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ADVANCED NANOMETROLOGY TECHNIQUES OF CARBON NANOTUBES CHARACTERIZATION

It has become evident that carbon nanotubes (CNTs) possess exceptionally high physical, mechanical, electrical, and structural properties that made them attractive for researchers to investigate. In this paper, CNTs synthesized by submerged DC arc in deionized water were subjected to six different characterization techniques in order to have an insight into their intrinsic properties. Stages of CNTs growth scenario during their synthesis were captured by Transmission Electron Microscopy (TEM). Images of Scanning Tunneling Microscopy (STM) depicted the spaghetti-like nature of nanotubes sized in the range from 6 to 8 nm diameters with bends and kinks observed. Transmission Electron Diffraction Microscopy (TEDM) images declared the purity of the synthesized CNTs. Also, Fourier Transformation Infra Red (FTIR) spectrum analysis depicted the transmittance and frequency band widths of peaks relevant to the functional groups. In addition, Raman spectrum analysis disclosed the G and D modes with no radial breathing mode (RBM) for a random sample of the synthesized CNTs indicating some defects, strain, oxidation stated of the SWCNTs with the possibility of multiwalled carbon nanotubes existence as well. Thermo Gravitric Analysis (TGA) reflected the thermal stability of the synthesized CNTs as they sustained temperatures approaching almost 1000°C. Thus, it can be concluded that the used techniques proved to successfully characterize the synthesized CNTs, so that they can be reasonably nominated for suitable potential application.

Keywords: Nanometrology, CNTs characterization, STM, TEM, TEDM, FTIR, Raman spectroscopy, and TGA.

1. INTRODUCTION

CNTs have been subjected to extensive investigation over the past decade due to their discovered attractive structural features and amazing properties [1]. CNTs have fascinated researchers worldwide as it has been confirmed that their nano-scale dimensions with high aspect ratio, together with their structural geometries has resulted in

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exceptionally high intrinsic mechanical and electrical properties [2]. Compared to the known conventional materials, CNTs are characterized by light weight, high mechanical strength, controllable electrical and thermal conductivities, as well as chemical and thermal stability. Thus, CNTs are recognized as the ultimate carbon fibers for high performance, multifunctional, and structural nanocomposites [3]. They have great potential for many novel applications; such as ultra strong wires, nano-electronic devices, field electron emitters, nanoprobes, nanocomposite materials, and more [4-7].

CNTs are seamless hollow cylinders composed of rolled graphene sheets either in the form of single-walled (SWCNTs) or multi-walled (MWCNTs) configurations [8-9]. Within the same sample of SWCNTs, there exists a distribution of diameters and atomic structural geometries such as armchair, zigzag, and chiral. Each tube consists of two separate regions with different physical and chemical properties. The first is the sidewall of the tube and the second is the end cap. The end cap structure is similar to or derived from a smaller fullerene, such as C_{60} where carbon atoms are arranged in hexagons and pentagons to form the end cap structures. It can be easily deduced that twelve pentagons are needed in order to obtain a closed cage structure; another five pentagons or hexagons form the desired curvature of the surface [5, 10]. The combination of a pentagon and five surrounding hexagons results in the desired curvature of the surface to enclose a volume.

MWCNTs can come in an even more complex array of forms, because each concentric single-walled nanotube can have different structures, and hence, there are a variety of sequential arrangements. The simplest sequence is when concentric layers are identical, but different in diameter. However, mixed variants are possible, consisting of two or more types of concentric CNTs arranged in different orders [2, 6].

CNTs may be synthesized by arc discharge [11-14], laser ablation [15-19] or chemical vapor deposition processes [20-23]. The main idea is to apply an intensive amount of energy to a carbon source (gas or solid), within an inert medium (gas or liquid). Thus, the resulted high temperature causes the carbon target to evaporate and hence CNTs starts to nucleate, grow up, precipitate on a collector, and purified afterwards if needed. The structure of the nanotube influences its properties including electrical and thermal conductivity, density, and lattice structure. The larger the diameter of the nanotube, the more it behaves like graphite. On the other hand, the smaller the diameter of the nanotube, the more its intrinsic properties depending on its specific type. Bulk production of CNTs often results in a dense entangled network of nanotube bundles. Thus, separation of CNTs bundles, their dispersion, and their alignment are elementary crucial problems in practice. Characterizing the CNTs becomes therefore mandatory before recommending them for a reasonable use.

The objective of the present paper is to focus on characterizing CNTs produced by an adopted simple technique (submerged DC arc in water) [11-14]. Scanning Tunneling Microscopy (STM), Transmission Electron Microscopy (TEM), Transmission Electron Diffraction Microscopy (TEDM), Fourier Transformation Infra Red (FTIR) and Raman

Spectroscopy, and Thermo Gravimetric Analysis technique (TGA) have been applied for the sake of characterizing the synthesized CNTs.

2. SYNTHESIS OF CNTs

Carbon nanotubes are generally produced by three main techniques namely; arc discharge, laser ablation, and chemical vapor deposition. DC arc-discharge seems to be the most commonly used method to produce carbon nanotubes in water [11-14]. It is a technique that proved to economically produce high yield of pure carbon nanotubes which do not require post costly micro-filtration process afterwards.

Therefore, arc discharge technique has been adopted throughout this experimental work in which the arc was triggered between extra pure graphite electrodes submerged to a depth of 3 cm in distilled water where the gap in-between was maintained fixed at 1mm. The anode was 3 mm diameter while the cathode was 12 mm diameter. A current intensity up to 60A through a potential of 24v was applied. The forwarded plasma to the anode was found to be stable as long as the gap was being maintained fixed during experimentation. The arc-discharge in this case can be referred to as anodic because the anode was the smaller one which was consumed more during the process. Purification of CNTs refers to the processes used to separate the CNTs from other unwanted entities and species. A centrifugal apparatus designated (Hermle Z-230) with a variable speed range from 0 up to 5500 rpm and 60 minutes timer was used for this purpose. The purification was achieved by successive separation and decantation by using the centrifugal effect over four successive steps with incremental speed increase in each step. Eventually, the separated carbon nanotubes were dried and subjected to the following different characterization techniques to have an insight into their intrinsic properties.

3. CNTs GROWTH MECHANISM

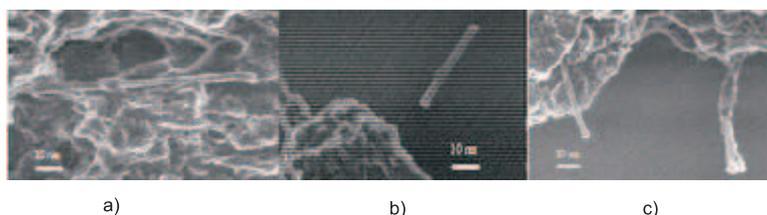


Fig. 1. TEM images illustrate the growth mechanism of CNT.

Fig. 1 shows TEM images disclosing the growth mechanism of carbon nanotubes in different stages and time intervals of plasma discharge. Fig. 1a depicts a rod like tubes

coming out of its carbon mother base which may be considered incomplete growth stage of carbon nanotubes. Fig. 1b shows the start of the separation of a CNT from its base after completion of their growth, while Fig. 1c exposes a completely separated CNT of which its length and diameter could be assessed.

4. NANOMETROLOGY MEASUREMENTS

The synthesized CNTs were characterized and morphologically inspected using nanometrology measuring devices such as Scanning Tunneling (STM), Transmission Electron (TEM), and Transmission Electron Diffraction (TEDM) Microscopy. In addition, Fourier Transform Infra Red (FTIR) and Raman spectrum analysis, and Thermo Gravimetric Analysis (TGA) techniques were used as well.

4.1. Scanning Tunneling Electron Microscopy (STM)

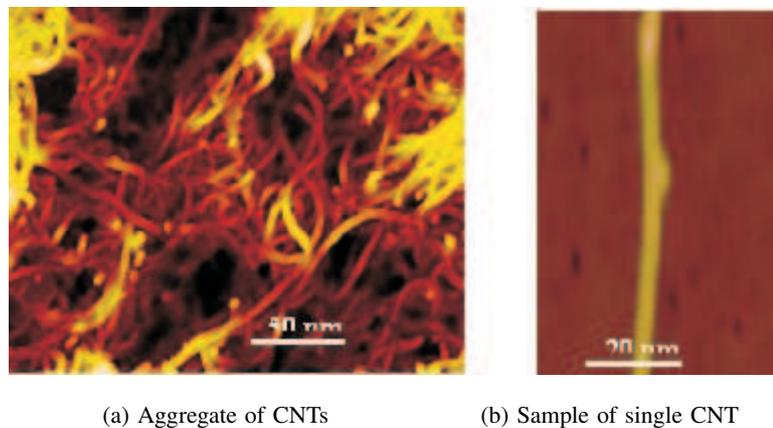


Fig. 2. STM images for carbon nanotubes suspended and coated on Au III.

Carbon nanotubes sample was prepared for STM by spin coating of CNTs suspension on Au III substrate. Fig. 2a shows the STM image of a bulk CNTs sample where the image depicts nonaligned spaghetti like tubes having bends with different angles and lengths which can be well determined. The tubes are averaged to be of 7 nm diameter and a few micrometers of length. The kinks and bends depicted in the image can be explained by either the mechanical nature of CNTs or its structural deformation. The deformations may arise from the insertion of a pentagon–heptagon pair in the hexagon network [18]. The length of the tube could not be precisely measured while its diameter could be assessed with reasonable accuracy and found equal to 7 nm on the average.

Fig. 2b shows a single tube with a knee-like in its middle. The disclosed knees and bends in Fig. 2 agree well with some other research findings [19].

4.2. Transmission Electron Microscopy (TEM)

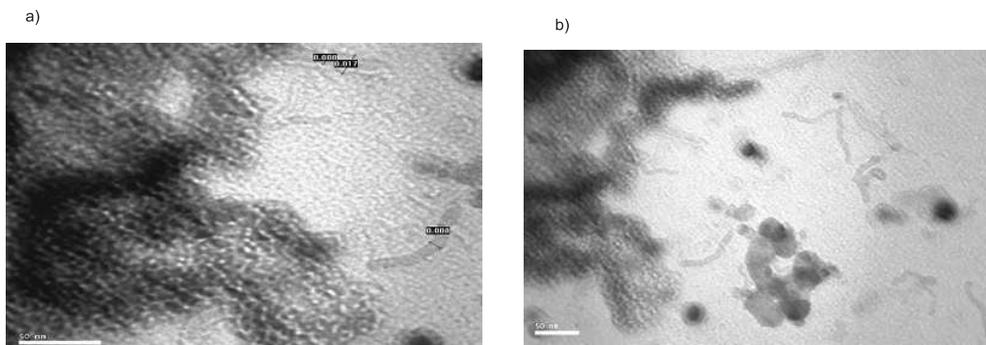


Fig. 3. a) TEM image of CNTs of different sizes; b) TEM image shows bends and kinks in CNTs.

Samples of carbon nanotubes were sonicated in de-ionized water and then put on a copper grid and allowed to dry slowly. Fig. 3a illustrates the TEM image for purified and dried samples of carbon nanotubes. A honey-comb arrangement is depicted through most of these samples with a few single tubes observed. The length of the tubes was found to be between 60-80 nm and the diameter was 7 nm on the average, as shown in Fig. 3b. The tubes showed kinks and bends at angles of 60° to 90° . Honey-comb like structure of orientation of carbon nanotubes agglomerates due to the charge intensity on its surface. This can be explained by the hexagonal arrangement of graphite layers made of carbon nanotubes. Tubes of the same sort of orientation of the honey-comb like have been found by other researchers [20-21].

4.3. Transmission Electron Diffraction Microscopy (TEDM)

The diffraction pattern of TEDM image was used to identify both the diameter of the tube and its chirality vector. The diameter was determined from the equatorial oscillation, and the chiral angle is determined by measuring the distance from the different lines to the equatorial line. While it was possible to obtain the diffraction pattern of the carbon nanotubes images, it was not possible to obtain the diffraction lines [22].

Fig. 4 depicts the TEDM image of the CNTs sample deposited on a copper grid as aforementioned in the TEM sample preparation. The shown sharp and clear light spot indicates that the sample is free of any contaminating crystalline or amorphous

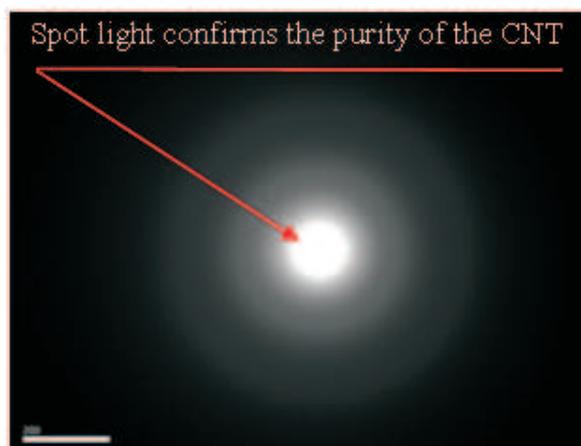


Fig. 4. TEDM electron diffraction of CNTs.

traces. The obtained image resembles a reported data of multi-walled carbon nanotubes (MWCNT) [23]. It is recalled here that the CNTs sample has been synthesized by the arc discharge method in absence of any catalyst or undesirable materials and then post centrifugal purification was performed. This explains the disclosed relative purity of carbon nanotubes in the obtained TEDM image of Fig. 4.

4.4. FTIR Frequency Spectrum Analysis

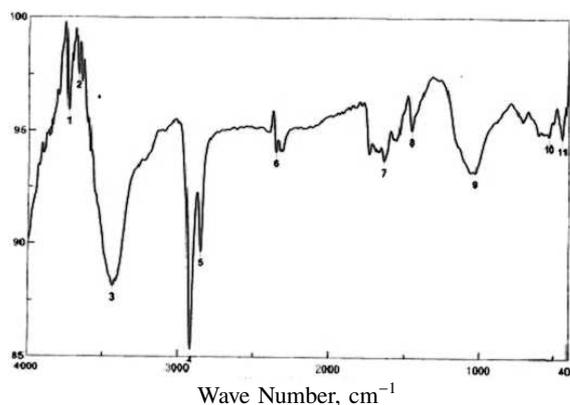


Fig. 5. FTIR spectra of functionalized carbon nanotubes.

Carbon nanotubes were dispersed in KBr by tweezers and then functionalized as they were exposed to IR beam of wave length range from 400 to 4000 cm^{-1} . Fig. 5 depicts the Fourier Transform Infra Red (FTIR) spectrum which contains eleven peaks

of transmittance percentages with the corresponding band widths and its functional groups described in Table 1.

Table 1. Characteristics of FTIR functionality groups of CNTs.

Peak No.	Bands, cm^{-1}	Transmittance, %	Functional Group	Remarks
1	3731.58	95.93	O-H (Stretch)	W, Sh
2	3667.94	97.53	O-H (Stretch)	W, V
3	3435.56	88.14	N-H (Stretch)	M
4	2921.63	85.37	C-H (Stretch)	S
5	2852.20	89.68	C-H (Stretch)	S
6	2353.69	94.10	C \equiv C (Stretch)	W, Sh
7	1643.05	93.72	C=H (Stretch)	M, W
8	1455.99	95.07	C-H (Bending)	W
9	1037.52	93.24	C-O (Stretch)	M, Br
10	539.97	94.83	C-H (Bending)	W, V
11	440.66	94.72	C-H (Bending)	W, V

W: weak, M: medium, S: strong, Sh: sharp, Br: broad, and V: variable.

4.5. Raman Spectroscopy

Fig. 6 discloses the Raman spectrum of a random sample of the synthesized CNTs. The Raman test was carried out at room temperature in range of Raman shift of 100 to 1800 cm^{-1} by Raman spectroscopy system (HORIBA Jovin. Yvon, LabRAM HR-800) available at Venture Laboratory, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan. Argon ion laser at laser excitation wavelengths of 488 and 633 nm corresponding to excitation energies of 2.54 and 1.96 eV respectively was used. These two energy levels were adopted as they usually point at metallic and semiconducting laser-generated SWNTs, respectively. The first excitation wavelength of 633 nm (1.96 eV) did not reveal a clear spectrum, whilst, the excitation wavelength of 488 nm (2.54 eV) produced the spectrum shown in Figure 6. The regular D and G modes were detected at Raman shift ranges of 1300-1400 cm^{-1} and 1500-1650 cm^{-1} , respectively. The relatively exposed low ratio of D/G modes and the absence of the radial breathing mode (RBM), which is usually expected at the range of 100-300 cm^{-1} for the SWCNTs, may be interpreted by the possibility of multiwalled CNTs existence in the sample. In addition, defected SWCNTs in the test sample may also be present.

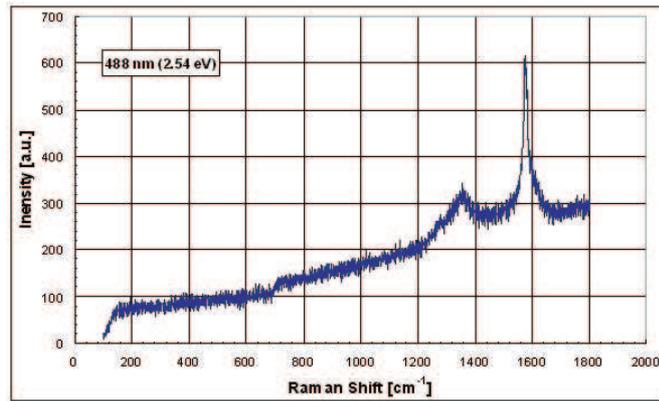


Fig. 6. Raman spectroscopy of CNTs.

4.6. Thermo-Gravimetric Analysis (TGA)

The thermal stability of the synthesized carbon nanotubes samples was assessed by the TGA analysis technique. Fig. 7 discloses the weight loss percent due to the thermal degradation while heating up the test sample in an inert gas (nitrogen), at a constant rate of $10^{\circ}\text{C}/\text{min}$. The TGA results shown in Fig. 7 are also tabulated in Table 2 in which the degradation temperatures corresponding to weight percent loss values of 10, 20, 30, 50, 70, and 80% have been found 579.91 , 631.26 , 671.27 , 721.75 , 780.99 , and 859.85°C , respectively. In other words 20% of the test sample, representing 0.7192 mg, has endured as the temperature reached 859.85°C . This residual 20% of the sample may indicate some impurities existence.

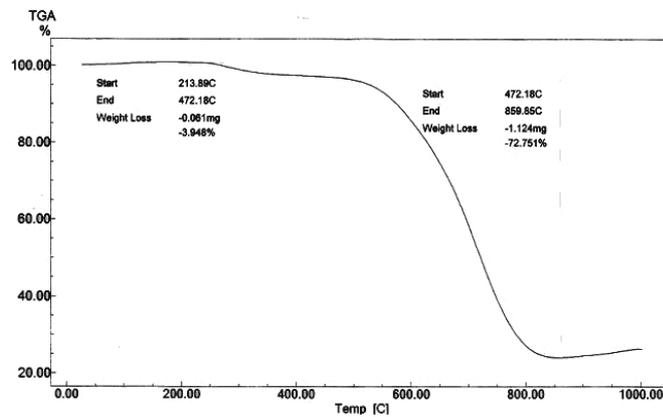


Fig. 7. TGA curve for proposed CNTs.

It can be concluded from both Table 2 and Fig. 7 that the thermal stability of the test sample of the synthesized CNTs is relatively high as it sustained a temperature rise up to 989.52°C. Fig.8 shows the TGA curve together with its time derivative to disclose the peaks which correspond to the characteristic degradation temperatures of the constituents of the test sample. Two Peaks are observed; the first is at about 283.5°C attained after about 25 minutes from the start of the heating program, while the second is attained at 714.5°C after about 68.3 minutes. The first may be a characteristic temperature of some associated impurities and the second may be related to the start of degradation of the CNTs themselves.

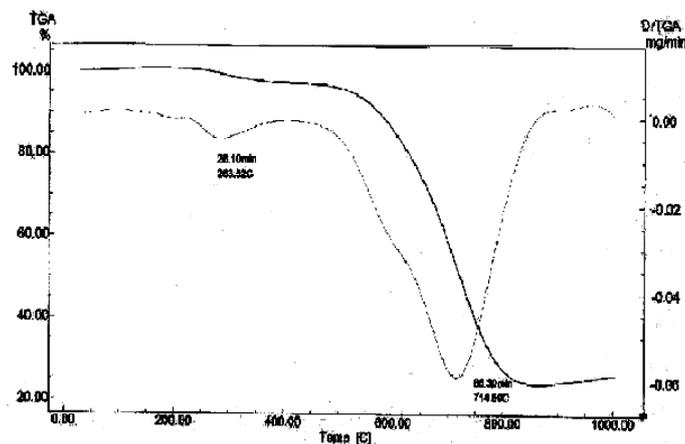


Fig. 8. TGA and its derivative (DrTGA) curves for CNTs.

Table 2. TGA results of CNTs.

Weight loss, %	Temperature, °C
10	579.91
20	631.26
30	671.27
50	721.75
70	780.99
80	989.52

5. CONCLUSION

Experimental nanometrology techniques have been proposed to characterize CNTs synthesized by submerged DC arc discharge in deionized water technique. The following conclusions have been drawn:

CNTs were characterized by Scanning Tunneling Electron Microscopy (STM) that depicted spaghetti-like tubes sized in the range from 6 to 8 nm in diameter with bends and kinks observed.

Transmission Electron Microscopy (TEM) was applied to have an insight into the growth mechanism of the CNT during its synthesis process until it became completely separated from its mother graphite base. In addition, TEM images illustrated the honey comb arrangement of the CNTs and the tubes sizes.

Transmission Electron Diffraction Microscopy (TEDM) images depicted a bright clear spot indicating the relative purity of the synthesized CNTs.

Fourier Transform Infra-Red (FTIR) spectrum analysis exposed the characteristic transmittance of the peaks corresponding to the absorption band widths of the functional groups of the synthesized CNTs.

Raman spectrum analysis disclosed a relatively low ratio of D/G modes with the absence of radial breathing mode (RBM) in the resulted trace. This can be explained by the possibility of MWCNTs existence in the sample, and/or defected SWCNTs possible presence.

Thermal analysis of the synthesized CNTs has also been performed using the Thermo Gravimetric Analysis technique (TGA). The CNTs have been found to start burning at about 714.5°C and they could sustain a temperature as high as 989.52°C, leaving 20% mass residue.

The used characterization techniques proved to successfully evaluate the synthesized CNTs, so that they can be reasonably proposed for suitable potential application.

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