MWCNT samples. The XRD measurements were performed with Ni-filtered and Cu-Kα radiation with 1.54 nm. The angle of scan was 10° per minute with step size of 0.01. XRD analysis was performed in the range of 10^0 to 90^0. The XPS experiments were carried out to detect the distribution of oxygen-containing functional groups (C—O, C═O) characterized by deconvolution of C-1s spectra in an ultra-high vacuum system. The Specs Flex Mode system with a 150 mm hemispherical electron analyzer attached to a Phoibos 150-CCD detector was used with pass energy of 100 eV for survey spectra and 10 eV for high-resolution spectra of C elements. The monochromatized Al-Kα (1486.6 eV) line was used for measurements. Shirley background subtraction was applied to an implemented fitting operation, which can decompose each spectrum into individual mixed Gaussian-Lorentzian peaks. In addition, structural changes of the samples were carried out with TEM HITACHI 7700 and SEM with ZEIS Gemini Sigma 300.

3. Results and discussion

Raman spectroscopy is an excellent tool to reveal the structural properties of CNTs, and it is commonly used in quantitative analysis to show radiation damages [11, 17]. The Raman spectra of virgin and irradiated MWCNTs are shown in Fig. 1. There are three characteristic bands, namely the D-band at ~1339 cm^{-1}, G-band at ~1572 cm^{-1}, and G'-band at ~2681 cm^{-1} (values for virgin CNTs) in the spectra for all the MWCNTs investigated in the present study. The D-band is known to be a disordered band due to structural defects, edge effects, dangling sp^2 carbon bonds, and the presence of amorphous structures, which all result in a break in the symmetry in the CNTs. The G-band originates due to an in-plane tangential stretching motion of the sp^2 carbon atoms [18]. The G' band displays the intrinsic property of well-regulated sp^2 carbon atoms. All the Raman spectra were taken at six different points and averaged over all the measurements for each sample. The evaluation of the quality was revealed by taking account of the integrated intensity ratio of the D-band to the G-band after baseline subtraction.

It is observed that the defect density (D-band) was highest in the sample subjected to thermal neutron radiation in which the ratio was 1.18. Increase in the I_D/I_G ratio was more than 25% compared to the virgin sample. On the other hand, compared to the virgin sample, the MWCNTs irradiated by 10 kGy gamma radiation (I_D/I_G = 0.88) showed a reduction of the D-band intensity. The I_D/I_G ratio of all samples is given in Table 1. It might be concluded that irradiating with 10 kGy