Study about characterization of CNTs through electron microscopy and Raman spectroscopy

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Abstract. Carbon nanotubes were produced by arc discharging process. Morphology and characteristics of carbon nanotubes were investigated through electron microscopy and Raman spectroscopy. Electron microscope reveals different shape and size, typical branching phenomena, randomly oriented, entangle CNTs and agglomerated CNTs. Raman spectroscopy reveals the deficiency of RBM (radial breathing mode), D-band corresponds to disorder band of graphitic structure and G-band corresponds to E²g mode of carbon atoms. Moreover, the ratio of I_D/I_G was found to be 0.24, which is attributed to high purity and crystalline in nature. Raman spectroscopy also exhibits G’ band attributed to overtone of D band, which furnish typical characteristics of different graphene layers.

1. Introduction
Since the discovery of CNTs by Iijima in 1991[1] through TEM (Transmission electron microscope) and subsequent report on synthesis of overwhelming quantities of nanotubes [2], it became intriguing for many researcher & invoke the depth studies for futuristic application. Carbon nanotubes behave like one dimensional structure (1D) made by rolled up of graphene sheets (2D) of sp² bonded carbon atoms into cylindrical shell [3]. There are mainly two types of carbon nanotubes characterized by their no of walls/layers, one of them is called SWCNTs (Single-walled carbon nanotubes), while other is called as MWCNTs (Multi-walled carbon nanotubes). Single walled carbon nanotubes are made of one layer of graphene tubes, while multi-walled carbon nanotubes consists of different co-axial tubes/cylinders made of graphene sheets. Carbon nanotube is defined by its tubule diameter d, and chiral angle θ [3]. Carbon nanotubes have important application in the field of nano-electronics, probe tips, chemical sensor, advance nano-composites etc. [4].

Characterization of CNTs is a vital task in order to find its morphological behavior. There are various techniques to characterize the morphology, texture, no of layers and structure of CNTs [5]. SEM, TEM and Raman spectroscopy are very important tool to characterize the morphological and structural behavior of CNTs. SEM analysis gives valuable information pertinent to morphological and structural behavior of CNTs. Nevertheless, it is not ample to establish ultimate nature of CNTs. Thus one proceeds for other analysis like TEM and Raman spectroscopy.

Mohammad Jafari eskandari et al [4] characterized the different nanotubes by transmission electron microscope and evaluated the diameters, thickness of wall, morphology and lattice structure of nanotubes.
C. branca et al [5] characterized the carbon nanotubes by TEM and Infrared spectroscopy and exhibited different degree of purity, nanotube concentration and vibrational characteristics behavior. A. M. kezler et al [6] studied on characterization of nanotube materials by Raman spectroscopy and microscopy. By Raman spectroscopy, they exhibited different types of band and Lorentzian analysis of D/G band and concluded that the relationship between D and G band indicates a low crystallinity of graphite sample. Similarly, from SEM analysis they observed a thick bundle of MWCNTs along with amorphous carbon.

Present work mainly emphasized on morphological behavior of carbon nanotubes through electron microscope and Raman spectroscopy.

2. Experimental
Carbon nanotubes were prepared by arc discharging process [7] under the atmospheric condition between cylindrical and rectangular graphite electrode. During arcing carbon cations were vaporized in the plasma region followed by quenching in air. With this technique more heat was liberated at anode due to thermionic and electron emission. As a result of that anode was consumed and deposited in the form of soot (‘figure 1’) on the face of rectangular electrode. Further collected soot was grounded into fine powder followed by heating in muffle furnace at 600°C for burning off amorphous carbon and other catalyst in order to get pure CNTs.

![Figure 1](image)

Figure 1. Deposited soot on the face of rectangular electrode

First characterization and morphological behavior of CNTs was done by FE- SEM (Model-SUPRA 55, Carl Zeiss) after gold coating to CNTs sample and then placed in microscopic grid. Further characterization of CNTs was done through Raman spectroscopy Via Reflex developed by Renishaw with an excitation of 514 nm.

3. Result and discussion

3.1 SEM Characterization:
Morphological studies were carried out on CNTs samples at different surfaces at different magnification using field emission scanning electron microscope. FE- SEM image (‘Figure 2A’) reveals the different types of carbon nanotubes, which are randomly oriented and some of them are encapsulating with nanomaterials. This image also depicts different shape and size of CNTs. It can be anticipated that it may be happened due to unstable plasma zone. Those who were remain in plasma zone for a durable period that appears to be longer in size. Appearance of few holes may be attributed to higher temperature and hence some of amorphous carbon may be burn off during arc discharging process. At few places agglomerated encapsulating CNTs with nanomaterials can be observed.

FE-SEM image (‘figure 2B’) depicts that overwhelming CNTs are encapsulating with nanomaterials and few blobs [6] of amorphous carbon. These polyhedral nanomaterials have more or less distorted spherical, cylindrical and conical shapes. By carefully looking at FE-SEM image, it appears that CNTs are not only randomly oriented and entangle with each other but also agglomerated. These entanglements and agglomeration occur due to Vander Waals forces among nanomaterials. These types of typical behavior invoke scientific temperament among researcher towards the depth investigation by AFM (Atomic force microscopy), TEM (Transmission electron microscopy) and SPM (Scanning probe microscopy) analysis. We have investigated in details Raman analysis.
Figure 2. A) Showing CNTs and B) agglomerated and entangles CNTs

Figure 3. A) showing the CNTs with nanomaterials and B) carbon nanotubes at higher magnification

Figure 4. Typical branching phenomenal behaviour of CNTs
‘Figure 3 A’ reveals the entangle carbon nanotubes along with polyhedral nano-materials, which have distorted conical and spherical shapes, while figure 3 B depicts cylindrical as well as twisted carbon nanotubes have negative curvature.

FE-SEM (‘Figure 4’) reveals different typical branching phenomenal behaviour in CNTs. These typical branching behaviour looks like L-type and Y-type structure. Y-type branching is a combination of non-coaxial tubes in which one of them is an arrangement of cylindrical shell, while other two are inclined to cylindrical tube axis. Similarly L-type of structure is a combination of two nanotubes in which one of them is along horizontal axis, while other is along vertical axis. These types of typical shapes attributed to introduction of pentagonal or heptagonal defects that leads to different types of curvature (Positive or negative) [8]. These types of branching phenomena were first observed by Dan Zhou and Seraphin [9]. Y-junction SWCNTs has been also observed by Y C Choi et al [10]. It can be anticipated that this types of branching phenomena may be attributed to fluctuation in temperature, unstable arcing and fluctuation in anode consumption [11]. From branching phenomena it can be demonstrated that carbon nanotubes are not always constructed by concentric linear growth phenomena. Average diameter of carbon nanotubes varied from 22 nm to 51 nm, while average diameter of branched nanotubes varied from 31.6 to 39.4 nm.

3.2 Raman Characterization

During SEM analysis it is very difficult to make distinction between carbon nanotubes (1D) and carbon nanofibers. In this situation, Raman Spectroscopy plays vital role to characterize the CNTs. Raman spectra gives information on vibration and electronic properties of sp² hybridized graphite crystallites. ‘Figure 5’ presents the Raman spectrum of CNTs, which depicts absence of first band/low energy radial breathing mode which directly relates with the diameter of SWCNTs by following equation:

\[ \omega_{RBM} = \frac{A}{d_t} + B, \]

where \( \omega_{RBM} \) is the vibration frequency, \( d_t \) is the tube diameter usually observed in SWCNTs and A, B are constant which fluctuates between individual graphene tube and bundle tubes [12].

![Raman Spectroscopy of CNTs sample with excitation wavelength of 514 nm](image)

But in our case non-existence of first band make confirmation of MWCNTs (Multi-walled carbon nanotubes). The second band or disorder band also known as D-band appears at 1352 cm⁻¹, which
invokes due to presence of defects like amorphous carbon, other impure materials. Third band also known as G-band as a sharp peak appears at 1575cm\(^{-1}\), which confirms to high crystalline graphitic structure and relates with photon vibration in sp\(^2\) carbon materials.

Moreover, the ratio of intensity of D-band and G-band namely (I_D/I_G) is usually determined to evaluate degree of disorder of graphene (2D). The ratio (I_D/I_G) of graphene decreases with increase in number of layers of graphene [13]. Jiao et al [14] reported that the average (I_D/I_G) value for single layer, bi-layers and tri-layers graphene were found to be 0.38, 0.30, and 0.28 respectively. In this context, present investigation shows that value of (I_D/I_G) is about 0.24, which demonstrate the multilayered graphene/multi-walled carbon nanotubes. The fourth band also known as 2D band shows a Raman peak at 2707cm\(^{-1}\). This band depicts the no of layers present in graphene, which is related with no of shoulders. By carefully looking at 2D-band, it appears as broader as compared with G-band and have more no of shoulders, which corroborates multi-walled carbon nanotubes [15]. Guixia zhao et al [15] reported nearly coherent results related to D-band, G-band and 2D-band, which constructed qualitative graphene. A separate band also appears at 1127cm\(^{-1}\), which depicts presence of undesirable substance.

4. Conclusion

1. Present study was mainly focused on characterization of carbon nanotubes by field emission scanning electron microscope (FE-SEM) and Raman spectroscopy.
2. FE-SEM depicts different shape & size of carbon nanotubes whose diameter varied from 22 to 51 nm. Branching phenomena of Y- type and L- type were also observed from FE-SEM analysis, which corroborate about complex growth phenomena during arcing process. These types of branching phenomena demonstrate that carbon nanotubes growth does not always occur in concentric linear direction.
3. Raman spectroscopy depicts the absence of low energy band which corroborate the presence of multi-walled carbon nanotubes (MWCNTs). Second order band of D-band (2D-band) reveals more no of shoulders, which corroborate multi-graphene layers.

5. References
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