Synthesis of multi walled carbon nano tubes by arc plasma discharge method and their characterizations

[1]R. K. Sahu, [2]T. Dash[#], [1]V. Mukherjee, [3]S. K. Pradhan,
[4]T. K. Rout, [3]B.B. Palei, [3]A.K. Sahu, [2]S. K. Biswal, [3]S.K. Biswal, [5]B. B. Nayak
[1]Sambalpur University, Odisha, India
[2]Centurion University of Technology and Management, Odisha, India
[3]CSIR- Institute of Mineral and Materials Technology, Odisha, India
[4]Tata Steel Ltd, Jajpur, Odisha, India
[5]CV Raman College of Engineering, Bhubaneswar, Odisha, India
[#]Corresponding author, E-mail: tapan.dash@cutm.ac.in; tapanphy@gmail.com

Abstract:

We developed a low-cost approach to prepare high-quality multi-walled carbon nanotubes (MWCNTs) using direct current (dc) arc discharge in Ar atmosphere. Multiwall carbon nanomaterial (MWNT)/tubes were synthesized by arc plasma melting of graphite samplesfollowed by *in situ* cooling has been carried out by employing a special 50 kW dc arc reactor. Graphite material was also chosen for preparing both electrode and crucible because of high temperature involved in carrying plasma melting experiments of samples. Carbon nanotubes of various forms have been found to grow in various plasma treated samples. A bunch of whisker structure (containing nanotubes) was formed on the electrode tip and bottom and wall of the crucible. Evaluation of properties of nanotubes has been identified by XRD, TEM and micro Raman studies. Electrical conductivity value (measured by four probe method) of arc plasma treated graphite samples has been found to increase in comparison to untreated graphite. This achievement is the consequence of formation of nanotubes in the plasma treated graphite samples.This process is quite favorable for the formation of nanotubes due to the easier condensation of carbon vapor quickly in the arc region. Fine MWCNTs with random orientation are obtained.

Key Words: carbon nanotubes; arc plasma;electrical conductivity;microstructure

1. Introduction:

Carbon nanotubes (CNT) were discovered by Iijima in 1991 [1]by arc discharge method and it belongs to fullerene family and got popularity due its unique and excellent mechanical and electronic characteristic.CNT is highly conductive (i.e. both electrically and thermally) with high aspect ratio and also

acts as electron field emitter because of their nano size. It can have used in various fields like in generating high magnetic field(*tokomak* application), Atomic force microscope tip, in fuel cells, in flat panel display [2-4].These are widely used in cutting tools such as Solar cells, Paper batteries,Actuators,Radar Absorption,Hydrogen Storage,Super Capacitors,Water Treatment,Environmental remedies,Electrical Circuit, Electrical Cables and Wires,Textile,Optical power detectors etc. due to several advantages.Depending upon layers of Carbon sheet CNT is categorized into single wall nanotube (SWNT), dual wall nanotube (DWNT) and multiwall nanotube (MWNT) having attractive properties, such as high sublimation point (~ 4200K), high hardness (up to 25 GPa for MWNT and 55GPafor SWNT), high Young's modulus (0.2-0.95TPa for MWNT and 1-5TPa for SWNT) and high tensile strength (11-63-150GPa for SWNT and 13-53 for MWNT), high thermal conductivity (3500 W/m.k along the axis and 1.52 w/m.k in radial axis direction) and have high temperature stability i.e. 2800 ^{0}C in vacuum and 750 ^{0}C in air[5].

Production of high-quality MWCNTs is extremely beneficial as these possess unusual properties and great potential applications [6, 7]. Generally, MWCNTs of high densityare usually prepared by laser ablation of carbon, chemical vapor deposition (CVD) and arc discharge, plasma torch (dc & rf) and electrochemical deposition are the common technique for synthesis of carbon nanotubes[8-10]. However,the laser ablation method is not extensively applied due to expensive equipment and high energy consumption. Though MWCNTs prepared by CVD have been commercialized, yet CVDgrown nanotubes usually have very disordered structures andmany defects because the growth temperature is normally below 1000^{0}C, moreover, they are always contaminated by residual catalytic particles [11]. Among all these methods, arc discharge is simple and used widely nowadays because arc-preparedCNTs with relatively uniform structure are known to be well graphitized and have less structural defects. Furthermore, the mechanical properties and the electric or thermal conductivity of arc-prepared nanotubes are one to two orders of magnitudebetter than those of the CVD-grown CNTs[12]. CNTs are the strongest and stiffest materials yet discovered having high elastic modulus and tensile strength [5].CNT is sp^2hybridized[13]. According to the theory, metallic nanotubes can carry an electric current density of 4×10^9 A/cm^2, which is more than 1,000 times greater than those of metal such as copper [10].

In arc discharge process fast and efficient condensation of carbonvapor generated from evaporation of solid carbon sources which is veryconducive leads to the formation of MWCNTs[14, 15]. However, in the conventional installation for preparingMWCNTs, the effect of condensation on the surface of cathodeis gradually insignificant due to high heat with theincrease of arc discharge time, which simultaneously causes thedestruction of existing nanotubes. In addition, the cathodedeposit continues to grow and the space between two electrodescannot be maintained constant, as a result the current is unstableand the electric fields are non-homogeneous [16]. As a result, it isquite unfavorable for the formation of MWCNTs.

The Production of CNT is highly costlier and requires a high amount of precision. It is not possible to achieve 3000^0C temperature by common furnaces. Hence, induction furnace, arc furnace, graphite furnace, etc. are usedin industries for melting of graphite [17]. All these heating processes are costly as well as energy intensive compared to arc plasma furnace (and take several hours to reach high temperature (~3000 ^{0}C). In contrast, arc plasma (thermal plasma furnace operating in transferred arc mode), is endowed with very high energy density (10^6 W/cm^2) and high ion temperature, the developed process is a very fast melting technology which takes notmore than 10 minutes to completely melt 100gm scale of charge (of high melting point ~ 3000 ^{0}C) [18]. Because of simple arc configuration employed in the reactor / furnace, the equipment cost becomes relatively cheaper without involvement of any high technology.It can significantly reduce the cost of preparing nanotubes.Moreover, it also simplifies the preparation process because of theabsence of pre-vacuum. So in contrast to the conventional arcdischarge, this technique with the high reliability and stability iseasier to control over the growth conditions and can be capable ofpreparing MWCNTs on a large scale and at low cost.

In the present research work, the systematic effect has been taken for treatment of graphite discs by employing thermal arc plasma. The arc plasma treated graphite discs and untreated graphite disc were compared by employing various advanced characterization techniques XRD, TEM, micro Raman and electrical conduct measurements.

2. Experimental:

Graphite of 99.999% purity (electrode grade) was taken as the staring material for production of carbon tubes by arc plasma melting technique. The graphite discs were treated in a 50 kW DC extended arc plasma reactor using Ar as plasmagen gas.Fig. 1shows the schematic view of arc plasma reactor used in our experiments. The arc discharge systemconsists of a horizontal anode(27mm diameter and250 mm,with adjustable ends) and a vertical cathode (27mm diameter and200 mm length having a5mm axial hole along the length for the flow of Ar gas) assemblyinstalled in a mica cylindrical chamber. A graphite based crucibleis suspended with the anode which acts as the reaction chamber.The crucible with the charge was connected to positive polarity of a dc power supply (served as the anode) via three graphite rods laterally positioned inside hearth of the reactor and mechanically fixing the crucible.Graphite samples were plasma treated in a special designed 50 kW extended arc plasma furnace/reactor using graphite crucible. The specialty of the reactor lies in its design which aims to utilize the waste heat of plasma by enrooting the hot exhaust gas / flame of the arc in a down draft mode so that heat energy / enthalpy supplied to melt graphite sample can be reduced. Water cooling device is used for theelectrodes and the arc chamber during the arc growth process.The arc discharge condition in this work is described in detailsas follow. A gap of 20 mm between the two electrodes wasmaintained, which wasfixed during the preparation process.

The sample was placed in a graphite crucible.The chamber was filled with Ar gasfor the plasma creation at a flow rate of 1-1.5 lts/min through the central axial hole provided in the top vertical graphite cathode.At first the top graphite cathode was brought to the close proximity of the charge (maintained with positive polarity) to produce a transferred arc type plasma discharge which transferred more energy to charge in the melting process. By upward and downward motion of graphite cathode (connected to a rack and pinion arrangement), the arc length between cathode and anode was maintained 20mm. The plasma treatment (melting) of graphite samples was carried out for 5-9 min. In the plasma reactor each electrical feed-through (total 3), the voltage and current conditions applied were: voltage 50-80 V (dc), current 180-260 A.

The total current is varying from 520-600A, Voltage from 59.1-75V with an energy supply range of 3.18-6.5038kWh.Whisker structure were clearly visible in various reacted samples. Further increase in energy the beyond 6.5038 kWh melting of graphite took place. After melting operation was over electrical power was switched off. The *in-situ* cooling of reactor / furnace was carried out around 4-5 h to attain room temperature. Argon flow of 0.5 lit per min was maintained for 20-30 min. during cooling cycle to prevent oxidation. The plasma treated graphite samples were collected from reactor / furnace at room temperature and taken for various characterization studies.XRD patterns of the arc plasma treated graphite sample were carried out by employing a PANalytical X'Pert Pro diffractometer equipped with CuKα radiation (λ = 0.15406 nm) (40 kV and 45 mA conditions). The spectra were taken in the 2θ range 20-80º at a scan speed of 0.017 min^{-1}.The surface morphology and microstructures of the treated samples were observed by FESEM using back scattered electron mode, model: ZEISS SUPRA 55 and TEM, model: TECNAI G^2 (200 kV), FEI (Netherland). EDS study of the treated samples were studied using the Oxford, X-Max system mounted on the FESEM instrument with 20 kV accelerating potential.The SAED pattern of the treated sample was studied by the facility available in the TEM instrument. The phase and plane identifications in the SAED patterns were interpreted using Gatan Inc.'s digital micrograph^{TM} software. Micro Raman spectra were recorded by employing a dispersive type Renishaw inVia Reflex (UK) spectrometer with a spectral resolution of 1 cm^{-1}(514 nm line of an Ar^{+}ion laser).

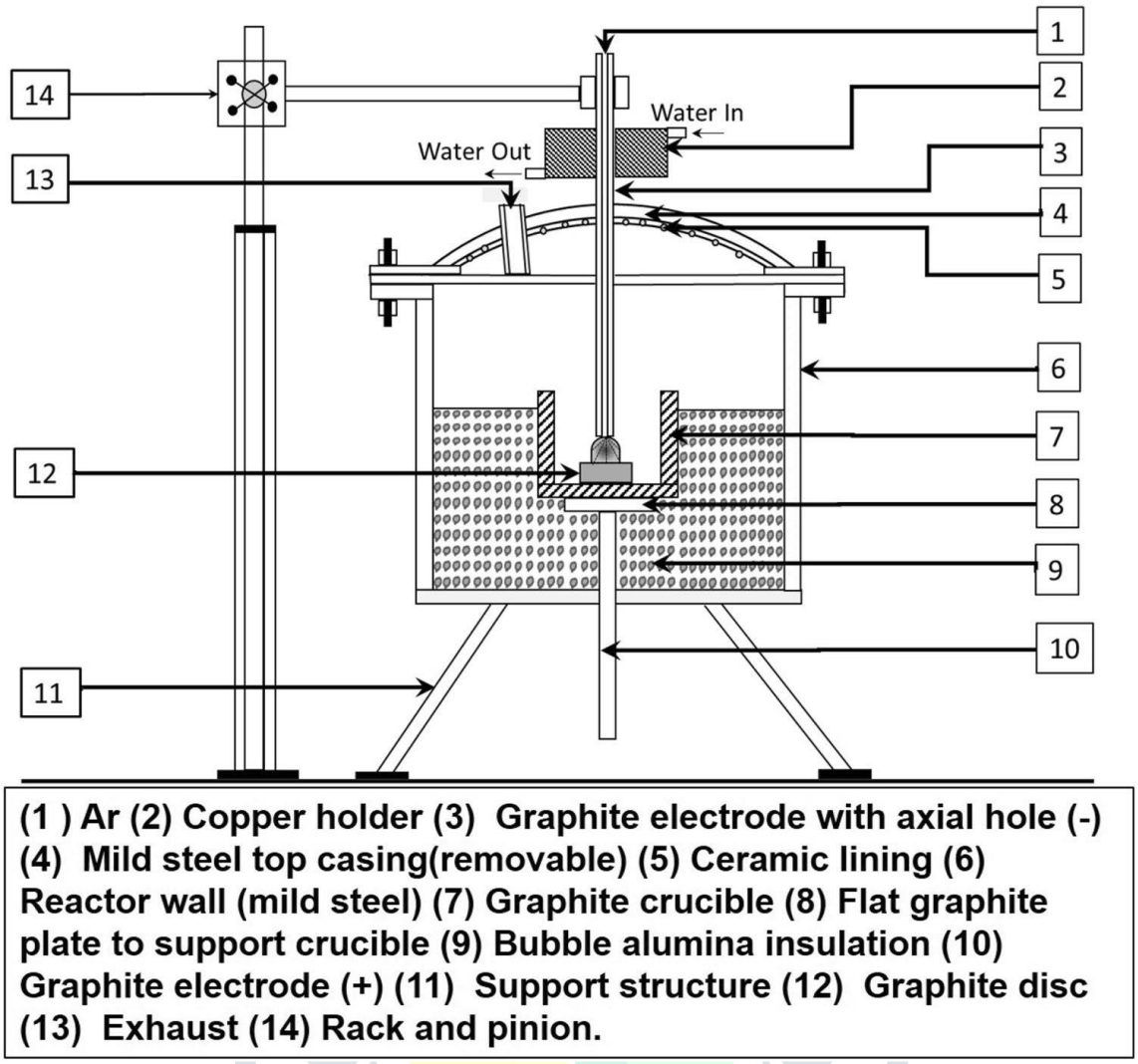

Fig. 1: Schematic diagram of the arc plasma reactor used in plasma treatment of graphite disc [19]

3. Results and Discussion:

The arc plasma treated graphite samples were evaluated by using various advanced characterization techniques. XRD patterns of the untreated and typical arc plasma treated graphite discs have been recorded and presented in Fig. 2.It is marked that all the samples show a strong intense peak of C(002), C(100), C(004) and C(110). It found that, its intensity of carbon peaks for plasma treated graphite is decreased significantly. This is varied possibly because of structural changes or modification occurred due to plasma treatment. The relatively larger d-spacing observed for plasma treated graphite of milling samples than that of high purity graphite is due to the lattice expansion (occurs in AB stacking order of graphite lattice).A sharp peak is seen around 26.4^0 angle shows the graphitic peak. The (100) peak reveals the order within the graphene plane. The (100) peak is narrower because within a graphene sheet, the carbon atoms are

connected by the strong covalent bonding. But broadening in the FWHM XRD of treated sample shows the formation of CNT [20].The deviation of crystalline and structural modification confirms the formation of CNT with few layer of graphene.

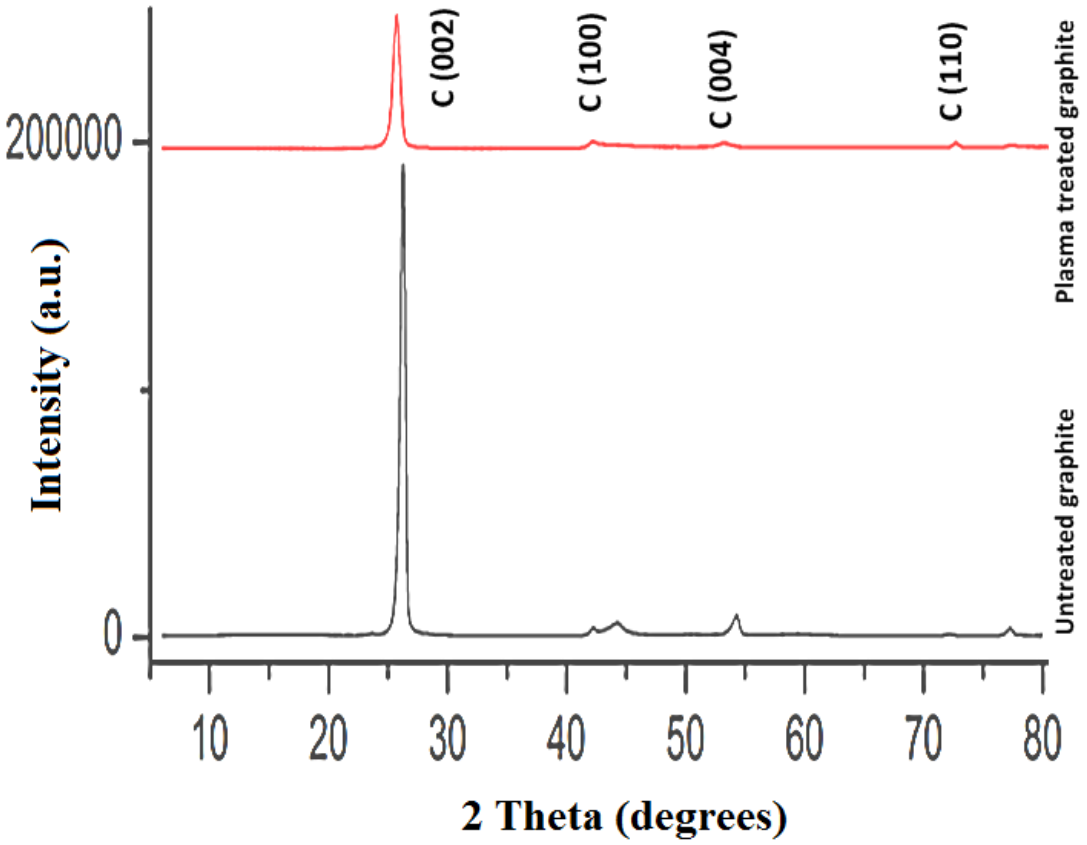

Fig. 2: XRD analysis of untreated and plasma treated graphite

The FESEM image of untreated and plasma treated typical samples are presented in Fig. 3. The Spheroid type of morphology is observed in the microstructure of plasma treated graphite. Spheroid is found uniformly distributed through the sample.It is possibly due to fine MWCNT filaments were vertically grown with randomorientation and there are nearly free of carbonparticles and curved graphite sheet.To confirm the formation of CNTs (MWCNTs) and graphene, TEM analysis of typical plasma treated graphite was carried out and presented in Fig. 4. The formation of the enlarged section of MWCNTs is carefully observed. Fine straight and rod-like MWCNT were seen with random orientation (whereas CVD-grown

nanotubes arealways curved and defect-rich [21]. The observed CNTS are found to form in bundle and expected to enhance the electrical conductivity of graphite.

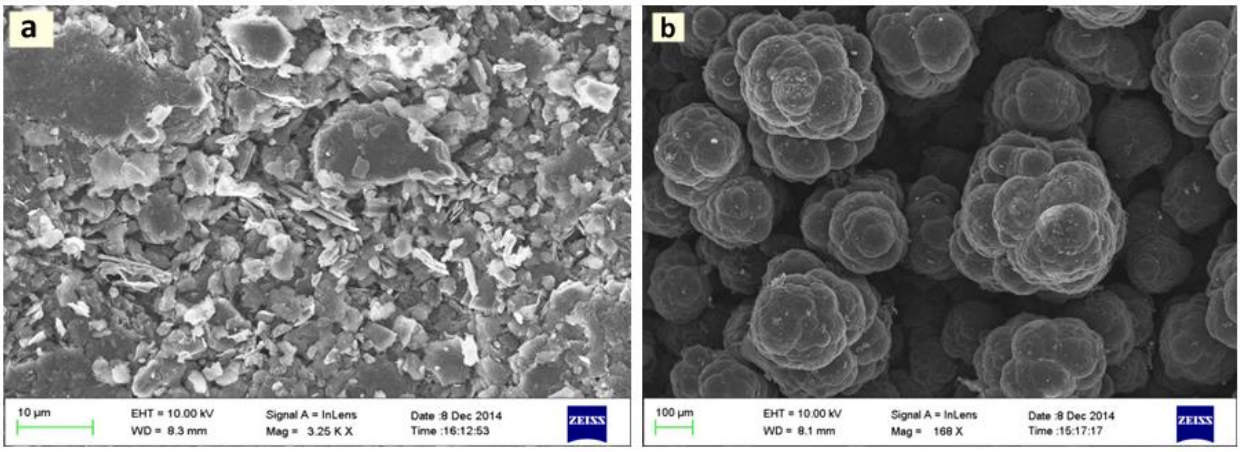

Fig. 3: (a) and (b) are FESEM images of untreated and plasma treated graphite

The electrical resistivity of graphite (carbon) exhibit a value of 3-60 Ωm having ampacity value is 25-30A/cm^2. However electrical conductivity value of CNT fiber have been generally reported in literature in the range of 10^4 - 10^6 S/m[15]. This is due to residue of the catalyst used for synthesis, structural defects in the CNTs, and contact resistance between the CNTs. Multiwall CNT (MWCNTs) has found to exhibit electrical conductivity of 1.9 ×10^7 S/m as great as copper at 6×10^7 S/m at 300^{0}K. We have CNTs in view of increasing electrical conductivity of graphite formed by arc plasma treatment. Among prepared sample, the sample prepared by 10 min plasma treatment was found to exhibit the conductance 8.6645 ×10^5S/m which is 10-fold higher conductivity than graphite.

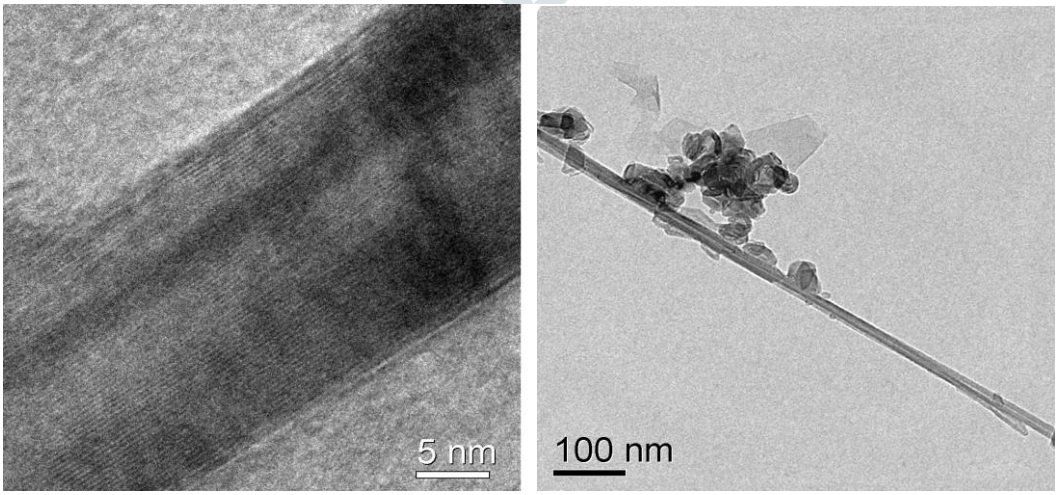

Fig. 4: TEM image of plasma treated graphite

4. Conclusion:

It has been possible to prepare CNTwith high electrical conductivity by arc plasma heat treatment of graphite. MWCNTs were formed by a d.c arc discharge between two graphite electrode. XRD pattern show the broad peak located at 26.5°, 44.3°, and 54.5° corresponding to planes (002), (100), (004) and (110). It is found from FESEM that spheroid uniformly distributed through the sample. This is the morphological view bundle of nanotubes in FESEM. The formation of MWCNTs with graphene is confirmed from TEM analysis.The typical CNT prepared by 10 min arc plasma treatment of graphite shows 10 fold increasing electrical conductivity (8.6645 $\times 10^5$S/m) than graphite and this enhances the potential of application of it electrode and other industrial electrical and electronics applications.

References:

1. Iijima, S.J.N., S. Iijima, Nature (London).1991. **354**: p. 56.
2. Che, G., et al., Carbon nanotubule membranes for electrochemical energy storage and production. 1998. **393**(6683): p. 346.
3. Rinzler, A., et al., Unraveling nanotubes: field emission from an atomic wire. 1995. **269**(5230): p. 1550-1553.
4. Yu, M.-F., et al., Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. 2000. **287**(5453): p. 637-640.
5. Popov, V.N., Carbon nanotubes: properties and application. Materials Science and Engineering: R: Reports, 2004. **43**(3): p. 61-102.
6. Yao, Z., C.L. Kane, and C.J.P.R.L. Dekker, High-field electrical transport in single-wall carbon nanotubes. 2000. **84**(13): p. 2941.
7. Zhang, Y., Y. Bai, and B.J.D.d.t. Yan, Functionalized carbon nanotubes for potential medicinal applications. 2010. **15**(11-12): p. 428-435.
8. Eatemadi, A., et al., Carbon nanotubes: properties, synthesis, purification, and medical applications. 2014. **9**(1): p. 393.
9. Ebbesen, T.J.N., TW Ebbesen and PM Ajayan, Nature (London) 1992. **358**: p. 220.
10. Purohit, R., et al., Carbon nanotubes and their growth methods. 2014. **6**: p. 716-728.
11. Harutyunyan, A.R., et al., CVD Synthesis of Single Wall Carbon Nanotubes under "Soft" Conditions. Nano Letters, 2002. **2**(5): p. 525-530.
12. Karthikeyan, S., P. Mahalingam, and M.J.J.o.C. Karthik, Large scale synthesis of carbon nanotubes. 2009. **6**(1): p. 1-12.
13. Kroto, H.W., et al., C60: Buckminsterfullerene. 1985. **318**(6042): p. 162.
14. Nayak, B.B., et al., Growth of carbon nanotubes in arc plasma treated graphite disc: microstructural characterization and electrical conductivity study. Applied Physics A, 2018. **124**(3): p. 220.
15. Subramaniam, C., et al., One hundred fold increase in current carrying capacity in a carbon nanotube-copper composite. Nat Commun, 2013. **4**: p. 2202.
16. Kim, K.S., et al., Large-scale production of single-walled carbon nanotubes by induction thermal plasma. 2007. **40**(8): p. 2375.
17. Savvatimskiy, A.J.C., Measurements of the melting point of graphite and the properties of liquid carbon (a review for 1963–2003). 2005. **43**(6): p. 1115-1142.
18. Heberlein, J. and A.B.J.J.o.P.D.A.P. Murphy, Thermal plasma waste treatment. 2008. **41**(5): p. 053001.
19. B. B. Nayak, R. K. Sahu, **T. Dash** and S. Pradhan, ", Applied Physics A, 2018 . **124:**(220), P.1-9,
20. Maldonado, S., S. Morin, and K.J.J.C. Stevenson, Structure, composition, and chemical reactivity of carbon nanotubes by selective nitrogen doping. 2006. **44**(8): p. 1429-1437.
21. Bower, C., et al., Nucleation and growth of carbon nanotubes by microwave plasma chemical vapor deposition. 2000. **77**(17): p. 2767-2769.