The synergistic effect of bremsstrahlung photons and intense laser radiation on the structural properties of carbon nanotubes

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Abstract
We present in this paper the influence of a synergistic radiation effect of both bremsstrahlung photons with maximum energy of 60 MeV and intense laser radiation (up to 60 KW cm⁻²) on the structural properties of carbon nanotubes (CNTs). The defect formation (damage) in CNTs under separate irradiations of 60 MeV bremsstrahlung photon or intense laser and their combined irradiations has been investigated by Raman spectroscopy. The experimental results show that (i) our obtained natural CNTs are multi-walled carbon nanotubes (MWCNTs) with a large number of structural defects, which are non-nanotube carbon impurities; (ii) the MWCNTs were not damaged by the irradiations of an intense laser and a bremsstrahlung photon beam with low electron fluency and the irradiation even leads to more purification/ordering; (iii) the reversible modification in non-irradiated and 60 MeV bremsstrahlung photon irradiated MWCNTs with variation of laser power density (LPD) have been received; (iv) the influence on the structural properties of MWCNTs induced by the combined irradiation was greater than the separate irradiation of a 60 MeV bremsstrahlung photon or intense laser radiation. The result also demonstrates that micro-Raman spectroscopy is a valuable, fast and non-destructive tool for the investigation of purification/ordering of CNTs.

Keywords: MWCNTs, Raman spectrum, bremsstrahlung photons, laser irradiations, synergistic radiation effect

Classification number: 5.14

1. Introduction

Over the past decade, both theory and experiments have shown that carbon nanotubes (CNTs) have unique electronic properties and extreme mechanical strength, as well as high thermal and structural stability. Consequently, CNTs are not only applied in advanced composite materials, thermal dissipation media, electro-magnetic wave absorption, scanning probe and electron field emitters in terrestrial systems [1–4] but could also be used in other areas, such as space shuttles, nuclear reactors and components of the next generation of optoelectronic devices for space applications [5–8]. For applications in the space environment, these materials are influenced not only by charged particles
and high-energy radiation, such as proton, electron, alpha and neutron, but also by a number of other environmental synergistic factors [9, 10]. Synergistic interactions can increase or decrease material degradation. Nowadays, these effects are not well understood and have to be investigated more and more carefully. For the purpose of simulating the interaction of space radiation with materials, one often conducts experimental research on the ground with artificial radiation sources, which are mainly generated from a particle accelerator. CNTs may have only one shell (single-walled carbon nanotubes (SWCNTs)) or many shells (multi-walled carbon nanotubes (MWCNTs)). However, all these structures retain graphitic arrangements of carbon atoms, and defects in CNTs can be created only if the interaction is energetic enough to displace carbon atoms. Micro-Raman spectroscopy is a widely used technique to study the vibrational modes of CNTs. This method is capable of detecting small changes in crystal structure and it has been used extensively in the analysis of the irradiation modification of CNTs. In this work, the CNTs fabricated by chemical vapor deposition (CVD) have been activated by a bremsstrahlung photon beam generated by an electron linear accelerator. To study defect formation (damage) in CNTs under separate irradiations of bremsstrahlung photon or intense laser and their combined irradiations, we consider the frequency shift, full-width at half-maximum (FWHM) of D, G and D’ Raman modes and a disorder parameter α = I_D/I_G with varied laser power density (LPD), where I_D and I_G are the intensities of the D and G modes.

2. Experimental

The CNTs used here were MWCNTs prepared by CVD using CaCO₃-supported iron salts, as described elsewhere [11]. They have diameters mainly in the range of 15–90 nm, with degree of purification ~97% and high yield ~78.61%.

The photon radiation experiments were carried out at Pohang Accelerator Laboratory (PAL), Korea. The MWCNTs were placed 10 cm from the central axis of a bremsstrahlung photon beam generated by the electron linear accelerator, and on thin W target (100 × 100 × 0.1 mm³), 10 cm away from the source. The energy of the bremsstrahlung photon can be varied from 0 to the maximum energy of a generated electron beam. These MWCNTs have been activated by bremsstrahlung photons with a maximum energy of 60 MeV, with an irradiation time of 80 min and average current of 35 mA.

The Raman spectra (632.8 nm excitation) of the MWCNTs were collected at room temperature by using a Micro-Raman Spectrometer Renishaw with a CCD detector and a ×50 objective in the range of 100–1800 cm⁻¹. The spectral resolution was about 1 cm⁻¹. The LPD was controlled as low as 3 kW cm⁻² to avoid any laser-heating effect to investigate the carbon shells of natural obtained CNTs and the influence of bremsstrahlung photon irradiation on structural properties of carbon nanotubes. The LPD was increased step-by-step from 3 up to 60 kW cm⁻² and then decreased in the reverse direction to 3 kW cm⁻² at the same point to investigate the intense laser power effect.

3. Results and discussion

The most important feature in the Raman spectrum of CNTs is the Radial Breathing Mode (RBM), which is usually located between 75 and 300 cm⁻¹. However, our obtained CNTs have diameters mainly in the range of 15–90 nm and we could not observe RBM modes. Figure 1 presents the Raman spectra of non-irradiated (a) and 60 MeV bremsstrahlung photon irradiated (b) MWCNTs excited by a 632.8 nm laser with increased LPD from 3 to 60 kW cm⁻² and then decreased LPD from 60 to 3 kW cm⁻² (curve 1: LPD = 3 kW cm⁻², curve 2: LPD = 15 kW cm⁻², curve 3: LPD = 30 kW cm⁻², curve 4: LPD = 60 kW cm⁻²).

Figure 1. Raman spectra of non-irradiated (a) and 60 MeV bremsstrahlung photon irradiated (b) MWCNTs excited by a 632.8 nm laser with increased LPD from 3 to 60 kW cm⁻² and then decreased LPD from 60 to 3 kW cm⁻² (curve 1: LPD = 3 kW cm⁻², curve 2: LPD = 15 kW cm⁻², curve 3: LPD = 30 kW cm⁻², curve 4: LPD = 60 kW cm⁻²).

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In our case, the intensity ratios (I_D/I_G) and FWHM of non-irradiated (a) and 60 MeV bremsstrahlung photon irradiated MWCNTs (b) with varied LPD of the 632.8 nm laser line.

| LPD (KW cm\(^{-2}\)) | D (cm\(^{-1}\)) | FWHM\(_D\) (cm\(^{-1}\)) | G (cm\(^{-1}\)) | FWHM\(_G\) (cm\(^{-1}\)) | D' (cm\(^{-1}\)) | FWHM\(_G\)' (cm\(^{-1}\)) | I_D/I_G |
|-----------------------|----------------|------------------------|--------|------------------------|-------------|------------------------|---------|
| (a) Non-irradiated MWCNTs |               |                        |        |                        |             |                        |         |
| 3                     | 1331          | 42.8                   | 1583   | 33.5                   | 1616        | 24.8                   | 1.09    |
| 15                    | 1331          | 42.3                   | 1583   | 37.8                   | 1617        | 23.2                   | 1.20    |
| 30                    | 1329          | 43.9                   | 1581   | 34.5                   | 1614        | 27.7                   | 1.20    |
| 60                    | 1327          | 45.2                   | 1578   | 37.3                   | 1611        | 28.0                   | 1.14    |
| 30                    | 1329          | 44.7                   | 1581   | 35.7                   | 1614        | 27.4                   | 1.17    |
| 15                    | 1331          | 43.4                   | 1583   | 34.4                   | 1616        | 30.9                   | 1.12    |
| 3                     | 1331          | 41.6                   | 1583   | 37.2                   | 1615        | 24.3                   | 1.12    |
| (b) 60 MeV bremsstrahlung photon irradiated MWCNTs |               |                        |        |                        |             |                        |         |
| 3                     | 1332          | 33.8                   | 1581   | 21.0                   | 1610        | 45.1                   | 1.22    |
| 15                    | 1331          | 38.7                   | 1581   | 27.7                   | 1611        | 41.5                   | 1.26    |
| 30                    | 1326          | 47.4                   | 1576   | 39.0                   | 1608        | 30.5                   | 1.23    |
| 60                    | 1323          | 46.3                   | 1571   | 38.0                   | 1602        | 30.4                   | 1.30    |
| 30                    | 1329          | 42.9                   | 1579   | 34.6                   | 1611        | 27.4                   | 1.34    |
| 15                    | 1333          | 33.8                   | 1581   | 25.2                   | 1612        | 44.0                   | 1.32    |
| 3                     | 1332          | 36.7                   | 1582   | 22.7                   | 1610        | 38.6                   | 1.28    |

3.1. Non-irradiated MWCNTs

We know that the Raman spectral bands for disordered graphite are located in the ranges 1570–1585 cm\(^{-1}\) and 1350–1300 cm\(^{-1}\), and besides the D and D' bands are usually attributed to the presence of amorphous or disordered carbon in the CNT samples, they should be due to the lattice defects and finite crystal size occurring inside the graphene atomic layer [15, 16]. The lines 1 in figure 1(a) and table 1, at exciting laser intensity about 3 kW cm\(^{-2}\) (to extract laser-heating effect), show two intense broadened bands at 1583 and 1331 cm\(^{-1}\) that evidence a larger number of defects and disordering of graphene layers in our samples. Moreover, the D band is observed at 1331 cm\(^{-1}\) lower than D-mode frequency from graphite, its intensity is quite large compared with that of the G band and this band has FWHM of about 42.8 cm\(^{-1}\). These two characteristics (frequency and line width) and the absence of RBM mode confirm that our sample is a nanotube and not graphite. We know that the intensity ratio (I_D/I_G), which allows the degree of ordering or graphitization of the carbon structure, is a good indicator of the quality of the CNTs. If both of these bands have similar intensity (I_D/I_G) \sim 1, this indicates a high quantity of structural defects, and if (I_D/I_G) < 1 and (I_D/I_G) > 1, these correspond to disordered graphite and amorphous carbon, respectively. In our case, the intensity ratios (I_D/I_G) of non-irradiated natural carbon nanotubes is about 1.09 and the FWHM of the G band is about 33.5 cm\(^{-1}\) (table 1). For these reasons, we could affirm that our obtained natural CNTs are MWCNTs with a large number of structural defects; they are non-nanotube carbon impurities, such as amorphous carbon and nanocrystalline graphene.

3.2. 60 MeV bremsstrahlung photon irradiated MWCNTs

To understand the modifications occurring under bremsstrahlung photon irradiation with maximum energy of 60 MeV for about 80 min, we compared the Raman spectra at exciting laser intensities of about 3 kW cm\(^{-2}\) of the non-irradiated MWCNTs with those irradiated by bremsstrahlung photon (lines 1 in figures 1(a), 1(b) and table 1). It was shown that the Raman spectra of 60 MeV bremsstrahlung photon irradiated MWCNTs comprise also three characteristic bands, i.e. the D, G and D' bands. The maxima bands of 60 MeV bremsstrahlung photon irradiated MWCNTs are located at 1332 cm\(^{-1}\) for the D band, at 1581 cm\(^{-1}\) for the G band and at 1610 cm\(^{-1}\) for the D' band (line 1 in figure 1(b)), while the bands of non-irradiated MWCNTs were located at 1331, 1583 and 1616 cm\(^{-1}\) (line 1 in figure 1(a)), respectively. We do not observe a significant shift after 60 MeV bremsstrahlung photon irradiation for the D band, which should be due to the fact that the width of our D band makes it difficult to detect any shift, while the position of the G band at 1583 cm\(^{-1}\) was slightly changed from 1581 cm\(^{-1}\). These slight shifts should indicate the removal of carbon particles adhered to the walls of the nanotubes [17]. In addition, the frequency of the G band is related to tangential stretching of the carbon–carbon bonds in graphene sheets, which is likely also associated with the softening force constant [17, 18]. Moreover, in comparison with MWCNTs before and after 60 MeV bremsstrahlung photon irradiation, the FWHMs of the D and G bands decrease significantly from 42.8 to 33.8 cm\(^{-1}\) and from 33.5 to 21.0 cm\(^{-1}\), respectively (table 1). These observed decreases in FWHMs for the D and G bands should be attributed to the removal of carbon impurities from non-irradiated MWCNTs by 60 MeV bremsstrahlung photon irradiation. Regarding a shoulder D' (at \sim 1616 cm\(^{-1}\), which originated from defective graphite, it shows clearly that the position was downshifted by 6 cm\(^{-1}\) (from 1616 to 1610 cm\(^{-1}\)) and FWHM increased from 24.8 to 45.1 cm\(^{-1}\) after 60 MeV bremsstrahlung photon irradiation. The spectra broaden consistently with the domain size decrease, which is attributed to the progressive relaxation of the wave-vector selection rule [12–14]. The positions, the intensity ratios (I_D/I_G) and FWHM of G, D and D' bands of non-irradiated and 60 MeV bremsstrahlung photon irradiated MWCNT spectra with varied LPD are listed in table 1.

![Table 1. The band positions, the intensity ratios (I_D/I_G) and FWHM of non-irradiated (a) and 60 MeV bremsstrahlung photon irradiated MWCNTs (b) with varied LPD of the 632.8 nm laser line.](image-url)
particle radiation. Thus, together with the bremsstrahlung photon beam generated by an electron linear accelerator, a number of electrons always exist. Under interaction of this amount of electrons, a number of carbon particles adhered to the walls of nanotubes should be knocked out and separation of nanotubes can be observed. This fact could be a cause of the decrease in crystallite size. Moreover, the energy transferred from the incident electron into the material is enough to enhance the local temperature at the irradiation site of MWCNTs during 60 MeV bremsstrahlung photon irradiation processes. With increasing temperature, the force constants of nanotubes could be softening. Therefore, the change in the force constants after 60 MeV bremsstrahlung photon irradiation should cause the bands downshift. Thus, through the interaction of 60 MeV bremsstrahlung photon (with an amount of electron) on MWCNTs, the irreversible changes in the spectrum indicated that these MWCNTs were not damaged and the irradiation even leads to more purification/ordering because an amount of native carbon impurities (amorphous carbon or nanocrystalline graphite) was removed, their force constants becomes softened and a separation of nanotubes that is related to decreasing crystallite size could be observed.

3.3. Intense laser irradiation effect on non-irradiated MWCNTs

As shown in figure 1(a) and table 1, when LPD increases step-by-step, the frequencies of both D and G modes shift towards a lower wavenumber from 1331 to 1327 cm$^{-1}$ and from 1583 to 1578 cm$^{-1}$, respectively, which further shifts towards a higher wavenumber with decreasing LPD. This behavior shows the reversible modification with varied LPD and is represented by a black square in figures 2(a) for D mode and (b) for G mode. In addition, the intensity ratio ($I_D/I_G$) of D and G modes, which is conventionally used to quantify the structural quality of carbon nanotubes, remains almost constant within the experimental error in the case where LPD increases and/or decreases (black square in figure 2(c)). This indicates that under intense laser irradiation the lattices of our MWCNTs were not damaged, but the carbon–carbon distances in the tubes changed. A reversible shift of the stretching frequencies correspondingly changes the carbon–carbon distances in the MWCNTs. This could result in the dependence of the diameters of the multilayer carbon nanotubes on the LPD [18].

3.4. Intense laser irradiation effect on 60 MeV bremsstrahlung photon irradiated MWCNTs

To examine the modifications occurring under synergistic bremsstrahlung photon and intense laser irradiations, the frequency variation of D and G modes and the intensity ratio ($I_D/I_G$) of 60 MeV bremsstrahlung photon irradiated MWCNTs as a function of varied LPD of the 632.8 nm laser line are plotted as red circles in figures 2(a), 2(b) and 2(c), respectively. Reversible modification of the frequencies of both D and G modes with varied LPD was also observed. When LPD increases (from 3 to 60 kW cm$^{-2}$), D and G modes shift toward a lower wavenumber (from 1332 to 1323 cm$^{-1}$ and from 1581 to 1571 cm$^{-1}$, respectively), which further shifts towards a higher wavenumber when LPD decreases (from 60 to 3 kW cm$^{-2}$). Similarly to the case of non-irradiated MWCNTs, the intensity ratios ($I_D/I_G$) of D and G modes do not change so much with increasing and decreasing LPD (red circles in figure 2(c)). In addition, table 1 shows that when the LPD changed from 3 to 60 kW cm$^{-2}$, the FWHMs of D and G modes increased from 33.8 to 46.3 cm$^{-1}$ and from 21.0 to 38.0 cm$^{-1}$, respectively. When the LPD returned from 60 to 3 kW cm$^{-2}$, these FWHMs decreased to 36.0 cm$^{-1}$ for D and 22.7 cm$^{-1}$ for G modes. All these indicate that under intense laser irradiation our 60 MeV bremsstrahlung photon irradiated MWCNTs were not damaged. The reversible modifications in these MWCNTs with varied LPD should be attributed to the changes in carbon–carbon distances that result in the dependence of the diameters of the multilayer carbon nanotubes on LPD and the softening force constants effects could play the role here for the depth of the frequency shifts.

4. Conclusion

The separate irradiations of intense laser beam or 60 MeV bremsstrahlung photons and the combined synergistic irradiation effects of a 60 MeV bremsstrahlung photon and the intense laser beam on structural properties of carbon nanotubes have been investigated. The experimental results show that (i) our obtained natural CNTs are multi-walled...
carbon nanotubes (MWCNTs) with a large number of structural defects, they are non-nanotube carbon impurities; (ii) the MWCNTs were not damaged by the irradiations of intense laser and a bremsstrahlung photon beam with low electron fluency and the irradiation even led to more purification/ordering; (iii) the reversible modification in non-irradiated and 60 MeV bremsstrahlung photon irradiated MWCNTs with variations in LPD have been received; (iv) the influence on the structural properties of MWCNTs induced by the combined irradiation was greater than the separate irradiation of 60 MeV bremsstrahlung photon or intense laser radiations. The results also demonstrate that micro-Raman spectroscopy is a valuable, fast, non-destructive tool for the investigation of purification/ordering of CNTs.

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