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Radiation damage to multi-walled carbon nanotubes and their Raman vibrational modes

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Abstract

The influence of the radiation damage to multi-walled carbon nanotubes (MWCNT) during the high-energy electron irradiation ($E_e = 1.8$ MeV) with different doses of absorption ($D_n = 0.5$; 1.0; 1.5 and 2.0 MGy) on their Raman vibrational spectra is studied in detail. The modification of both radial and tangential optical vibrations is observed depending on radiation dose. This is manifested both in the frequency shifts of the vibrational modes and in a change in the intensity of the Raman scattering, which corresponds to different optical vibrations. This behavior of Raman spectrum is explained by appearance and increase in the concentration of radiation defects and by seams of separate layers of nanotubes.

Keywords: Carbon nanotubes; Arc discharge; Raman spectroscopy; Defects

1. Introduction

The variety of the physicochemistry properties of carbon nanomaterials is determined by the possibility of influencing their structure, including the creating of different defects. One method for modifying properties is the formation of radiation defects resulting from electron irradiation [1–9]. In contrast to the irradiation by low-energy photons, which are mainly used to excite π-electron systems, and can lead to the polarization of the molecules of the nanostructures [10], electron bombardment is capable of creating radiation point defects. In order to displace carbon atoms from the surfaces of nanostructures, the energy transferred to them must exceed a certain threshold value E_d. This value in the carbon materials equals from $E_d = 15$ eV to $E_d = 80$ eV and is reached at the energies of the bombarding electrons, which exceed $E_e = 1$ MeV.

Other types of particles, ions and neutrons for example, can be used to initiate the radiation stimulated processes in the carbon nanostructures. However, the mechanisms of defect formation in this case are different. As a result, cascades of the defects for the fragments of the molecules for the atomized substance are created [10–13].

The most effective radiation influence is expected in the case of the electron irradiation of multi-walled carbon nanotubes (MWCNT). This is explained by the possibility not only that radiation defects occur during irradiation, which will contribute to the degradation of nanotubes, but also that seams appear due to the broken connections as vacancies are generated. This material, an amorphous, porous carbon, tends mainly to transform both diamond

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nanoclusters and the graphitized nanostructures [15–21]. In this case the presence of essential differences in the geometry of the graphitized component should also be considered. If amorphous, porous carbon and graphitized structures are related predominantly by plane clusters with the sp^2-hybridization of electron states, then the geometry of nanotubes assumes the presence of the higher degree of hybridization between sp^2 and sp^3. This means that the introduction of radiation defects in MWCNT can substantially influence the properties of nanotubes as a result of the changes in their electron and vibrational structures.

In the present work, we investigate in detail the radiation induced modification of the MWCNT vibrational spectra with a study of Raman scattering after the action of electron irradiation with the doses of absorption by $D_n = 0.5$; 1.0; 1.5 and 2.0 MGy. Irradiation was accomplished by using a linear electron accelerator. Raman scattering was excited by laser emission with the wavelength $\lambda = 514.5$ nm (Ar^+-laser).

2. Samples

The nanotubes used in this study were obtained as cathode deposits in the DC arc vaporization process of graphite. The arc discharge conditions and the apparatus used are described in details elsewhere [14]. The anode was a graphite rod (6.15 mm diameter, length 7–10 mm) in which a hole (5.1 mm diameter, deeper than the burned part of the electrode) was drilled and filled with a mixture of metal oxides (4.2% Ni and 1% Y) and graphite powder. The cathode was a graphite rod (15 mm diameter, 15 mm length). The purity of the graphite rods and powder was 99.999% (ash residue <500 ppm). The gap between the graphite electrodes was 0.5–1.5 mm, which was kept by manually advancing the consumed anode. The discharge voltage and current varied between 23–25 V and 35–45 A, respectively, during the arc discharge. The discharge time was between 50 and 120 s at N_2 pressure of 700 mbar.

The products were collected from the different parts in the apparatus. MWCNT used in this study were obtained as cathode deposit. Investigations showed that only in the cathode deposit the amount and the quality of the MWCNT is high. Soot was deposited around the metal rod behind the cathode and was not used in these experiments.

The characterization of the products was performed by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) and thermo gravimetric analysis (TG). From SEM and TG we estimated that the content of MWCNT in the samples was higher than 80%.

3. Results and discussion

The pattern of Raman scattering for MWCNT is analogous for the single-walled CNT [22–28]. However, it is nearer to the fine-crystalline, amorphous carbon [15,20] or thermocrushed graphite (Fig. 1).

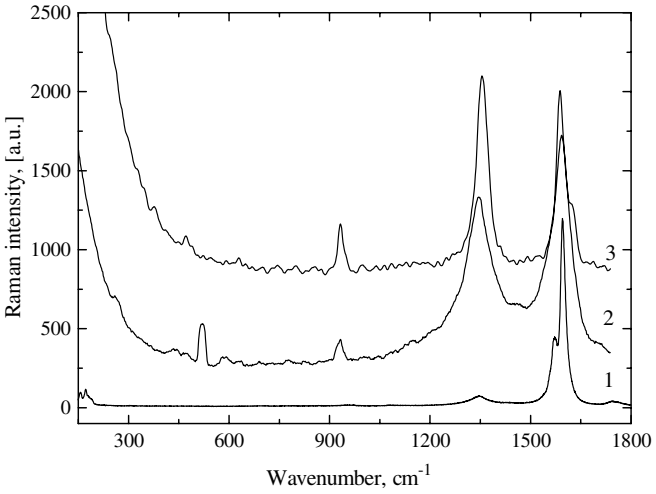

Fig. 1. Raman spectra for different carbon nanostructures: 1 – single-walled CNT; 2 – MWCNT; 3 – thermocrushed graphite.

However, with the exception of external similarity the differences are noticeable. In the low-frequency part of the MWCNT spectrum the intensive scattering near the position 116 cm^{-1} appears. This scattering is characteristic for the vibrational E_{1g} mode in armchair (10,10) CNT, which is usually optically "silent" and is revealed only with neutron scattering [24,25]. While for the single-walled CNT the D^*-band (~1350 cm^{-1}) of Raman scattering has weak intensity in comparison with the G^*-band (~1590 cm^{-1}), in MWCNT their intensities coincide. This behavior of Raman scattering is similar to analogous scattering from the amorphous carbon (thermocrushed graphite).

In the process of electron irradiation, the noticeable reconstruction of the Raman spectrum with an increase in the dose of absorption occurs (Fig. 2).

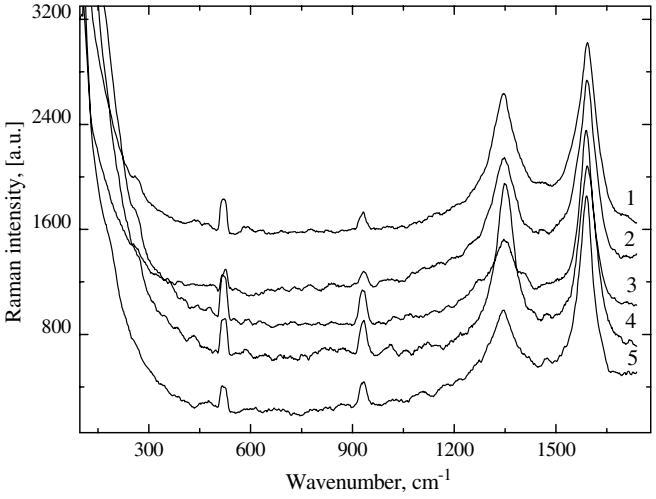

Fig. 2. Dose dependence of the spectrum of Raman scattering for the MWCNT during the electron irradiation ($E_e = 1.8$ MeV): 1 – initial (nonirradiated) state; 2 – dose of absorption is 0.5 MGy; 3 – 1.0 MGy; 4 – 1.5 MGy; 5 – 2.0 MGy.