

Defects and Structural Analysis of Multi-Wall Carbon Nano Tubes via Ball milling and Cryo-milling

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Abstract

Nano fillers are part of new studies to enhance various properties of fluids and solids. For example, adding nanoparticles as an enforcement in nanocomposites or as an additive to improve thermal or electrical properties in nano-fluids are of extreme importance in science and industry. There are numerous methods to uniformly disperse nanoparticles in fluid and solid phase. One of the well-used techniques is utilizing ball mills. Milling method is treated widely to uniformly disperse Carbon Nano Tubes (CNTs) in solid or fluid state materials. However, the issue is that this method abolishes some part of CNTs' structure. As a result, this defect adversely decreases the improvement of designated properties. In this research, two methods of milling conditions have been analyzed to find out their impacts on CNTs' structure. The first method is milling Multi-Wall Carbon Nano Tubes (MWCNTs) in ambient temperature. On the other hand, in the second method the temperature dwindled to -196°C by Retsch new generation ball mills (Cryo-mill). This apparatus flows liquid nitrogen (LN₂) around the shaking jar and decreases the temperature as low as -196°C. To analyze the impact of these methods of milling on MWCNTs, Field Emission Gun-Scanning Electron Microscopy micrograph, X-Ray Diffraction, Raman Spectroscopy, and Thermo Gravimetric Analysis are scrutinized on MWCNTs' structure. In conclusion, all the aforementioned experiments provide sufficient support to implicitly convince that cryo-milling method has less defective impact on initial MWCNTs.

Keywords:

Ball mill, Cryo-mill, MWCNTs, Raman spectrometry, TGA, XRD

1. Introduction

Researchers have illustrated the exceptional properties and potential of differences in nanomaterials since the revolutionary article on

CNTs was published by Iijima around 25 years ago [1]. A single-wall Carbon Nano Tubes, i.e. a nanotube made of only one graphite sheet rolled-up in cylinder, has a Young's modulus as high as 1.8

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TPa and a tensile strength as high as 63 GPa [2], which is one to two orders of magnitude superior to the best ever-made steels. MWCNTs displays lower but still outstanding mechanical properties, and this is easier to synthesize. These outstanding physical properties combined with a low density provide several enhanced properties for CNTs as an additive to solid and fluid state materials. CNTs have a strong tendency to form bundles due to their own high aspect ratio and molecular van der Waals bonding [3]. This extensive agglomeration is detrimental for CNTs' composites or fluids physical properties. This agglomeration is one of the main drawbacks when trying to mix them with other materials as an additive [4].

In mechanical milling, a solid state high-energy ball milling process, particles are repeatedly fractured [5]. Meanwhile, this technology has been successfully used to uniformly disperse a variety of additives in nanomaterials [6-8]. However, different studies show that CNTs can be modified when milled alone, going from simple shortening [9-12] and to amorphization [13]. For example, Rabi et al used ball mill to work on purification and fictionalization of CNTs [14]. In addition, I. Z. Pappa implemented plenary ball mill to study nitrogen adsorption by MWCNTs [15]. Moreover, study of CNTs milling with metals, such as iron [16] or magnesium for hydrogen storage [17-18] indicate accelerated CNTs' damages [19]. Characterization of milled MWCNTs was studied using X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM).

There is a great deal of studies on ball milling and MWCNTs properties in different aspects, however, study on one important factor which is working temperature condition is not that much. In this research, we tried to reduce the milling temperature condition down to -196°C and find out the effects on MWCNTs' structural defection.

2. Experiments

RIPI¹ grads MWCNTs, which is produced by chemical vapor deposition (CVD), was used in this research. The purity of MWCNTs is 95% and their diameter is between 30–50 nm. Moreover, they are around 30 μm long. Fig. 1 shows Field Emission Gun-Scanning Electron Microscopy micrograph (FEG-SEM) picture of MWCNTs.

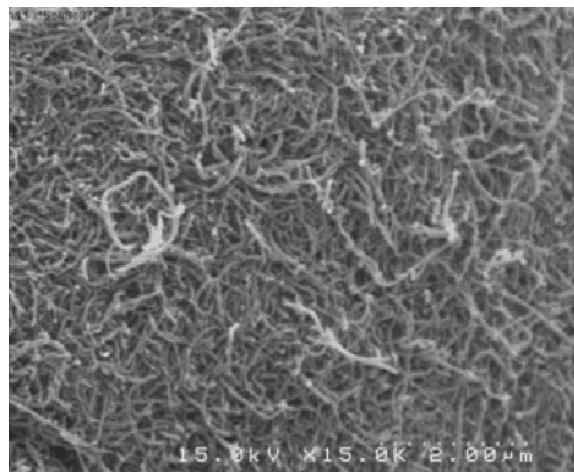


Fig. 1. Initial MWCNTs are clearly visible in the picture.
Scale: 2.00 micron

To study the reaction of MWCNTs after ball milling and cryo-milling *Retsch CryoMill* device was used. First sample was milled for 30 minutes in room temperature. Then, in the second test, LN_2 as a cooling system flowed around the shaking jar. This LN_2 reduces the milling temperature to the designated condition. In this method of milling, the grinding jar is shaken left and right with the frequency of 20 Hz. In addition, grinding jar becomes cold as low as -196°C via changing the state of LN_2 into gas which flows around the grinding jar in cryo-milling apparatus.

The impaction of the balls against the MWCNTs breaks them down, and results in milling sample. Steel balls and hardened jar were used in this study, and the ratio of balls to powder considered to be 100:1 which causes high number of impactions in a short time.

Morphology of the MWCNTs was analyzed using a Hitachi Field Emission Gun-Scanning Electron Microscopy (SEM). X-Ray Diffraction (XRD) characterizations of the MWCNTs were performed with a *PW1840* device type using $\text{Cu K}\alpha 1$ radiation, and Raman Spectra was explored with an *Almega Thermo Nicolet Dispersive*. The laser light wavelength in Raman test was 532 nm made by argon. Finally, the samples were scrutinized for thermogravimetric analysis (TGA) by *TGASDTA/851e mettle*.

3. Results and Discussion

3.1. Retsch CryoMill

One of the main purposes of cryo-mill is cryogenic grinding. The shaking jar is continually cooled by LN_2 (Fig. 2) from an integrated cooling system before and

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during milling process. The LN₂ circulates continually and fills the system automatically to keep the temperature at -196°C (Fig. 3). High energy ball milling brings about perfect grinding efficiency. The capability of this device is in the fields of biology, chemistry, engineering, pharmaceutical, etc. In addition, the main applications of this tool are categorized in size reduction, mixing, homogenization, and cell disruption. Depending on feed materials, this device is able to reduce the size up to 5 μm, and the shaking jar can be adjusted from 5 to 30Hz in dry, wet or cryogenic grinding conditions. It comes with hardened steel, stainless steel, or zirconium oxide jars with the capacity of 5, 10, 25, 35, and 50 ml [20].



Fig. 2. The picture a cooled jar

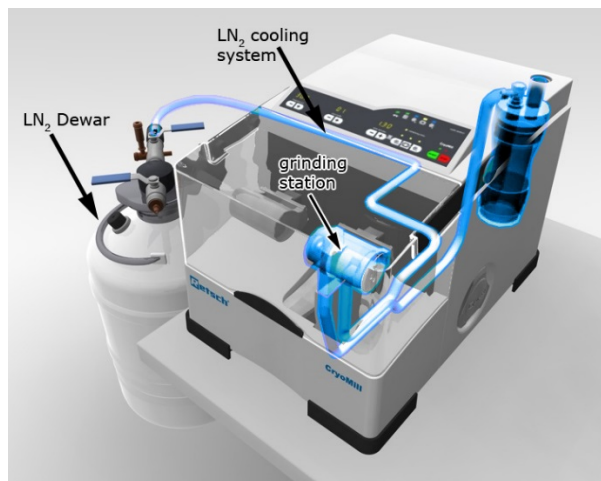


Fig. 3. Retsch CryoMill and LN₂ auto cooling system

3.2. Field Emission Gun-Scanning Electron Microscopy Micrograph

The morphology of initial, ball milled, and cryo-milled MWCNTs has been studied using Scanning Electron Microscopy (SEM). Morphology plays an important

role in determining the structure of MWCNTs. The SEM images of initial, ball milled and cryo-milled MWCNTs are depicted in Fig. 4-6, respectively. The initial MWCNTs is long and smooth. On the other hand, the milled one seems shorter, damaged, and more agglomerated. In other words, milling condition brings about compacted MWCNTs [21].



Fig. 4. Initial MWCNTs micro structure Scale: 500 nm

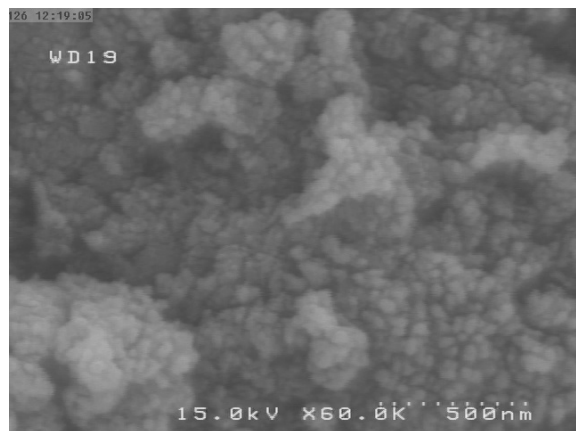


Fig. 5. Ball milled MWCNTs micro structure Scale 500 nm

3.3. X-Ray Diffraction Discussion

X-Ray can be made from different sources such as X-Ray generator or synchrotron equipment [22]. The wavelength depends on the metal used in anode. For the copper, this is 0.154 nm. The most well-known and simplest scattering theory is Bragg Law. By considering crystals reflection layers for x-Ray, W.H. Bragg applied following equation:

$$d = n\lambda / 2\sin\theta \quad (1)$$

where λ is the wavelength of the X-ray beam, 2θ is the scattering angle, n is an integral number, and d represents the distance between successive crystal

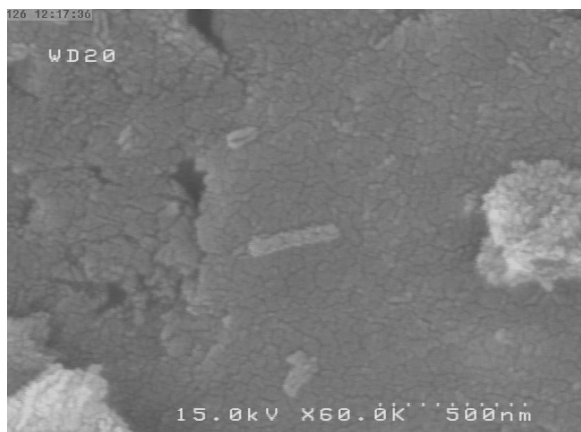


Fig. 6. Cryo-milled MWCNTs micro structure Scale: 500 nm

planes of atoms. Scheme to derivate the Bragg law is shown in Fig. 7.

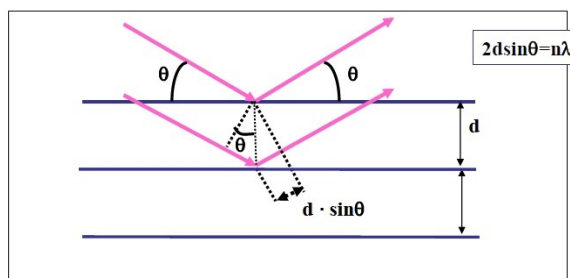


Fig. 7. The Bragg law. X-rays (arrows) are reflected by crystallographic planes separated by a distance d

The Miller index (hkl) defines different crystallographic planes in a crystal. These three integral numbers are linked to the related values of the intersection of a given plane with the crystallographic unit cell axes [19]. If the sample is a single crystal, the diffraction pattern is made of a series of spots corresponding to a particular plane in the crystal matrix [19]. However, many materials are not single crystal. Therefore, in a polycrystalline state, the diffraction spots change into circles because the sample has different orientation of the crystallites. When an X-Ray beam reaches the sample and is reflected, beams with different intensity are detected. Then, the diffraction pattern can be obtained as a graphic of the diffracted intensity versus either the s -vector ($s=2\sin(\theta)/\lambda$) or the q -vector ($q=2\pi s$) or even versus 2θ [23].

X-ray diffraction graphs were obtained for the initial, ball milled and cryo-milled MWCNTs to evaluate the effects of ball milling and cryo-milling on the MWCNTs structure. The peak at around 26° is similar to graphite layers peak and shows the spacing

of 0.34 nm between the tubes of the MWNTs (Fig. 8). The intensity in cryo-milled MWCNTs is more than ball milled sample. In addition, this peak is wider in ball milled MWCNTs (Fig. 9). It means that, the tubular structure is conserved better in cryo-milling rather than ball milling [5, 18, 24, 25, 26].

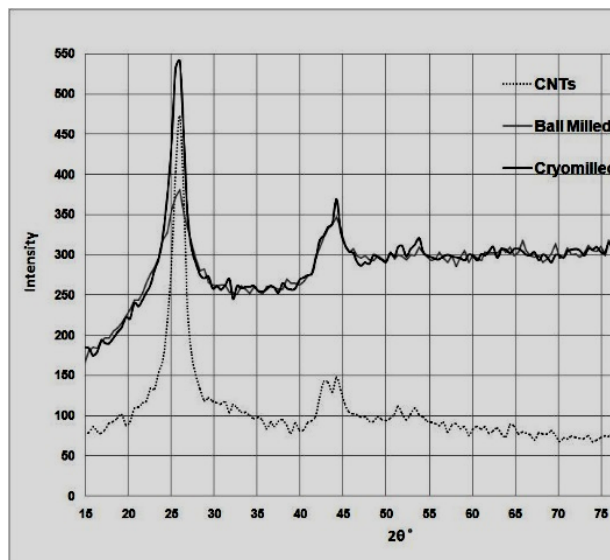


Fig. 8. X-Ray Diffraction of Initial, Ball milled, and Cryo-milled MWCNTs

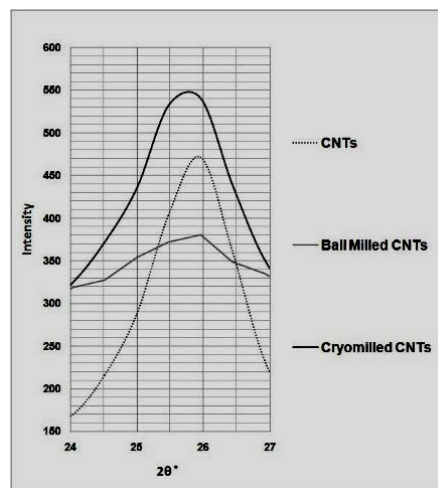


Fig. 9. Magnification of the peaks of Initial, Ballmilled, and Cryo-milled MWCNTs at 26°

3.4. Raman Spectroscopy

The Raman spectra for initial, ball milled and cryo-milled MWCNTs are indicated in Fig. 10. The first order peaks of the D band is around 1350 cm^{-1} , and the G band is almost located at 1580 cm^{-1} [27, 28]. Sites of sp^2 bands cause D and G bands. The

breathing modes of sp^2 atoms in rings causes D band, and stretching of all pairs of sp^2 atoms in chains and rings causes G band [29]. Undamaged hexagonal graphite makes The G band sharper. Therefore, defect in MWCNTs makes the G band peaks wider and shorter. As a result, based on G band, it can be concluded that cryo-milled MWCNTs with an intensity of 115 has less undamaged hexagonal structure compared to ball milled one with the intensity of 100.

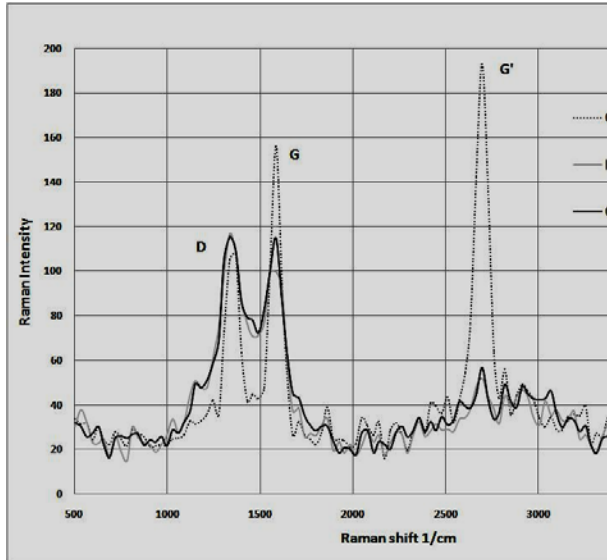


Fig. 10. Raman Spectroscopy of Initial, Ball milled, and Cryo-milled MWCNTs

Moreover, D band peak represents lattice defects and finite crystal size which cause a breaking of the 2D translational symmetry (Fig. 11); as a result, it will increase and become wider via raising number of defects [28]. Therefore, according to D band intensity, ball milled (117) and cryo-milled (115) ones, both, have more lattice defects compared to the initial MWCNTs. G' band is like D band, at around 2700 cm^{-1} Raman Shift. This band is decreasing with milling and represents amorphous defect as well [28] (Fig. 12).

The ratio of D Band to G band intensities (ID/IG) can identify quantified factor of defect which are calculated in Table 1. Thus higher creation of lattice defects increases, the D band peaks while the G band is decreased. Wider D and G peaks with milling show more amorphous defect in MWCNTs structure [30]. According to ID/IG as a factor of defectiveness, therefore, it is easy to estimate that the defect of cryo-milled MWCNTs is around %48; however, it is around %72 for ball milled MWCNTs

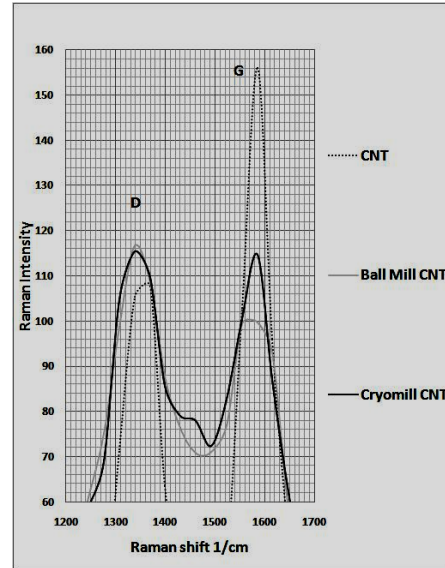


Fig. 11. Magnification of Peaks D and G

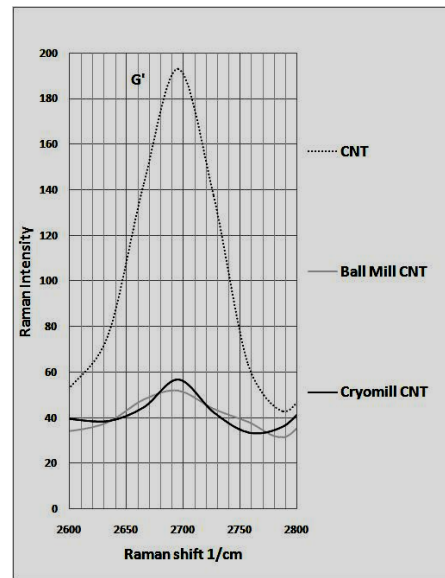


Fig. 12. Magnification of G'

In brief, scrutinizing D, G, and G' bands intensities, all of the peaks prove that ball mill in ambient temperature has more adverse impact on MWCNTs structure compared to cryo-mill.

3.5. Thermogravimetric Analysis

Thermogravimetric analysis was tested under synthetic air for initial, ball milled and cryo-milled MWCNTs and their corresponding results are depicted in Fig. 13. Different carbon structures have different oxidation behaviors. As a result, TGA and DTG studies are

Table 1. Raman spectra characteristics of Initial, Ball milled and Cryo-milled MWCNTs

Band	D	G	G'	Ratio ID/IG			
Milling type	<i>position (cm⁻¹)</i>	<i>ID</i>	<i>position (cm⁻¹)</i>	<i>IG</i>	<i>position (cm⁻¹)</i>	<i>IG'</i>	
Initial CNTs	1354	108	1583	157	2692	195	0.68
Ball milled CNTs	1338	117	1569	100	2696	052	1.17
Cryo-milled CNTs	1343	115	1592	115	2696	057	1.00

useful to understand carbon structure presenting in the carbonaceous material. Amorphous carbon starts burning at lower temperature because of lower activation energy for active sites and open bonds [31-36]. The oxidation range of amorphous carbon structure is less than 450°C [35-37]. While MWNTs sample oxidation starts from 590°C and ends at 885°C. In this analysis, initial MWCNTs start burning at around 590°C and end at 885°C (Table 2) which is compatible with other works in [38]. It resulted in %93.7 of losing weight during TGA. This lost weight can be quantified to the purity of MWCNTs (Table 3).

TGA on ball milled MWCNTs shows that oxidation starts at 390°C and ends at 775°C. As a result, weight analysis estimates that this structure is composed of %51.3 Amorphous Carbon or other Carbon Structures, %39.5 MWNTs, and %9.2 Unburned Structures.

On the other hand, in cryo-milled structure, oxidation starts at 430°C and ends at 830°C. Therefore it is obtained that %36 Amorphous Carbon or other Carbon Structures, %55.5 MWCNTs, and %8.5 Unburned Structures are synthesized. In other words, MWCNTs in cryo-milled sample is %55.5 which is

almost %16 more than that of ball milled one (Table 3). Overall, ball milling has adverse effects on MWCNTs structure since bonding between Carbon atoms is broken during milling and open bonds are created [34-36].

However, the TGA provide another proof that defect of MWCNTs via cryo-milling is less than ball milling.

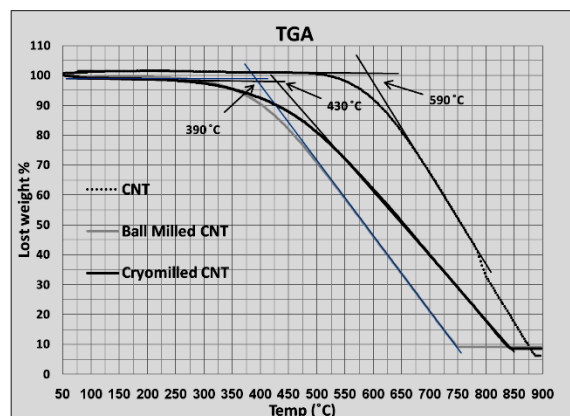


Fig. 13. thermogravimetric analysis the Initial, Ball milled and Cryo-milled MWCNTs

Table 2. Oxidation start and end points of Initial, Ball milled and Cryo-milled MWCNTs in TGA

MWNTs	Oxidation Start Point °C	590
	Oxidation End Point °C	885
Ball milled CNTs	Oxidation Start Point °C	390
	Oxidation End Point °C	775
Cryo-milled CNTs	Oxidation Start Point °C	430
	Oxidation End Point °C	830

Table 3. Weight ratio of different structures in Initial, Ball milled and Cryo-milled MWCNTs

Temperature Range °C	weight %		
	CNTs	Ball milled CNTs	Cryo-milled CNTs
Amorphous Carbons Oxidation or Other Carbons Structures temp. $T \leq 590$ °C	-	51.3	36
MWNTs Oxidation temp. 590 °C $\leq T$	93.7	39.5	55.5
Unburned Structures	6.3	9.2	8.5

4. Conclusions

Shortened MWCNTs should be easier to disperse but it changes its own physical properties [39-42]. Milling has been used as an effective way to uniformly disperse MWCNTs [19, 40, 43]. For example, nanocomposites or nanofluids are fields of study that deal with dispersion of nanoparticles, such as MWCNTs. Less defective dispersed MWCNTs directly affect physical property of nanocomposites or nanofluids, which comes from MWCNTs' behavior. To enhance dispersion with less defects, all aforementioned experiments prove that ball milling damages MWCNTs to amorphous structure more than cryo-milling. In high energy ball mills, the impaction between balls and jar generates an immense instant amount of thermal energy. This local impaction energy is high enough to damage the MWCNTs structure and increase free bonding between carbon atoms [34, 35]. Changing the phase from liquid to gas in LN₂ can absorb thermal energy resulted from impaction in the system during ball milling. Although, reduction in temperature via cryo-milling increases the brittleness of the material, absorbing massive generated energy brings about less deflection due to high temperature. Another study which was investigated by J.H. Lee et al. shows the same trending results on X-Ray diffraction and Raman Spectroscopy in cryogenic condition on MWCNTs, and these trends and results are correlated with our study [25].

Consequently, as it is shown qualitatively and qualitatively in Field Emission Gun-Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Raman spectrometry, and thermogravimetric analysis (TGA), the amount of amorphous carbon is highly likely to reduce in cryogenic condition. In other words, the TGA result shows that defects after ball milling the MWCNTs is almost %51.3 which is %15.3 more than that of cryo-milled sample. Similarly in Raman spectrometry, ratio of ID to IG which is a factor of impurity in MWCNTs estimates that defectiveness in cryo-milled MWCNTs is 1.00 while it is 1.17 for the ball milled one.

Accordingly, wrapping up these results which have same trends with other studies, it is concluding that cryo-mill is less defective than ball mill.

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