THE INTERNATIONAL JOURNAL OF SCIENCE & TECHNOLEDGE

Carbon Nanotubes: A Review of Synthesis and Characterization Methods/Techniques

Yahaya Saadu Itas

Assistant lecturer, Department of Physics, Bauchi State University, Gadau, Nigeria

Chifu Ebenezer Ndikilar

Professor, Department of Physics, Federal University, Dutse, Nigeria

Tasiu Zangina

Senior Lecturer, Department of Physics, Federal University, Dutse, Nigeria

Abstract:

This review on the different methods of synthesis and characterization techniques of carbon nanotubes was done via precise consultations of different works on carbon nanotubes and the recent developments made in the process. Understanding of the total properties of carbon nanotubes still remain limited due to their novel characterized features such as high strength, high young's moduli, high thermal and electrical conductivities and many more uncountable features that are yet to be discovered. This paper summarizes the most adopted method of synthesis and the most adopted technique of characterization of CNTs and highlighted the reason why these methods and techniques are considered best. The review however recommends further reviews on CNTs as information of the complete and reliable method and technique remained the major challenge.

Keywords: Characteriation, composites, grapheme, nanotubes, synthesis,

1. Introduction

With the discovery of lower dimensional forms of carbon with unique mechanical properties in many areas of technology especially in nanotechnology (Popov V. , 2004), over the years until recent, the discovery was not made about nanostructure, particles and fibers and their applications are also not known. In 1991 carbon nanotubes were discovered by Iijima (Resel Das, Sharifah Bee Abd Hamid, 2015) and they have received much attention because of their usefulness in mechanical (Qingyue Yu et al, 2916), (Yu, 2004), (Qingzhong Zhao et'al, 2002), (Rodney S. Ruoff and Donal C. Lerents, 1995), electrical (A/\J. Nelson et'al, 2015), (A Szentes et'al, 2012) and thermal properties. They play key role in areas of applications such as polymer, composites, hydrogen storage media and biomedical sciences, field emission dipoles etc. CNTs show unique structural and physical properties (Medjo, 2013), the discovery of CNTs in 1991 shows that there is improvement in the potential of nanostructures for in nanotechnology (Popov V. , 2004). There had been a lot of researches on the synthesis of nanostructures from organic materials, the nanostructures such as nanoparticles, nanofibres and carbon nanotubes have far been extracted from different substrates.

The result of the growth of CNTs in the absence of metal show that CNTs growth need catalytic environment, this is indicated by wide energy drop difference (81.9-51.7 Kcal) during the first way and second way growth process. The wide margin shows the growth process terminates immediately (Murugesan, 2001). The CNTs exist in two phases which are single walled CNTs and multi walled CNTs (D. W. Lee and J. W. Seo, 2014), the properties of each phase depends on the method used in the synthesis, the arrangements of the grapheme in CNTs is represented by a chiral vector (n, m) which determines the classification of CNTs as armchair ($n = m$), zigzag ($m = 0$) and chiral. SWCNTs show all the three structures while MWCNTs show only armchair and zigzag structure. Although CNTs are promising candidates for nanotechnology applications, the synthesis is difficult due to high temperature conditions (about 500°C and above). However they can be synthesized at room temperature under catalytic environment (D. W. Lee and J. W. Seo, 2014), this can be achieved when pure graphite is added to a mixture of fuming nitric acid and sulphuric acid (H_2SO_4) slowly for 30 minutes. The mixture is then cooled down to 5°C in ice bath, potassium chlorate ($KClO_3$) is then added slowly to the solution and then stirred for 30 minutes, the solution will then be heated up to 70°C for 24 hours and then allowed to cool in air for 3 days. It will be found that the graphite will precipitate at the bottom while some reacted carbons will be floating, the floating carbons will be filtered and washed with distilled water and then allowed to dry. CNTs of diameter 14.6 nm are seen in the sample through SEM and TEM analysis and then electron diffraction pattern demonstrates its zigzag edge structure.

Because of their Nano-sized structure, the synthesis of CNTs increases proportionally with the size of the catalyst particle, it is worth noting that the catalyst particle size is an important factor in the nanotube growth (Khursed A. Shah, 2016). The catalyst with large particles size is not effective for growth of SWCNTs, the increase of average catalyst size lead to decrease in surface area. Different methods of synthesis have been used to synthesize catalyst nanoparticles from

materials, this literature will therefore review and look in to the use of three methods; physical vapor decomposition method, sputtering method and chemical methods. The physical vapor decomposition method is also called thermal evaporation method and is the most common technique adopted for the decomposition of metal nanoparticles on a substrate. In this method, the material will be heated to a very high temperature (500 °C and above) and a very low pressure range between 10^{-6} – 10^{-12} Torr on to a cooler substrate and this results in the yield of thin films. The physical vapor decomposition method of preparing metal catalyst nanoparticles is aided via the use of electron bombardment heating method where by a heated material such as Tungsten filament (W) will supply high energy electrons and then accelerated on to the material for evaporation to take place. The target material becomes molten as a result of the bombardment, the atoms will evaporate and then then be collected on the substrate. Nano-sized Nickel (Ni) catalyst are prepared in this way on silicon oxide surface. A 100 Kw electron beam was used to supply energy of 1.4 MeV under the beam power density of 5 MW/cm². The vaporizing temperature was 550 °C under atmospheric condition of 10^{-5} Torr. The evaporated Nickel material the collects on the SiO₂ surface to form thin film. The annealing process then follows through a nitrogen atmosphere at 740 °C for 15-45 minutes and these results in forming a nano-sized Ni-particles on the substrate.

The sputtering technique involve the surface bombardment by high energy particles, during the process, ejected or sputtered atoms will be condensed and collected on to a substrate and the whole sputtering process is aided by DC-diode sputtering and DC magnetron sputtering. The chemical method for nano-sized catalyst particle preparation is the use of transfer media (gas or liquid) to deliver chemical compound which serve as precursors on the surface of the substrate and then chemically modified to obtain nanoparticles. This method is also divided in to sol-gel precipitation technique and deep dry technique. The sol-gel technique is popularly used in the preparation of metal catalysts because it results in highly homogeneous materials with high degree of metal dispersion. It involves the formation of materials in gel type solution. The deep dry technique is obtained by dipping the substrate in appropriate solution which contains metal salts without the application of electric filed.

The metal catalyst nanoparticles synthesized from different methods are used in the synthesis of CNTs using different methods such as laser ablation(et'al J. C., 2015), electric arc discharge (et'al A. E., 2014) and chemical vapor decomposition methods (CVD) (Ritu Sharma, 2015). The nature and property of each type of CNT produced depends on the method used in the synthesis. Some among these methods require high temperature and costly while others like CVD is cheaper and easier in obtaining CNTs though it is best for MWCNTs synthesis but they are produced with defects. Laser ablation method is limited to the laboratory scale, crude production, so the CNTs produced need to be purified. Detailed description of the CNTs synthesis methods are given in the subsequent sub-sections.

2. Methods of Carbon Nanotubes Synthesis

The synthesis of both SWCNTs and MWCNTs depends on the type of needs for CNTs ranging from small scale needs such as CNTs needed for study purposes in the laboratory. This type of CNTs can be prepared using local method, however they are not pure and may contain defects and some other imperfections. CNTs needed for industrial purpose such as CNTs for electrical, mechanical and thermal applications need to be pure, purified, perfect and free of deformations. They therefore require high precision method for their synthesis, for example the plasma enhanced chemical vapor decomposition method was used to investigate the factors determining the properties of MWCNTs(al M. S., 2007). The growth of CNTs can be from different methods such as the popular chemical vapor decomposition method (CVD)(et'al J. C., 2015), (Ritu Sharma, 2015), (Ping'an Hu, 2002), (Amin Termeh, 2014), electric arc discharge (Ritu Sharma, 2015) method and laser ablation method (et'al J. C., 2015)(et'al Y. D., 2010). CNTs can also be grown locally at room temperature when graphite powder is placed in a mixed solution of nitric acid and sulfuric acid with potassium chlorate (D. W. Lee and J. W. Seo, 2014). MWCNTs were first discovered in 1991 by Iijima(Popov V., 2004) through electric arc method, this was the method used in the preparation of carbon fibres and fullerenes long time ago. Progress was subsequently made when SWCNTs were synthesized using the laser ablation method and later the catalytic growth of CNTs by CVD method was first discovered by Yacamanet'al. Three main methods of producing both type of CNTs can be cauterized as follows (Varshney, 2014)

Plasma based method

- Arc discharge
- Laser ablation

Thermal synthesis method

- Chemical vapor decomposition
- PECVD
- Alcohol catalytic CVD

Hydrothermal method

2.1. Chemical Vapor Decomposition Method

It is widely known that the thermal decomposition method otherwise known as chemical vapor decomposition (CVD) is the commonly used method for decomposition of hydrogen vapors (et'al A. S., 2010). Many studies on the preparation of CNTs has shown that CNTs are prepared from different materials such camphor oil, synthesis of tree-like CNTs, CNTs from coconut shell activated carbon, from byproduct of oil (al S. H., 2014) such as petroleum coke, and many other materials used CVD method.

The CVD method uses hydrogen gas such as acetylene and methane, they are decomposed at a very high temperature range of 700°C and above, as the gas decomposes, carbon atoms are then produced through condensation by

a cooler substrate containing metal nanoparticles catalyst such as Nickel and Iron nanoparticles. In the experiment carried out on analyze CNTs morphology, dispersion and functionalization characteristics, the CNTs were produced by CVD method in which nickel was used as the catalyst and acetylene as carbon containing gas. The synthesis took place at temperature of 750°C under a flow of argon gas. The as-synthesized samples are examined via various analysis methods and CNTs of 200-800 nm were seen. Synthesis was also made to obtain tree-like carbon nanotubes with multi junction via CVD method, the experiment obtained a web-like or tree-like CNTs containing two and three dimensional junctions over a cobalt supported magnesium oxide at 1000°C. Figure 2.1 shows an SEM image of chemical vapor decomposition method in which CNTs were synthesized from Azerbaijan oil (al S. H., 2016).

Figure 1: SEM Images of Carbon Structures Obtained At Atmospheric Pressure in the Reactor From: (A) Gasoline Fraction; (B) Fraction Jet Fuel; (C) Diesel Fraction

In all experiments ferrocene in concentration of 20 mg/ml of the solvent was used as a catalyst. Raw material with a dissolved catalyst was injected to the reaction zone as an aerosol using an ultrasonic apparatus. The reactor consists of quartz tube of a length of one meter and an internal diameter of 33 mm. For uniform deposition of carbon material the electric furnace (35 cm of length) automatically moved with a velocity of 10 mm/min over the length of quartz reactor during the synthesis process. Deposited carbon materials have been studied using analytical scanning electron microscope (ASEM). Purification of synthesized carbon nanotubes was carried out by two known successive methods-by washing with solvents (cyclohexane, toluene), with simultaneous action of ultrasound and a half-hour burning at 420°C in a muffle furnace in air atmosphere(al S. H., 2016). The research carried out on the synthesis of carbon nanomaterials reported CVD method as the best approach for CNTs synthesis with controlled properties (al K. A., 2011), the CNTs were synthesized by spray pyrolysis assisted CVD using ferrocene as a source of iron catalyst at 850 °C and castor oil was used as carbon source.

2.2. Laser Ablation Method

The experimental arrangements for the synthesis of carbon nanotubes by laser evaporation method is shown in figure 2. The arrangement contains quartz tube containing argon gas and a sample target (graphite). The furnace provides temperature maintained at 1200°C. a water-cooled copper collector is mounted with the tube at one of its ends, lying outside the furnace. The graphite target contains small amounts of cobalt and Nickel that act as catalytic nucleation sites for the formation of the nanotubes.

The method involves passing of high laser beam on the target so that carbons can be evaporated. The argon from the tube then sweeps the carbon atoms from the high temperature zone to the colder copper collector on which they condense in to nanotubes of relatively 10-20 nm size and 100 :m long.

Figure 2: Laser Evaporation Set-up

The effect of laser wavelength was investigated on carbon nanotubes by laser ablation method (al J. C., 2015), the experiment took place at the institute of fundamental technology research, Poland using a double pulse Nd. YAG laser with working wavelength of 355 or 1064 nm.

Figure 3: Reactor for Laser Ablation of CNTs (al J. C., 2015)

The ablation of the target was performed in argon background gas at a pressure of 6.6×10^4 Pa flowing slowly (5 mm/s) in a quartz tube 25mm in diameter inserted in an outer 50mm tube, the results showed that SWCNTs were obtained according to the SEM images shown in figure 4

Figure 4: SEM Images of Carbon Nanotubes Obtained In (al J. C., 2015)

The laser ablation process depends on factors such as wavelength dependence, pulse width and repetition rate dependence, energy power/density dependence, single-laser and multiple sequencing etc (Arepalli, 2004)

2.3. Electric Arc Discharge Method

In the electric arc method, a potential of 20-25 V is applied across carbon electrodes of 2-20 mm diameter separated by 1 mm at 500 torr pressure of flowing helium. Carbon atoms are ejected from a positive electrode and form nanotubes on the negative electrode. An arc is produced in between the electrodes by DC power supply capable to produce 100-200 A current. Deionized water is used in the process so as to serve as good cooling agent, this is because deionized water is less evaporative than liquid nitrogen.

Figure 5: Electric Arc Method

Being one of the most abundant elements on Earth, carbon exists in many different forms called allotropes with widely different properties. The discovery of novel carbon allotropes or carbon nano structures (CNSs) has attracted intensive attention due to their fundamental and technological interests. CNSs are promising to revolutionize many areas of fundamental science and technology because they exhibit unique structure. They are large contributors in nanotechnology because they exhibit unique physical properties, they can be used as composite materials and other uses such as hydrogen storage and medical uses. The table 1 below gives the summary of methods used in the synthesis of carbon nanotubes, it also indicates other relative parameters obtained from different methods.

S/no	Carbon source	Synthesis method	Catalyst	CNT type	CNT diameter (nm)	CNT length (nm)	Synthesis temperature (°C)	Reference
1	Graphite	CVD	HNO ₃	MWCNT	146	1000	70	[24]
2	NC 7000	CVD	Fe-Co	MWCNT	12.6	540.6	700	[8]
3		CVD	Fe-Co	MWCNT	Jun-20	400-500	860	[3]
4	Graphite	Electric arc		MWCNT	15-150	45.7	710	[15]
5	Methane	CVD	MgO-CO	MWCNT	130	540	700	[8]
6	Graphite	Laser ablation	Ni-Co	SWCNT	125	1.3		[15]
7	Wood char	CVD	Fe-Ni	MWCNT	124	450	900-1110	[18]
8	Coconut shell	CVD		MWCNT	0.45	174	700	[4]
9	Camphor oil	CVD	Ni-Co	MWCNT	0.56	109	750-850	[2]
10	Flame	Thermol		MWCNT	20	200		[6]
11	Graphite	Electric arc	Co-Ni or Fe	SWCNT	123	1.2		[20]

Table 1: Different Sources and Method of Synthesis of Carbon Nanotubes

The table 1 shows that graphite is most the direct carbon source that is employed in the synthesis process, the chemical vapor decomposition method by this literature is the most frequently employed method deployed to synthesize MWCNTs under catalytic ambient. The synthesis of SWCNTs does not however require catalyst in some cases as can be seen in synthesis in serial number 6 in table 1

3. Characterization Techniques

Of all the CNSs, CNTs are the most important ones due to their variety of applications. The study of the properties of CNTs can be given by qualitative analysis through the use of the electron microscopes. This research will however try to review the use of different electron microscopy techniques to analyze the properties of CNTs synthesized from neem bark. The following techniques are thus considerable;

- Scanning electron microscopy (SEM)
- Transmission electron microscopy (SEM)
- X-ray photoemission spectroscopy (XPS)

- Atomic force microscopy (AFM)
- Raman spectroscopy
- Fourier transform infra-red spectroscopy (FTIR)

3.1. Electron Microscopy Technique

Electron microscopy is an essential tool for characterizing CNTs because it allows direct observation of size, shape and structure (K. Saarova, 2007). TEM, SEM, AFM and STM are the most popular electron microscopy approaches that are used for the investigation of material characterization with SEM and TEM being mostly used to checkmate the exfoliation of bundles and purity of the material. They are however limited in the sense that they cause damages on the sample because of the high beam of electrons. SEM and TEM reveal information about the material topography, its morphology and its composition. On the recent research conducted on the usage of AFM, SEM, and TEM for the research on CNTs, AFM method gives information about the length of CNTs and the diameter of their bundles, it was however not possible to observe the accurate value of the diameter due to CNTs did not lie directly on a mica and oscillated under the daze (N. S. Anas, 2017). SEM method was used to determine the accurate diameter of the CNTs bundles, it gives information mainly about surface morphology of the sample (et'al A. A., 2016), (Tan Win Hon, 2016) and also about chemical composition of the sample. TEM method was used to determine the diameter directly of the nanotube and bundles. The study showed that the best method for detailed analysis of CNTs is TEM because of its ability to observe nanotubes even on atomic resolution and its ability to give information about surface morphology. Synthesis of CNTs by HF, PE COUD on SiO₂/Si (100) substrate using electron microscopies and X-ray absorption spectroscopy near edge reveals that CNTs are highly oriented under optimized conditions, notably when the ammonia concentration is 1 % of gases mixture (Medjo, 2013). This information is further obtained by the use of SEM, TEM and XANES spectra. The diameter of CNTs obtained was 20 nm, length of 100-400 :m, the CNTs morphology depends on the transition metal used as catalyst, so also the structure. It also depends on the experimental parameters used during the growth process.

3.2. Diffraction Technique

The principle behind the diffraction technique involves the focusing of monochromatic ray beam on a material sample in order to obtain its structural information that is hidden in its crystal lattice (Espinosa, 2014). Various diffraction techniques include, small angle X-ray scattering/diffraction (SAXS/SAXD), X-ray powder diffraction (XRD), and energy dispersive X-ray diffraction (EDX). Among all these methods, XRD is considered to be the most confident method for crystal characterization (Popov V. N., 2004) though it also has its own limitations. The monochromatic beam is obtained from polychromatic beams produced in a special tube called cathode ray tube, the monochromatic rays then hit on to the sample atomic planes. This results in the creation of diffracted, transmitted, reflected, scattered and absorbed beams in accordance with bragg's law given by

$$n\lambda = 2d \sin \theta \quad \dots (2.1)$$

Where n is an integer, λ is the wavelength of the incident monochromatic beam, d is the distance between near atomic planes called d-spacing, θ is the angle of the incident X-ray beam.

C. XRD experiments for CNTs

Although CNT is considered as a non-crystalline material, its periodic structure results in distinct X-ray diffraction peaks (Resel Das, Sharifah Bee Abd Hamid, 2015). XRD has successfully been utilized to enlighten the morphology and structural features of CNT aligned at different angles. The carbon atoms in CNTs act as 3D optical diffractors that scatter light at different, but specific angles. From the diffracted angles, it would be possible to extract information on aligning graphene sheets of CNT from the position and intensity of diffracted beams.

XRD pattern of CNTs has shown some distinct similarities to those of graphite probably because of their similar intrinsic graphene properties. Turbostatic atomic carbon structure in graphene has random orientations and translation rather than graphite sheet has piled up sequential carbon atoms. Therefore, there is no lattice atom plane existing especially (001) and it makes diffraction pattern peaks specific and different from other sp² carbon based crystals. In addition, because of curvature and cylindrical structural shapes of CNTs, dipole moment of carbon atoms could be different with the direction of 2D graphite. Analysis of the direction of dipole moment or atomic dipole vector of nano-tube structure could help to characterize CNTs and give differentiating points between CNTs and graphite.

3.3. Peaks Analysis in XRD Patterns

CNT diffraction peak intensities depend on CNTs' morphological orientation. When X-ray beam strikes single wall of CNTs, it produces (002) peaks with some parallel (h k l) reflections. On the other hand, when X-ray beams pass through an empty central core of CNTs, it produces some extra hexagonal peak arrays (h ko). It may occur multiple times at different azimuths depending on the number of helix present, also the intensity of (002) peak decreases monotonically with higher nanotube alignment (et'al A. C., 2001). However, a peak (002) that occurs at integer $2\pi/C_0$ (Fig. 2.4) is generated possibly by the reflections from basal hexagonal carbon atomic networks and parallel nanotube stacking layers (et'al A. C., 2001), (et'al T. J., 2015). Position of prevailed peak gives rise to the information on the spacing (C_0) between the nanotube layers. The positional value of interlayer spacing was observed to be larger than in HOPG (highly ordered pyrolytic graphite) and closed to the value determined in turbostratic graphite (et'al Y. X., 2017). It has symmetric shape, but slight asymmetrical changes could occur because of increasing diameter of sheets with decreased interlayer distance (et'al L. Z., 2012). However, there are some reasons, which might affect intensity and width of the XRD family peaks for

layer numbers, interlayer sheets distances, distortion lattice and CNT orientations (Masdania Zurairah, 2015). Compared with graphite peaks, 002 peak families might often weaken and even broadened on its low-level diffractions angle part (Resel Das, Sharifah Bee Abd Hamid, 2015). Such asymmetrical behavior might suddenly occur because of the presence of multiple crystalline species.

Figure 6: XRD Pattern of MWCNTs (size 60 nm, CVD synthesis, $\delta = 0.154056$ nm, source: Elsevier)

4. Conclusion

The review studies of the synthesis methods of characterizing carbon nanotubes was carried out in this paper. The investigation was carried out so as to update the global Nano scientists and nanotechnologists about the new findings, problems and recommend how to go about possible ways to improve synthesis and characterization processes. The chemical vapor decompositions method is the most popular and most productive method for the synthesis of CNTs even though it has its own limitations of being under higher temperature, it is more promising and a very cheap method. CVD method was used to synthesize CNTs and understood that their length to diameter ratio was greater than 1000. The CVD method is simple, low temperature and produced high quality CNTs [14], it however failed to produce SWCNTs in large quantity. The electric arc discharge method is simple and inexpensive which produces high quality nanotubes but require high temperature and purification but it produces both SWCNTs and MWCNTs. The laser ablation method produces high purity nanotubes even at room temperature but it is limited to the laboratory scale and also requires purification.

The review discovered that the synthesis process is still faced with some problems such as the problem of development of low cost, the problem of large scale process for synthesis of high quality nanotubes, control over structure and electronic properties of the nanotubes, the problem of development of the thorough understanding of the growth mechanism of nanotubes.

The review understands that XRD is still the best technique of characterization because it gives information about most of the physic-chemical aspects of CNTs in both small and large scale productions. Beside information on crystalline phase, domain size, impurities and lattice microstructure, XRD diffraction angle also made it possible to know the how grapheme sheets are aligned and the intensity of the diffracted beams. There is however lack of symmetry of the XRD profiles for carbon anions and MWCNTs

5. Acknowledgement

Much appreciation and thanks to the staff of department of physics Bauchi State University, Gadau for their kind motivation and contribution during the review process. Dr. Tasiu Zangina of the department of physics, Federal University, Dutse has been the supervisor of this work together with Professor N. J. Chifu, department of physics, Federal University, Dutse.

6. References

- i. V. Popov, 'Computational Studies on Formation and Properties of Carbon Nanotubes,' California, 2004.
- ii. Resel Das, Sharifah Bee Abd Hamid, 'Carbon nanotubes Characterization by X-ray Powder Diffraction- A Review,' Current Nanoscience, vol. 11, no. 1, pp. 1-9, 2015.
- iii. Qingyue Yu et al, 'Mechanical Strength Improvements of Carbon Nanotube Threads through Epoxy Cross-Linking,' Materials, pp. 2-8, 25 January 2016.
- iv. M.-F. Yu, 'Fundamental Mechanical Properties of Carbon Nanotubes: Current Understanding and the Related Experimental Studies,' Journal of Engineering Materials and Technology, vol. 125, pp. 272-276, 2004.
- v. Qingzhong Zhao et al, 'Ultimate Strength of Carbon Nanotubes: A Theoretical Study,' Physical Review B, vol. 65, pp. 144105-1-6, 2002.
- vi. Rodney S. Ruoff and Donald C. Lerents, 'Mechanical and Thermal Properties of Carbon Nanotubes,' Pergamon, U.S.A, 1995.

- vii. A/\J. Nelson et'al, 'Effect of Proton Irradiation on the Electrical Resistivity of Carbon Nanotubes-Epoxy Composites,' *Nanoscience and Nanotechnology Letters*, vol. 7, no. 157-161, pp. 157-160, 2015.
- viii. A Szentes et'al, 'Electrical Resistivity and Thermal Properties of Compatibilized Multi-walled Carbon Nanotube/Polypropylene Composites,' *eXPRESS Polymer Letters*, vol. 6, no. 6, pp. 494-497, 2012.
- ix. R. E. Medjo, 'Characterization of Carbon Nanotubes,' in *Intech Open Science*, Intechopen, 2013, pp. 171-180.
- x. A. Murugesan, 'Neem Tree- A Review,' *The Indian Forester*, pp. 1337-1341, 2001.
- xi. D. W. Lee and J. W. Seo, 'Preparation of Carbon Nanotubes from Graphite Powder at Room Temperature,' Cambridge, 2014.
- xii. M. A. M. Khursid A. Shah, 'A Study of Preparation for Synthesis of Carbon Nanotubes,' *Chemical Science Transactions*, vol. 5, no. 1, pp. 1-7, 2016.
- xiii. J. C. et'al, 'Synthesis of Carbon Nanotubes by the Laser Ablation Method: Effect of the Laser Wavelength,' *Physics Status Solide B* 252, vol. 8, pp. 1860-1867, 2015.
- xiv. A. E. et'al, 'Carbon Nanotubes: Properties, Synthesis, Purification and Medical Applications,' *Springer Open Journal Nanoscale Research Letters*, vol. 9, no. 393, pp. 2-12, 2014.
- xv. A. K. S. a. V. S. Ritu Sharma, 'Synthesis of Carbon Nanotubes by Arc-discharge and Chemical Vapor Decomposition Method,' *Materials Engineering Research Article*, vol. 2, pp. 3-7, 2015.
- xvi. M. S. B. e. al, 'Factors Determining the properties of Multi-walled Carbon Nanotubes/Fibres deposited by Chemical Vapor Decomposition,' *Journal of Physics D. Applied Physics*, vol. 40, no. 2007, pp. 2285-2292, 2007.
- xvii. Y. L. X. W. Ping'an Hu, 'Synthesis of tree-like Carbon Nanotubes with Multi junction by a Catalytic Chemical Vapor Decomposition Method,' in *8th International Conference on Electronic Materials*, Xian, 2002.
- xviii. S. B. K. S. J. R. Amin Termeh, 'Fast Synthesis of Multilayer Nanotubes from Camphor Oil as an Energy Storage material,' *Biomed Research International*, pp. 1-5, 2 September 2014.
- xix. Y. D. et'al, 'Synthesis of Carbon-encapsulated Metal Nanoparticles from Wood Char,' *Forest Products Journal*, vol. 10, no. 00041, pp. 528-530, 2010.
- xx. K. Varshney, 'Carbon nanotubes. A review on Synthesis and Applications,' *International Journal of Engineering and General Science*, vol. 2, no. 4, pp. 660-677, July 2014.
- xxi. A. S. et'al, 'Synthesis Methods for Carbon Nanotubes and Related Materials,' *Material*, vol. 3, pp. 3094-3097, 7 May 2010.
- xxii. S. H. A. e. al, 'Synthesis of Carbon Nanotubes from Byproducts of oil Refines,' *World Journal of Condensed Matter Physics*, vol. 4, pp. 93-100, August 2014.
- xxiii. S. H. e. al, 'Synthesis of Carbon Nanotubes from Azerbaijan Oil,' *Advances in material Physics and Chemistry*, pp. 105-112, 5 May 2016.
- xxiv. K. A. e. al, 'Synthesis of Carbon Nanomaterials,' *Bulletin of Material science*, vol. 34, no. 4, pp. 607-614, July 2011.
- xxv. J. C. e. al, 'Synthesis of carbon nanotubes by laser Ablation method. The Effect of Laser Wavelength,' *Physics Status Solide B*, vol. 252, no. 8, pp. 1860-1867, 31 March 2015.
- xxvi. S. Arepalli, 'Laser Ablation process for Single-walled Carbon Nanotubes Production,' *Journal of nanoscience and Nanotechnology*, vol. 4, no. 4, pp. 317-325, May 2004.
- xxvii. e. K. Saarova, 'Usage of AFM, SEM and TEM for the Research of Carbon Nanotubes,' *Modern Research and Educational Topics in Microscopy*, pp. 513-516, January 2007.
- xxviii. R. K. D. T. N. R. a. R. V. N. S. Anas, 'Effect of Carbon nanotubes as Reinforcement on the Mechanical Properties of Aluminum-Copper-magnesium Alloy,' *Journal of Materials Engineering and Performance*, 26 May 2017.
- xxix. A. A. et'al, 'Analysis on the Effect of ZnO on Carbon Nanotube by Spray Pyrolysis Method,' *Mechanics of Advanced Materials and Modern Process*, vol. 2, no. 3, p. 2, 2016.
- xxx. L. S. L. a. C. C. T. Tan Win Hon, 'TEM and XRD Analysis of Carbon Nanotubes Synthesized from Flame,' *Key Engineering Materials*, vol. 723, pp. 471-473, 12 December 2016.
- xxxi. L. I. Espinosa, 'Determination of the Thermal Expansion Coefficient of Single Walled Carbon Nanotubes by Raman Spectroscopy,' *International Journal for Rapid Communication*, pp. 139-145, 15 September 2014.
- xxxii. V. N. Popov, 'Carbon Nanotubes: Properties and Application,' *REports: A Review Journal*, vol. 43, pp. 61-67, 2004.
- xxxiii. A. C. et'al, 'X-ray Diffraction Characterization on the Alignment Degree of Carbon Nanotubes,' *Chemical Physics Letters*, vol. 344, no. 1-2, pp. 13-17, 2001.
- xxxiv. T. J. et'al, 'Carbon Nanotubes Characterization by XRD,' *Current Nanoscience*, vol. 11, no. 1, pp. 1-6, 2015.
- xxxv. Y. X. et'al, 'Synthesis and Characterization of Carbon Nanotubes Doped Carbon Aerogels,' *IOP Conference Series: Materials Science and Engineering*, vol. 275, no. 1, pp. 1-5, 2017.
- xxxvi. L. Z. et'al, 'Synthesis and Characterization of MWCNTs/Polyurethane Composites via Surface Modification Multiwalled Carbon nanotubes using Silane Coupling Agent,' *Polymer Composites*, 11 October 2012.
- xxxvii. Z. A. H. A. a. H. M. Masdania Zurairah, 'preparation and Characterization Carbon Nanotubes-Chitosan nanocomposites by using Oil Palm Shell and Horseshoe Crab Shell,' *international Journal of Advanced Research in Chemical Science*, vol. 2, no. 1, pp. 6-13, January 2015.