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# QUALITY ASSESSMENT OF CARBON NANOTUBES: CHOOSING CHARACTERIZATION METHOD

***Abstract:*** Properties of carbon nanotubes (CNTs) have been drawing attention of scientists since its discovery in 1991 by Iijima. Different types of CNTs can be synthesized by various methods and catalysts. These methods and materials affect to the properties of CNTs. Furthermore, purification and functionalization processes of CNTs also have important effect on the structure of these nanomaterials. There are plenty characterization techniques such as electron microscopy, X-ray diffraction, Raman spectroscopy to investigate the structure of CNTs. In this paper, these methods are summarized by explaining the interesting features for each technique. The aim is to facilitate the selection of characterization method for quality assessment of CNTs.

***Keywords:*** *Carbon Nanotubes, Characterization, Quality*

## 1. INTRODUCTION

Nanotechnology has become prevalent with its all-inclusive range of disciplines that are progressively important nowadays. With applications in materials, electronics, biomedicals, and other related technology areas, the common factor is that the materials, techniques, devices and systems have at least one or more critical dimensions on the nanometer scale [1]. The prefix “nano” is derived from the Greek word “nanos,” meaning dwarf or extremely small. Nanotechnology is the science and engineering of fabricating and investigating materials, structures, and devices on a nanometer scale [2]. Nanostructured materials may have existed in nature since the evolution of life on Earth. Some examples for proof are fine-grained minerals in rocks, nanoparticles in bacteria, and smoke. From biological area, the DNA double helix has a diameter of about 2 nm, whereas ribosomes have a diameter of 25 nm. Atoms have a size of ~1 - 4 Angstroms.

Carbon is literally a versatile element in the periodic table, owing to the type, strength, and number of bonds it can form with many different elements [3]. The diversity of bonds and their geometries enable the existence of structural and geometric isomers, and enantiomers. Experimental evidence of the existence of the best known nanomaterials, CNTs, came in 1991 by the study of Iijima where multi-wall CNTs (MWCNTs) were investigated by using a transmission electron microscope (Figure 1) [4]. CNTs are the strongest and stiffest materials discovered in terms of tensile strength and elastic modulus respectively. The strength of the carbon–carbon bond gives rise to the interest in the mechanical properties of CNTs [5].

CNT synthesis has been shown to occur in a wide range of environments such as using a high-powered laser, two arcing graphite electrodes, in a hot furnace full of hydrocarbon gas, or even in the middle of a flame [3]. By this means, various CNT synthesis techniques were enhanced and being used. Diversified results of these techniques introduce a quality difference between CNT products. Not only the synthesis method but also extra processes such as oxidation, magnetic purification, ultrasonication and so on. The main objective is to determine these differences before the usage of CNTs and prevent the production from any inadequacy in application. Especially in electromechanical applications such as nano/micro electro mechanical systems. For this reason, a great number of characterization techniques are used to investigate the properties of CNTs. Within a wide range of techniques, selection of the examination methods is vital to eliminate the unnecessary costs.

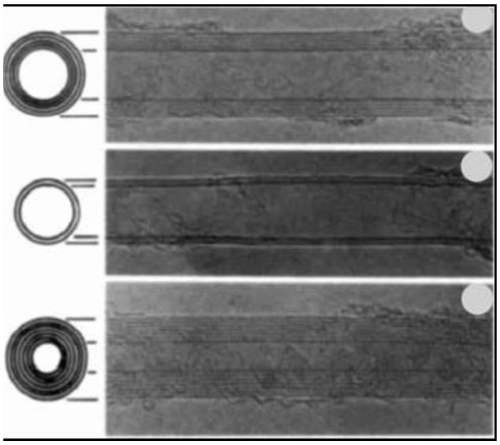

***Figure 1. Transmission electron micrographs (TEMs) of the first observed multi-wall carbon nanotubes reported by Iijima in 1991 [4]***

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## 2. CHARACTERIZATION METHODS

In this Section, the characterization methods of CNTs are explained.

### 2.1 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a contactless, nondestructive method of examining the electronic structure of materials [6]. In this method, light is directed onto a sample. In general, light is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of luminescence. The energy of the photoluminescence relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process.

As known, CNTs could be either in metallic or semiconducting type. The energy gap of the semiconducting tubes is approximately proportional to the inverse of the tube diameter [7]. Photolimunescence method is used to differentiate semiconducting CNTs from all. However, it’s difficult to realize this method, because CNTs are generally grouped in bundles. Because of Van der Waals force, metallic CNTs are placed in these bundles and counteract the photoluminescence signal. In order to achieve healthy results, CNTs must be seperated into individual tubes by succesfull dispersive methods like ultrasonification with surfactants. One of the most popular technique is the ultrasonication treatment of the nanotubes with sodium dodecyl sulfate (SDS) [8].

As a consequence, the electrical properties (semiconducting or not), the geometries and the diameters of CNTs could be obtainable by using the photoluminescence technique. Moreover, the luminescence spectra seems to be very sensitive to the purity of the samples and the presence of internal defects [9].

## 2.2 Electron Microscopy

The electron microscope uses a beam of electrons to screen an image of the specimen [10]. It is capable of much higher magnifications and resolutions than light microscopes. Thus, it is able to see smaller objects in fine details. Transmission electron microscope (TEM) is able to show two-dimensional, black and white images of internal structure of material with an quite high magnification and resolution. On the other hand, scanning electron microscope produces images by detecting secondary beams reflected from the material surface. Images of structures are achieved in three-dimensions.

TEM technique is useful for measurement of the outer and inner radius and linear electron absorption coefficient of CNTs [11]. SEM technique can only show outer dimensions and characterisics of CNT bundles. High resolution TEM images are also used for measuring the intershell spacing of MWCNTs. The intershell spacing is investigated between 0.34 and 0.39 nm varying to CNT diameter. However, these values are greater than the graphite interplanar distance (0.336 nm). The reson ot the increase is probably the curvature of the graphene sheets which is modified by the CNT radius.

## 2.3 Scanning Tunneling Microscopy (STM)

The STM is cabable of acquiring remarkable images on the most extreme scale, easily resolving atomic structure in the right environments [12].

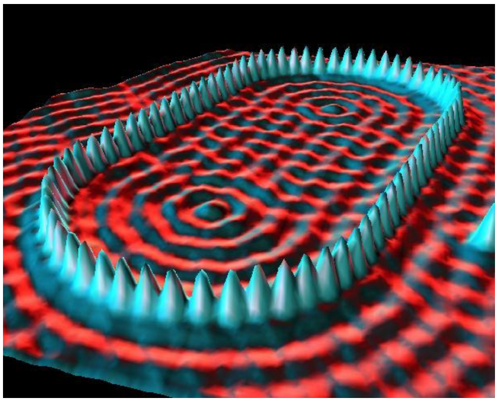

***Figure 2. Scanning Tunneling Microscope (STM) image of density of electron states for a corral of Fe atoms on a Cu metal surface [13]***

Chirality of CNT can clearly be determined with STM investigations. As known, electronic properties of CNTs are also related to the chirality of CNTs [11]. Moreover, energy bands and density of states (DOS) can be calculated by a STM. This technique can also be used to determine the properties of intramolecular SWCNT junctions. In addition, it can also be used to investigate influence of symmetry, electronic contacts, defects, doping etc.. In order to use this technique, CNTs must be deposited on a flat conducting substrate such as Au or Highly ordered pyrolytic graphite.

## 2.4 X-Ray Diffraction

X-ray diffraction (XRD) is a rapid analytical technique in CNT examinations that primarily used for phase identification of CNT material and can provide information on unit cell dimensions. This technique is used to obtain information about the interlayer spacing, the structural strain and the impurities of CNTs. However, XRD pattern of CNTs are too close to graphite due to their intrinsic nature. For this reason, XRD profile is not useful to understand microstructural differences between CNTs and graphite, but it may help to determinate the sample purity. XRD is also been used for investigating the finite size of the bundles, the mean tube diameter, and the diameter dispersivity of the tubes.

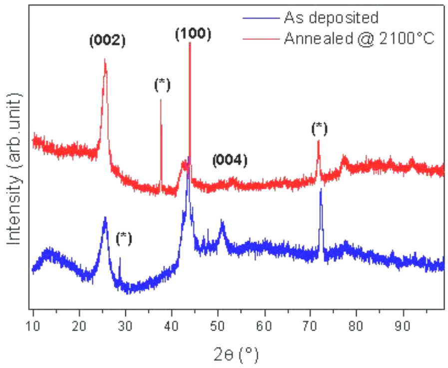


***Figure 3. XRD spectra of CNT where (*) is the difference peak of CNT [14]***

### 2.5 Raman Spectroscopy

Raman Spectroscopy is a vibrational spectroscopy technique used to collect a unique chemical fingerprint of molecules of materials [15]. Each molecule has a different set of vibrational energy levels, and the photons emitted have unique wavelength shifts [11]. Vibrational spectroscopy involves collecting and examining these wavelength shifts and using them to identify what the sample includes. Raman spectroscopy is a powerful method to characterize CNTs in the fastest way without sample preparation. Breathing mode, disorder line, G band (CNT frequency), second order observed band (G') and the relation between all these bands give us information about CNTs. Type of CNT, purity and density distribution can be understood from Raman investigations. Physical properties and the diameters can be characterized by studying on G band line shape.

Raman spectroscopy gives quite good qualitative and quantitative information on CNT diameter, electronic structure, purity and crystallinity, and distinguishes metallic and semiconducting, chirality (for single SWCNT). However, XRD or neutron diffraction is needed to investigate CNTs at larger scale.

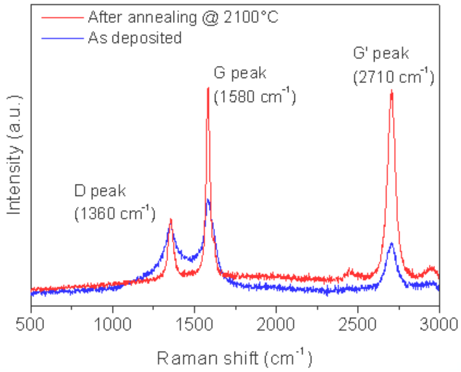


***Figure 4. Raman spectra of CNTs [16]***

### 2.6 Thermal Analysis

Thermal gravimetric analysis (TGA) and derivative thermal gravimetric (DTG) analysis methods are used to obtain quantitative data on the weight fractions of carbon and metal catalyst in the sample, and the temperatures of bulk oxidation events [11]. By using thermal analysis methods, observing the response of these materials to a change in temperature in an easy way is possible. Thermal analysis methods are used to identify relative changes due to processing and the degree of CNTs purification can be measured.

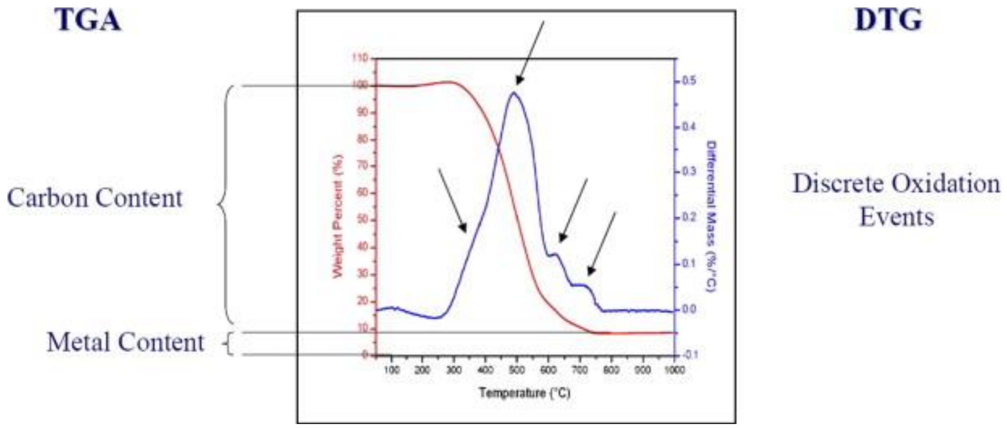


***Figure 5. Explanation of thermal analysis result***

### 2.7 Other Methods

There are also different other methods to investigate the other properties of CNTs such as functionalization properties and so on. X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared Analysis methods are used to investigate these properties. Furthermore, absorption spectroscopic technique is very useful as a relative purity measurement of CNT.

Moreover, contrary to X-ray diffraction, Q neuron diffraction method is used because a wide range of scattering vector can be explored due to the weak decrease of the atomic factor with this vector.

## 3. CONCLUSION

Production of CNTs is not enough by itself. It is important to characterize the properties to decide the application area of the product or to examine the convenience of the CNT to the application area. While choosing the characterization method, it is important to select the proper method. Moreover, useful method selection is helpful to provide to choose the most economic way for examination. For this reason, it is important to decide the need of the application area. If there is more than one property required, the characterization method selection must be in optimum number to keep prices low.

## REFERENCES:

[1] Kucukyildirim, B. O., & Akdogan-Eker, A. (2012). Comparison of Calculated Prediction Model Results with Experimental Strengths of Carbon Nanotube Reinforced Aluminum Matrix Composite Materials. *Sigma Journal of Engineering and Natural Sciences 30*, 364-373.

[2] Schwartz, M. (2006). *New Materials, Processes, and Methods Technology*. Boca Raton: CRC Press Taylor & Francis Group.

[3] Michael, J. O. C. (2006). *Carbon Nanotubes: Properties and Applications*. Boca Raton: CRC Press Taylor & Francis Group,.

[4] Iijima, S. (1991). Helical Microtubules of Graphitic Carbon. *Nature, 354*, 56-58.

[5] Gogotsi, Y. (2006). *Nanotubes and Nanofibers*. Boca Raton: CRC Press Taylor & Francis Group.

[6] Barron, A. R. (2012). *Physical Methods in Chemistry and Nano Science*. Creative Commons Attribution.

[7] Liu, X.., Pichler, T., Knupfer, M., Golden, M. S., Fink, J., Kataura, H., & Achibra, Y. (2002). Detailed analysis of the mean diameter and diameter distribution of single-wall carbon nanotubes from their optical response. *Physical Review B - Condensed Matter and Materials Physics, 66*(4), 454111-454118.

[8] Weisman, R. B., Bachilo, S.M., & Tsyboulski, D. (2004). Fluorescence spectroscopy of single-walled carbon nanotubes in aqueous suspension. *Applied Physics A: Materials Science and Processing, 78*(8),1111-1116.

[9] Lauret, J. S., Voisin, C., Cassabois, G., Roussignol, P., Delalande, C., Filoramo, A., … Jost, O. (2004). Bandgap photoluminescence of semiconducting single-wall carbon nanotubes. *Physica E: Low-Dimensional Systems and Nanostructures, 21*(2-4), 1057-1060.

[10] Retrieved from: http://www.jic.ac.uk/microscopy/intro_em.html

[11] Aqel, A., Abou El-Nour, K. M. M., Ammar, R. A. A., & Al-Warthan, A. (2012). Carbon nanotubes, science and technology part (I) structure, synthesis and characterization. *Arabian Journal of Chemistry, 5*(1),1-23.

[12] Retrieved from: http://www.nanoscience.com/education/STM.html

[13] Retrieved from: http://www.phy.duke.edu/~hsg/464/

[14] Retrieved from: http://areeweb.polito.it/ricerca/carbongroup/fac_xrd.html

[15] Retrieved from: http://www.st-andrews.ac.uk/seeinglife/science/research/Raman/Raman.html

[16] Retrieved from: http://areeweb.polito.it/ricerca/carbongroup/fac_microraman.html