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Research Article

Enhancing the Surface Properties and Structure of MWNTs by Effective Ion Beam Irradiation

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Abstract: The effects of irradiating multiwalled carbon nanotubes (MWNTs) with 100 keV He ions on the surface morphology were examined. Due to irradiation effects, the tube diameter reduced as revealed by scanning electron microscopy (SEM). Raman spectroscopy was used to investigate MWNTs by analyzing the principal bands in the spectra of virgin and radiated MWNT specimens. The effects of irradiation fluences on the disorder (D-band) and the graphite (G-band) modes were investigated. The possibility and prospects of using ion irradiation for controlling the wettability of the MWNT surface were investigated. The irradiation facility produces an MWNT coating that is either hydrophobic or hydrophilic to certain liquids. This analysis demonstrates that ion beam irradiation could be used as an alternative tool to change the structure of CNT and enhancing their wettability application, especially in water treatment. According to Raman spectra, when the fluence increases, the MWNTs become disordered due to the defect produced. The amorphous state of MWNTs could be attained with greater ion irradiation fluences.

Keywords: ion irradiation effects, multiwalled carbon nanotubes (MWNTs), amorphization, wettability enhancement, Raman spectra

1. Introduction

Carbon nanotubes (CNTs) have captivated researchers' interest since their discovery in 1991 by S. Iijima due to their unique physicochemical characteristics [1]. The unique properties of CNTs have led to a never-ending quest for new ways to use their properties to improve contemporary technological processes [2-4]. Investigation of the nature of CNT interactions with various liquids is one of the market trajectories. Irradiation with energetic particular beams (electrons or ions) is a common and effective method for the alteration of the material properties [5, 6]. Irradiation allows foreign atoms to enter the sample, as well as the creation of local amorphous areas, faults, and lattice recrystallization. Recent research has shown that irradiating CNTs with energetic particles may be used for a variety of nano-engineering processes. Making atomic crossings between nanotubes, nanotube-based quantum specks, and framing composite materials with improved mechanical characteristics are only a few examples [7]. Low-energy ion beams (eV to a few keV) irradiated CNTs produce fascinating fundamental modifications [8-10], Nanotube welding, bending, and fixing, nano-capsule formation, and amorphization are only a few possibilities. Numerous endeavors were examined to irradiate multiwall carbon nanotubes (MWNTs), energetic particles-ions irradiation [11], electron beams

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[12, 13], gamma irradiation [14, 15], and ultraviolet light irradiation [16]. Misra et al. investigated the supplementary damages of MWNTs with nickel epitomized insides using high energy gold (Au) ions in prior work [17]. Their research revealed that irradiation caused amorphization of the encapsulated nickel nano-rods by delivering limited defects via the tube walls. Other research used 1.3 MeV gamma rays to irradiate single-walled carbon nanotubes (SWNT) and graphite and then used Raman spectroscopy to evaluate the results [18]. Their study showed that irradiation produces surrenders in both systems. The Raman spectroscopy of MWNTs under electron irradiation was studied by Ritter et al. [19]. According to their study, irradiating MWNTs with 1.8 MeV electrons revealed both the shift and change the intensity of the vibrational mode under the influence of irradiation. While various methods of irradiation are generally used today to modify the properties of the material, the mechanism of their effects on CNTs has not yet been entirely implicit.

The Raman spectrometry (RS) technique is well-known for its ability to depict diamond nanostructures [20]. RS technique enables the observation of alteration kinetics as well as the collection of time-stamped data on structural changes during irradiation treatment. The occurrence of four bands characterizes this intense inquiry; two of them pertain to precise graphite structure, equal to in-plane optical phonon modes, and are termed G-and G′-bands, respectively, and are positioned about 1580 and 2700 cm^{-1}. The other peaks, known as the D-and D″-bands, are situated at 1350 and 2950 cm^{-1} respectively and are caused by intelligent spiral vibrations of six-atom rings. The (D) and (G) band intensities have both been used to indicate the chemical alteration of carbon nanotubes. The ratio of the D-and G-band Raman intensities may be used not only as a qualitative estimate of the number of defects in a carbon material but also as an indicator of the cleanliness of these nanostructures.

According to the current study, 100 keV He ion irradiation of MWNTs causes evident changes in the morphology of the CNTs surface, introduces flaws, and leads to amorphization at high fluences. In this study, we explore the imperfection configuration in MWNTs samples caused by He ions irradiation with unusual doses. The irradiation effects are investigated by efficient tools including RS and SEM. The feasibility of changing the wettability of MWNTs via 100 keV He ion irradiation was investigated.

2. Methods

2.1 *MWNTs preparation and irradiation*

As previously shown, MWNTs were made using the chemical vapor deposition (CVD) process [21]. The setup of the reactor consists of a 2.5 cm × 120 cm quartz tube, situated in a laboratory furnace. The system provided with a carrier gases supplier and a ferrocene catalyst solution disbanded in a hydrocarbon. The substrate for MWNTs growth is made of silicon plates and fixed into the middle of the working district inside the quartz tube. The evaporation of ferrocene in cyclohexane started in the first part of the tube at a temperature of 200°C (low-temperature zone). At 850°C, a stream of support Ar gas saturated with active vapor components passed through the high-temperature sector, where the active catalyst crumbles to a nano-sized metallic segment (Fe), which deposits on the silicon substrate, and the hydrocarbon decomposes to generate carbon. MWNT growth proceeds in this effective zone. The amendable growth factors are the gas carrier flow rates, the nourish rate of the active mixture and the zone temperature. On the silicon substrate, consistent MWNTs arrays up to 25 × 85 mm^2 were generated using the disclosed approach.

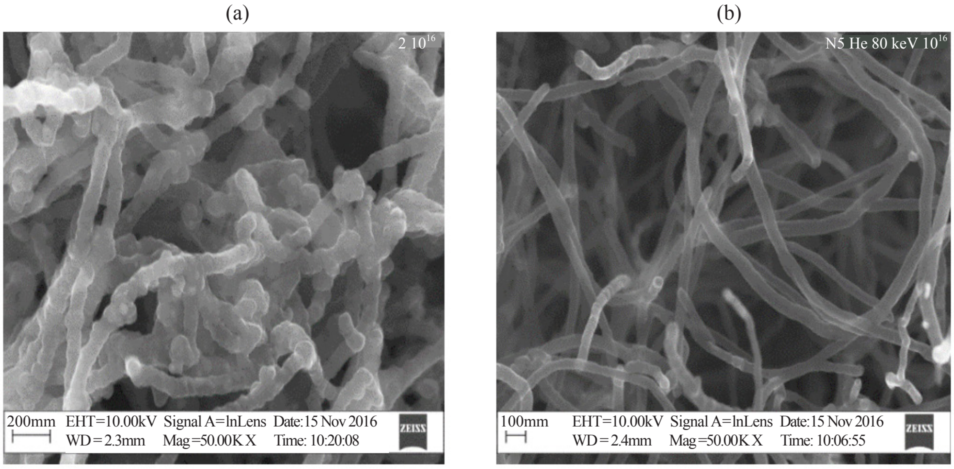
A scanning electron microscope was used to examine the raw and irradiated MWNT samples. It came with Digimizer software, which was used to determine the average tube diameter. The MWNTs attained by the previous methodology eradicated from the Si-substrate and smashed into powder structure. A pressure piston was used to compress the powder to obtain a round tablet having a diameter of 25 mm and a thickness of 4 mm, respectively [2].

The MWNT tablets were irradiated with 100 keV He ions at SINP MSU's (HVEEE-500 ion accelerator), with fluencies ranging from 5×10^{14} to 5×10^{16} ion/cm^2. During the irradiation, the sustained pressure within the accelerator chamber did not exceed 0.0002 Pa. Two arrangements of averting plates in a round chamber positioned in the beam procession after electrostatic triplet focal points, a generator, and a broad signal intensifier for electrostatic ion beam diversion in the two directions, (x) and (y), with a 103 Hz frequency were included in the ion ray examining apparatus. MWNTs are heated to roughly 1°C during the ion beam irradiation procedure.

The structure and chemistry of raw and ion beam irradiation MWNTs were studied using Raman spectroscopy and SEM methods. The SEM image analyzer was used to evaluate the normal diameter and diameter distribution of nanotubes. Micro-Raman (NTEGRA) Spectra using a blue laser of wavelength 473 nm, a 100× confocal magnifying apparatus, and a laser spot distance across of 2 μm were used to describe defect generation in the structure of MWNTs. The contact angle was calculated using the spontaneous emulsification approach with the following conditions: P = 1 atm pressure and room temperature. To conduct this estimation, we utilized high purity distilled water. A mechanical pipette was used to deposit water droplets onto the MWNT samples. The droplet shape was analyzed on a discernible picture obtained at the instant of placing the droplet onto the MWNTs surface to determine the contact angle.

3. Results and discussion

3.1 *The structural changes of raw and irradiated MWNTs*



(c) Typical external diameter = 65 nm

(d) Typical external diameter = 40 nm

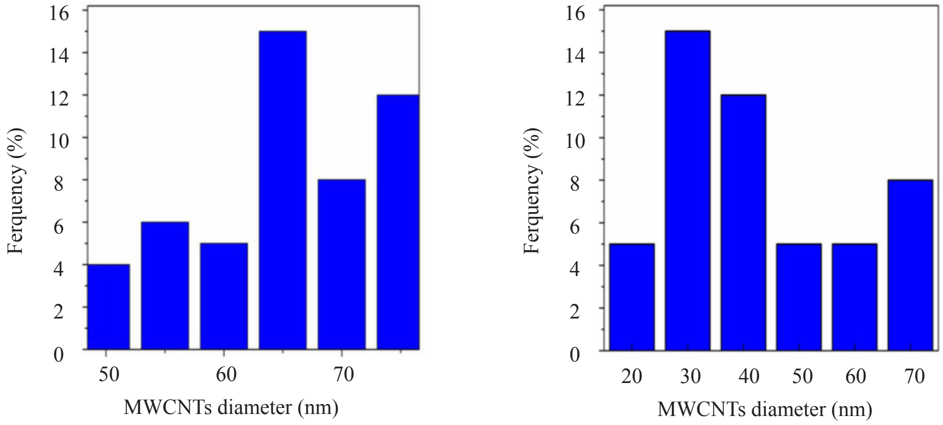


Figure 1. The SEM pictures demonstrating the structure and morphology of initially MWNTs (a), and the irradiated MWNTs (b). The average external diameter allotment of as grown MWNTs (c) and ion irradiated MWNTs (d)

The surface and morphology of MWNTs were investigated by SEM, Figure 1. Figure 1(a, b) shows pictures of two separate samples, one as grown and the other after being bombarded with 100 KeV He ion beams at a fluence of 5 × 10^{15} ions/cm^2. From the SEM pictures, we can observe that MWNTs have a lower average length, Figure 1(b). The tube boundaries are clearer than the pristine MWNTs shown in Figure 1(a). In addition, the exterior diameters of the tubes in the pristine and irradiated MWNTs were measured. Our investigation showed that the typical diameters of as grown MWNTs are around 65 nm, Figure 1(c), however, for irradiated one is 40 nm, Figure 1(d). Our findings showed that (Figure 1(c)) and 40 nm (Figure 1(d)) for ion irradiated MWNTs. These observations demonstrate that, on the average, the ion irradiated samples have misplaced their furthest walls followed by induced defect structure. The diminution of the MWNTs diameter could be explained by roughly, two unusual mechanisms, thermal heating effect and athermal effect which are the most postulated mechanisms as explained before in previous published work [20].

3.2 *The characterization of MWNTs by FTIR analysis*

The qualitative method of Fourier transform infrared (FTIR) spectroscopy is mostly used to assess the presence of functional groups. The FTIR spectra of MWNTs were measured in the region of 500 to 4000 cm^{-1} before and after He ion irradiation, as shown in Figure 2. In the irradiated MWNTs spectra, the hydroxylic group band, (-OH), at 3445 cm^{-1} and the carboxylic group (-COOH) peak at 1635 cm^{-1} seem to be more significant than those in the pure spectra of MWNTs.

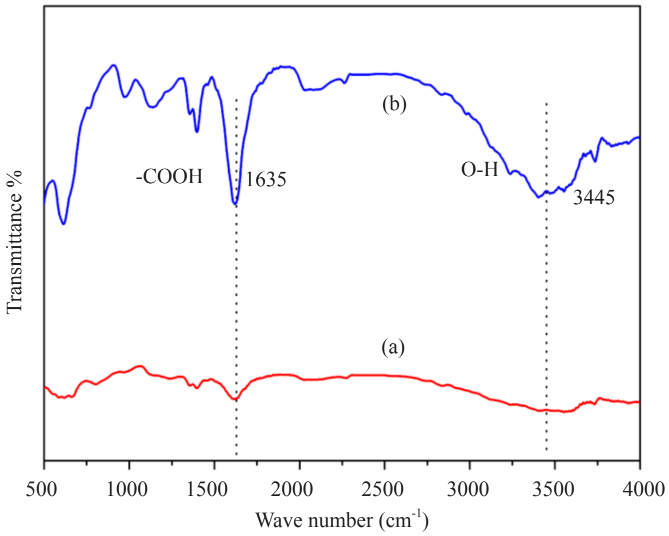
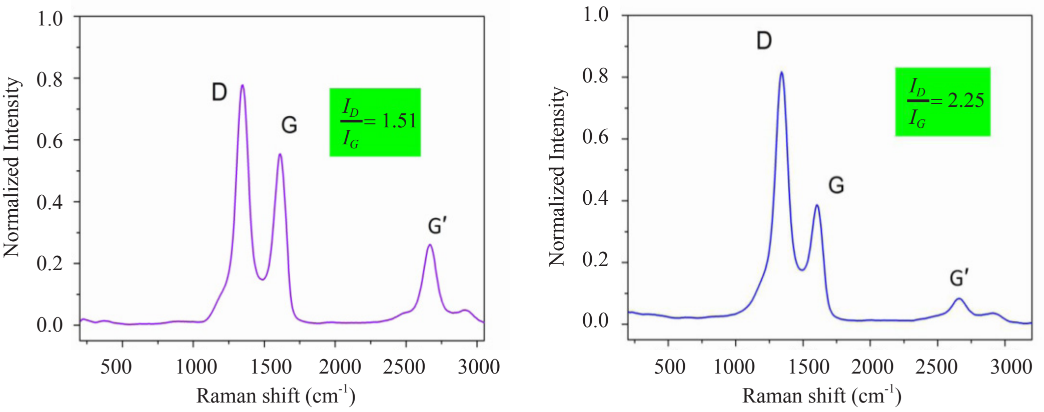


Figure 2. The spectra of FTIR technique of before irradiation MWNTs (a), and the MWNT sample irradiated with He ions (b) that showing the functional groups

3.3 *Investigating the Raman modes of as grown and irradiated MWNTs*

To account for the quality of MWNTs, the technique of Raman scattering is usually conducted [22]. Raman spectrum of as grown and irradiated MWNTs with a certain fluence of 1 × 10^{16} ions/cm^2 and radiation energy of 100 keV, were traced in the 100-3200 cm^{-1} range, are observed in Figure 3. The two most common characteristic bands in Raman spectra; named G- and G′-bands appeared approximately at 1580 and 2700 cm^{-1}, respectively, correspond to the crystallinity of graphite configuration, and correlate with the in-plane optical phonon modes. For the defect formation in the graphitic sheets, another band called D-band located approximately at 1350 cm^{-1} related to the defects, they begin from the six-atom rings' coherent radial vibrations. All these bands show a significant role in examining the arrangement and the morphology of nanotubes [22]. Both qualifying intensities of the D-and G-peaks are well-known markers of the number of structural deficiencies [23, 24]. After ion irradiation, the ID/IG proportion increased from 1.51 to 2.25, indicating that the experiment was successful, (Figures 3(a) and 3(b)). This rise in the ID/IG ratio indicates that defects and vacancies in irradiated MWNTs are increasing. The intensity of the other G′-band is different, which keeps our ongoing research. More graphite structure is associated with higher G′-band intensity, which is followed by a lower number of defects in non-irradiated MWNTs. The overall results of Raman spectroscopy demonstrate that following He ion irradiation, the crystallographic disorder of MWNTs is enhanced.



(a)

(b)

Figure 3. The analysis of Raman band intensities and the ID/IG of as grown (a), irradiated MWNTs by 100 keV He ions (b)

3.4 *The effect of irradiation fluences on Raman spectra*

Pristine and 100 keV He ions irradiated MWNT samples with fluence ranging from 5 × 10^{14} to 5 × 10^{16} (ions/cm^2) are recorded with the wavelength range from 500-3200 cm^{-1}, Figure 4. The relative strength of the D-to G-bands increases with increasing irradiation dosage, followed by the disappearance of the G′-band, which accounts for the crystalline arrangement of the tubes. Further increase in the fluence up to 2 × 10^{16} (ions/cm^2) causes the MWNTs to be more disordered. This might be due to the destruction of certain nanotube walls, Figure 4. The amorphization of MWNTs appears to be necessary for further raising the fluence up to 7 × 10^{16}, Figure 4. The current findings show that the quantity of ion beam irradiation specified is important in controlling defect development and MWNT transition to amorphization [25].

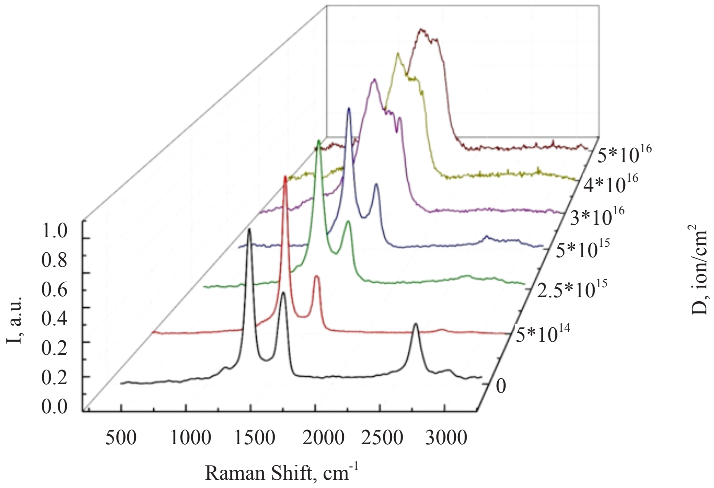
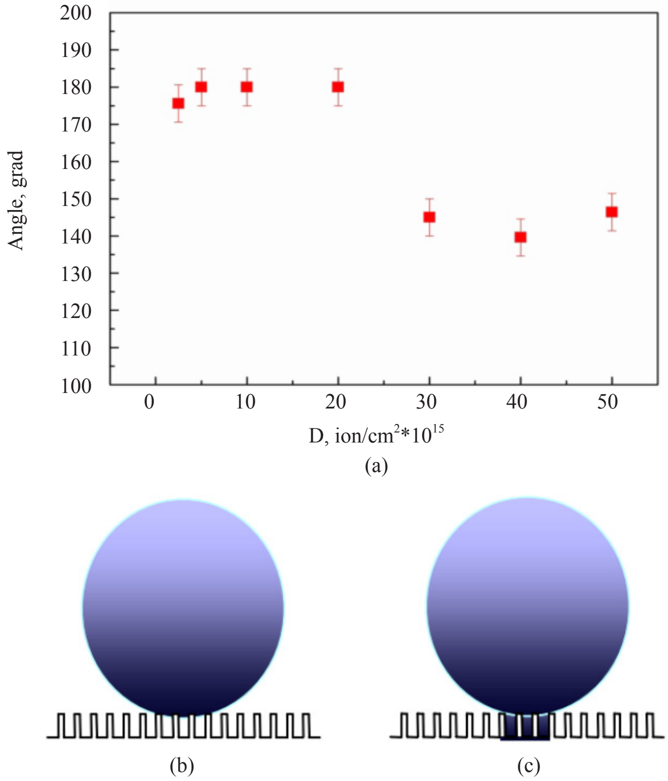


Figure 4. The MWNT Raman modes with the range 500-3200 cm^{-1} at various fluencies

3.5 *The effect Ion Irradiation on the Wettability of CNT*

The contact angle of the MWNT samples was measured before and after ion irradiation with varied fluences, and the contact angle for distilled water was significantly reduced Figure 5. For all studied liquids, a minor change in the contact angle is seen after irradiation with various fluences. At a fluence of 2 × 10^{15} cm^{-2}, a change in the wettability angle coincides with an increase in MWNT average diameter, an increase in oxygen content concentration, and a rise in the defectiveness of the MWNTs.



(a)

(b)

(c)

Figure 5. The contact angle variation with different irradiation fluencies as shown in (a), and the wettability of raw MWNTs (b), and ion irradiated MWNTs (c)

4. Conclusions

The effects of irradiating compressed MWNT samples with a 100 keV He ion beam were investigated. In the irradiated locations of the nanotubes, a noticeable increase in the D-to-G bands' intensity proportion in the Raman spectra verified the defect creation on the nanotube surface. Amorphization of the MWNTs demanded that greater fluences be used. The exterior diameters of the irradiated tubes are lowered on average, indicating that the MWNTs misplace their exterior walls owing to irradiation impacts, according to SEM image analysis. Optimizing the values of He ion fluences, it is possible to analytically eliminate the outermost wall of MWNTs. The contact angle for distilled water is reduced; the change in wettability with water is minimal at lower fluences. The MWNT average diameters in the analyzed samples have a direct impact on the contact angle variation for distilled water. Using ion irradiation, it is possible to modify the surface layer and affect both the filtration properties of the material and the filtration rate without introducing any impurities into the structure.

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