



A review on carbon nanotube: An overview of synthesis, properties, functionalization, characterization, and the application

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ABSTRACT

A foremost and inimitable invention in the part of nanotechnology is carbon nanotubes (CNT). Crystal structures are nearly analogous to the nuclear atomic arrangement of graphite and diamond. While graphite belongs to sp^2 -bonded carbon whereas diamond is owned by sp^3 -hybridized carbon. The evolution of CNTs began in 1991. CNTs contain some important traits such as lightweight, small in size, good strength, and high conductivity. CNT make useful in various materials like polymers, ceramics, and metallic surfaces. From an application perspective of CNTs, it can use in the nanotechnology field, nanomedicine, transistor, vacuum electronic devices, biosensors, membranes, and capacitors. Various types of synthesis techniques for CNTs are the arc-discharge method, laser ablation method; chemical vapor deposition method, vapor-phase growth, flame synthesis method, and plasma-assisted growth of CNTs. CNTs have inimitable kind of properties like mechanical, electrical, and optical. These properties can even be measured on single nanotubes. For commercial application, large quantities of purified nanotubes are needed. This present review covers the types, synthesis, characterization method, properties, applications, and toxic effect. The purification and sorting process of CNTs for applications are also presented in a summarized form.

1. Introduction

In the current, research has pivoted on nanotechnology and nano-material. Nanotechnology is a pathway to each innovation or science to the nanoscopic level. In nanotechnology, nanotubes have stimulated interest from the foundational research as well as form an advanced point of view. A tube is nothing but a cylindrical shape structure this is utilized for different applications for a different prospect. As for time is considering till now we have so many types of tube, such as SiC tube, silicon tube, carbon nanotube, etc. Carbon takes part in a major role in the CNTs. Carbon is a component that is found all over the place and in all things. Carbon is the sixth component and accessible in segment IV of the periodic table. Due to the half-filled outer most valance electrons; it forms more compound easily than any other element. In emerging technology, nanotechnology will be the base for other technology in the perspective at a microscopic level.

1.1. Nanotechnology

The word “NANO” is from the Greek, meaning dwarf (small) [1]. The

first concept was presented in 1959 by the famous professor of physics Dr. Richard P. Feynman. The expression “Nanotechnology” had been imagined by Norio Taniguchi in 1974, in Japan. He expressed “Nanotechnology” is a procedure of partition, union, and twisting of materials by molecules or atoms. A nanometer is one-billionth of a meter which significantly more diminutive than the wavelength of evident light. The impact of nanotechnology is both on technology and also on the health, a wealth of the human being, which explores the fact of structures and materials.

1.2. History

Till 1980 we are well known for the different forms of carbon like diamond, graphite, and amorphous carbon. After that, we have now the knowledge of all forms of carbon. In 1985 a new form of carbon came into the picture that is fullerene, discovered by Kroto et al. [2], and recent to that means in the year 1991 another form of carbon discovered which nothing but carbon nanotube [3]. The group of discovered research lead by Iijima. Specific character due to which CNT become so influential parameter in the theory of research as well as application

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perspective is its length and diameter. CNT has a length up to micron and a diameter of range in nanometers which result in a large aspect ratio. It is in the form of 1D, which leads to change or adds different attractive properties such as mechanic, electronic as well as molecular [4]. As in structure, it looks like a cylindrical molecule with a hexagonal arrangement of carbon atoms that are sp₂-hybridized. Its inner structure is hollow and the surface is consisting of single or multiple layers of graphene sheets. Then in 1993, NEC [5] and IBM [6] reported that CNT is made of a single graphene layer.

Depends on the presence of the layer it is differenced into two categories such as single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). Inbuilt properties of CNT of both types will describe in the below section with proper references. MWNTs have less stable CNT compare to SWNTs because of their inbuilt structural defects and undefined diameter [7]. Along with CNT the different and other new forms of carbon are buckyballs, rugby balls, and carbon nanotube. Buckyball is a molecule whose other name is buckminsterfullerene of structure like a ball made of 60 carbons so its other name is also C₆₀ fullerene. Then next is a combination of fullerenes which are a family of linear molecules which is called carbon nanotubes. In the C₆₀ fullerene, carbon atoms are arranged in the shape of a soccer ball with a combination of five-membered and six-membered rings. The rugby ball structure is different from buckyball and here carbon molecules are spherical in structure and slightly elongated too. Here the number of presence of carbon is 70. The advanced feature of C₇₀ is the presence of a five-membered ring, a six-membered ring, and a seven-membered ring. Summarize of CNT evolution is shorten in table 1. When CNT comes into the picture, the first thing of consideration of its preparation and which will able to prepare a well and properly defined structure CNT. The different researchers have been published various work where the preparation and discovery of CNT explained in detail [7–18].

Before entering to CNT discussion, we should have some basic knowledge of graphite, graphene, and its reduced form. CNT is a form of carbon and which is formed from another allotrope of carbon called graphite. Graphite is nothing but an arrangement of carbon atoms in a proper manner where the structure is planar-layered. Arrangement of carbon in graphite is like honeycomb hexagonal lattice where carbons are

separated by a distance of 0.142 nm in each plane and planes are separated by a distance of 0.335 nm [22]. Graphite occurs in meteorites, igneous rocks, and metamorphic rocks and is associated with micas, calcite, tourmalines, etc. Graphite is available in two geometry forms with alike physical properties such as hexagonal geometry and rhombohedral geometry which are also named alpha and beta respectively.

It is a very good conductor of electricity due to the presence of delocalized electrons. Application perspective, it is used in lamp ac electrodes, a pressure sensor in carbon microphones, batteries, brake linings, pencils, lubricants, and many more [23,24]. The next after graphite which is another form of carbon is graphene and it has described in 1962 by researcher Bohem [25] which is a one-atom layer made of similar carbon packed in a 2D honeycomb crystal lattice where

Table 1
Evolution of CNT.

Year	Inventor	Outline	References
1985	Kroto et al.	Fullerene was discovered	[1]
1990	Krätschmer et al.	Mass production of fullerene	[19,20]
1991	Iijima	Discovered of CNT	[2]
1993	NEC	Presence of layer in CNT	[5]
1993	IBM	Presence of layer in CNT	[6]
1995	Smalley et al.	Prepare SWCNT via laser vaporization of graphite	[21]
1996	Thess et al.	Prepare CNT ropes via laser ablation method	[87]
1996	W.Z. Li et al.	Prepare MWCNT via CVD	[104]

the arrangement of carbon is 1:3 that is one carbon atom is coupled with the other three adjacent carbon atoms. The various carbon forms such as graphite, fullerene, charcoal, and CNT has a basic unit of structure and that is the basic structural unit of graphene. Graphene was discovered in 2004 [26] which were produced from graphite by scotch tape method. Properties associated with graphene are lightweight, thin, strong, and transparent, a conductor of both electric and heat [27]. The top-down and bottom-up techniques for the production of graphene are highlighted by a researcher group [28]. In the top-down process, graphene sheets are produced from graphite which is available in graphene oxide and graphite fluoride, and in the bottom-up process, it is prepared by epitaxial growth, reduction of graphene oxide, micromechanical exfoliation, arc discharge methods, etc. [29,30].

Another form of carbon is graphene oxide which is a form of 2D carbon layers and synthesized from graphite flakes by oxidation of it [31]. The various methods of preparation of GO are categorized as Brodie, Staudenmaier, and Hummer's methods [32,33–37]. GO has been considered as an undetermined structure in nature because of various reasons such as the non-stoichiometric composition of atoms and the complex amorphous structure of GO. During the preparation of GO, oxidizing agents and strong acids are uses. Epoxide, hydroxyl, and carboxylate may fix with each carbon of GO. The location of the attached site is different for different polar groups such as the carbonyl group is attached on the edges of layers and hydroxyl and epoxide attached lower and upper surface of layer [38]. Due to the functionalities of polar groups, GO act as hydrophilic and isolated in water without any change. Epoxy group (-O-) was proposed by Hofmann and Holst [38] and they suggested that there unavailability of another group on GO. But in Ruess's suggested the presence of hydroxyl groups and epoxide in GO at 4th and 1st, 3rd position on GO. In addition to the presence of the group he also altered the sp₂ hybridized planes to sp₃ hybridized planes. Various [39–41] research groups suggested the presence of the different groups in GO. By this brief discussion of

Table 2
Evolution of different forms of carbon.

Carbon Form	Year	Inventor	Outline	References
Graphite	1789	Abragamgottlob werner	Named graphite as a writing stone	
Graphene	1952	Radushkevich	First TEM image of Nanoscale carbon filament	[42]
	1962	Bohem	One atom-thick layer of carbon	[25]
	1973	Bohem	Hollow carbon fiber	[43]
	2004	A. geim and K. novoselov	Discover Graphene	[26]
	2010	A. geim and K. novoselov	Got novel prize due to Graphene	[26]
Graphene	1859	Brodie	GO prepared by Oxide (GO) exploring the reactivity of graphite flake	[44]
	1958	Hoffman	Preparation of GO using graphite oxidation with a mixture of sulfuric acid, sodium nitrate, and potassium permanganate	[45]
	1946	Ruess's	Variation by incorporating hydroxyl groups into the 4 th position of cyclohexane in GO.	[46]
	1969	Scholz and Boehm	GO that may completely substitute ether and epoxide functionality by ketones and quinoidal groups	[41]

different forms of carbon, we have a clear picture of carbon and its properties. Below [table 2](#), gives a clear idea of different carbon forms and their history of evolution.

1.3. Carbon nanotubes (CNTs) and their structure

CNTs were found by Sumio Iijima [3] in 1991 and his first attempt to synthesizing multi-walled carbon nanotube was done by a simple arc evaporation method. CNTs are arranged in hexagon and Pentagon which are made up of carbon atoms with a diameter of 3–15 nm. CNT is the subfamily of the fullerene which is its carbon allotropes, which was discovered by Kroto et al. [2] in 1985. The name is gotten from its size where the diameter of a nanotube is a request of a couple of nanometers. These are enormous macromolecules that are idiosyncratic for their size, shape, and properties. CNTs structure is a hollow cylindrical structure, which is framed by moving of single or multiple layers of graphene sheets.

Rely upon the quantity of essence of the outer layer or wall CNTs are for the most part in two kinds that are single-single-walled carbon nanotube (SWNTs) and multi-walled carbon nanotube (MWNTs). When we have started to discuss the structure of nanotube we must become through fullerene because nanotube constitutes fullerene. When a sheet of Fullerene is rolled at specific and separate angles then a proper structure of nanotube will be formed with a fixed inner radius. Due to the roll of a graphene sheet, by itself it forms various allotropes of carbon; also incorporate with graphite and fullerenes its form CNTs [5].

1.4. Types of carbon nanotubes

CNTs are arranged into three groups on the base on its inner wall present in the CNTs. Different images of CNTs are shown in the below figure.

1.4.1. Single-walled CNTs

The term single-walled carbon nanotubes (SWNTs) were first described in 1993 [5]. SWNTs are a single layer of graphene sheet with a diameter of 1–2 nm. [Fig. 1](#) shows the surface and internal view of an SWNT. Catalyst is required for the preparation of CNTs for appropriate control over improvement and atmospheric state. Depend on the preparation methods the length of CNT can vary with less purity.

1.4.2. Double-walled CNTs

Double-walled carbon nanotubes (DWNTs) are made up of two carbon nanotubes where they are distinguished from each other where the outer tube encloses the inner tube. The outer tube has a diameter of 2–4 nm and the inner diameter is 1–3 nm. [Fig. 2](#) shows the surface and internal view of doubled walled carbon nanotubes.

1.4.3. Multi-walled CNTs

Due to the presence of various layers of graphene sheet rolled with a diameter range from 2 to 50 nm. Depending on the presence of graphene

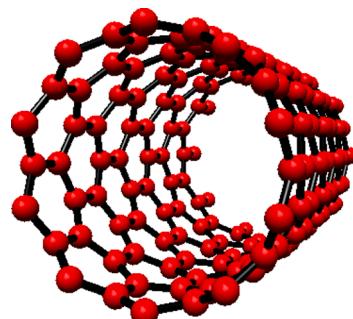


Fig. 1. Surface and Internal view of single-walled carbon nanotubes.

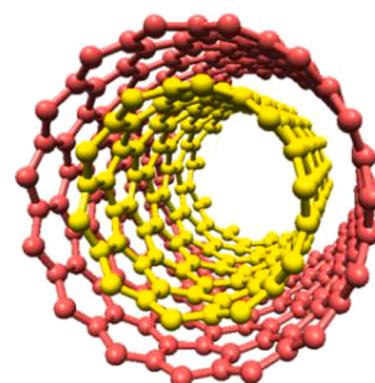


Fig. 2. Surface and Internal view doubled walled carbon nanotube.

sheets MWNTs are naming and numbering too. The inner layer radius of the tube is 0.34 nm and the outer layer radius is of the order is 2 nm up to 20–30 nm [47]. MWNTs are ordered into two structural models are Russian doll and the Parchment model. [Fig. 3](#) shows the surface and internal view of multiwall carbon nanotubes. Arrangement of graphene sheet in concentric cylinders is called Russian doll and wrapping of the single graphene sheet around itself many times, lead to the rolled-up scroll of paper [48].

1.4.4. Basis of chirality

As we are aware that CNT is nothing but a modified version of the graphene sheet, so to understand the CNT structure we should first know the structure of graphene. The graphene sheet shown below [Fig. 4](#) is the one plane sheet from graphite. Graphene lattice is formed by two basis vectors a_1 and a_2 which are shown in [Fig. 4](#). The basis vector $a_1 = (\sqrt{3}/2, 0)$ and $a_2 = a(\sqrt{3}/2, 3/2)$ are valued as $|a_1| = |a_2| = \sqrt{3}a$ where “ a ” is the C–C bond length of value of 0.142 nm. The unit cell of graphene has two atoms (X & Y) which are also shown in [Fig. 4](#). When the centers of the two hexagons are linked together with vector additions are called the chiral vector. Chirality is the main feature to know the electrical properties of CNTs. It is expressed by two integer's n and m which depends upon the integer's numbering and relation to them, many structures are formed. For, $m = 0$, the structure will be zigzag on the nanotubes. While $n = m$, the nanotubes will show the armchair structure and the remaining state is showing chiral structures.

CNT is a cylindrical structure which is forms after cutting the graphene sheet into the rectangular strip. The process of conversion of rectangular graphene sheet to a zigzag structure CNT is demonstrated in the below [Fig. 5](#). [Fig. 5](#) explains the conversation of graphene sheet of $n, m = 13, 0$ to a zigzag structure CNT of $n, m = 10, 0$ where tube length is 15 Å°. Chiral vector, $C = na_1 + ma_2$ (a_1 & a_2 are the base cell vectors of graphite) which “D” define the tube diameter and also finds the direction of rolling of graphene sheet respectively [3,5]. [Figs. 6a, 6b, 6c, and 6d](#) show the different chirality of CNTs.

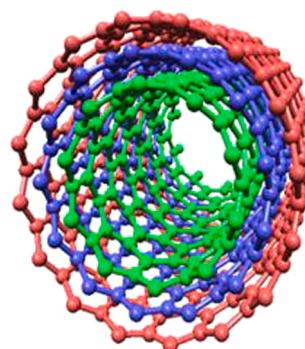


Fig. 3. Surface and Internal view of a multiwall carbon nanotube.

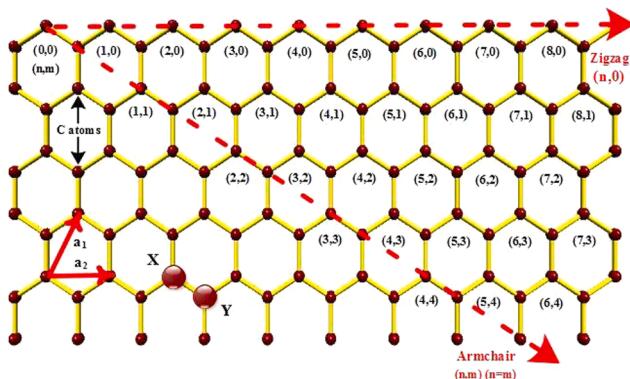


Fig. 4. One plane graphene sheet from graphite with chirality (n, m).

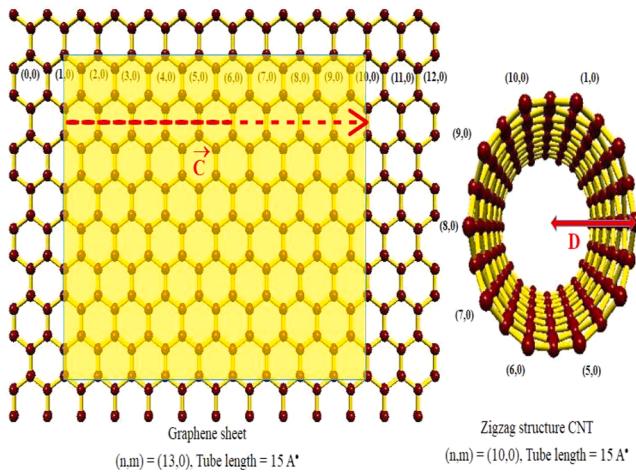


Fig. 5. Zigzag CNT (n, m = 10, 0) from graphene sheet (n, m = 12, 0).

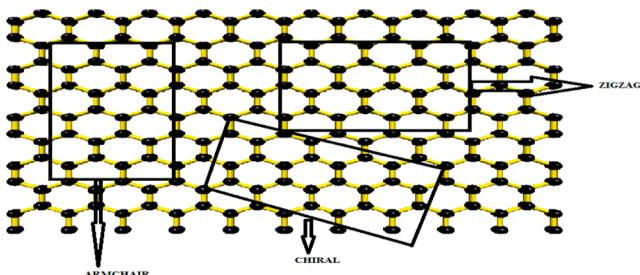


Fig. 6a. The basis on the chirality of CNTs.

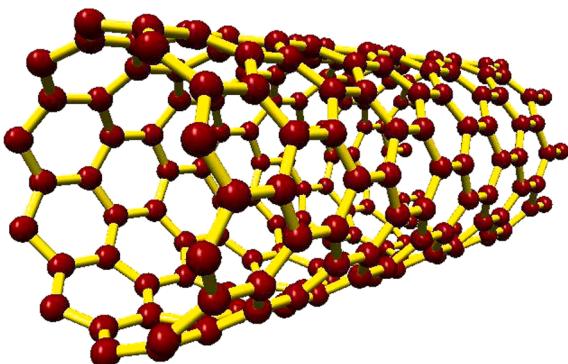


Fig. 6b. Zigzag chirality (n, m = 10, 0/Length = 20 Å/Bond length = 1.5 Å).

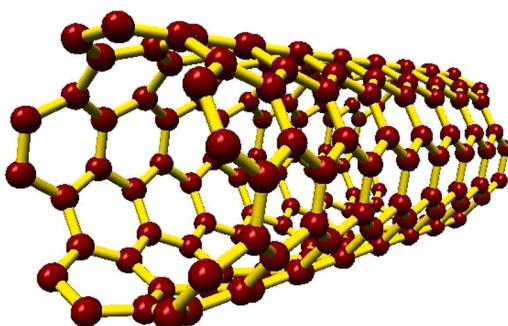


Fig. 6c. Armchair chirality (n, m = 5, 5/Length = 20 Å/Bond length = 1.5 Å).

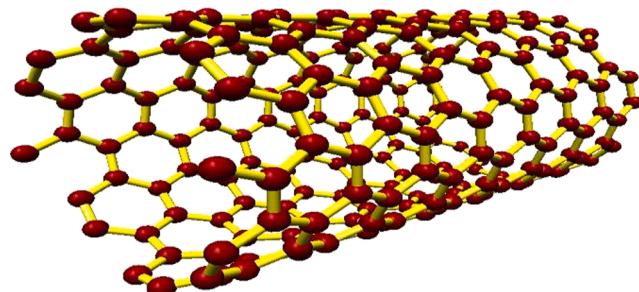


Fig. 6d. Chiral chirality (n, m = 8, 6/Length = 20 Å/Bond length = 1.5 Å).

Chiral vector (C) of rectangular strip and diameter of CNT are related as,

$$D = C/2\pi = (\sqrt{3}/2\pi)a\sqrt{(m^2 + n^2 + mn)} \quad (1)$$

where C = Chiral vector = $na_1 + ma_2$,

D = Diameter of CNT.

Bonding between carbon atoms in the graphene sheet is placed in a symmetrical way compare to carbon bonds in CNT. This difference in carbon atom bonding is due to the rolling up of the graphene sheet.

2. Synthesis of CNTs

2.1. Electric arc discharge method

In 1991, Iijima delineated the synthesis of the tube using the arc discharge evaporation method which is like that old arrangement strategy utilized for fullerene synthesis. The yield rate of the arc discharge method is (>75%). High temperature (above 1,700) uses the arc discharge method for CNTs synthesis with fewer structural defects as compared to another method. For the synthesis of CNT, carbon needles of diameters 4 to 30 nm and length, up to 1 mm were developed on the negative end (cathode) of the carbon base electrode. The chamber constitutes graphite as a cathode and evaporated carbon molecules as an anode and metal catalysts such as; cobalt, nickel, and iron [49]. Fig. 7 shows the high-resolution electron micrographs of CNT at 500tr under helium described by Iijima [3], where Fig. 7c is a magnified view of Fig. 7b and Fig. 7b is a magnified view of Fig. 7a. A connected source generates the current which is passed through the arcing process directly. The chamber gets under pressure and heated to 4000 K (approximately). Power supply connected to the two graphite rod with a distance of few millimeters. After switching on the source by maintaining the power at 100 amps, the carbon starts to vaporizes, and it forms a hot plasma.

Arc discharge method for synthesis of CNT can be performing under two conditions that are synthesis with the presence of catalyst precursors and synthesis without a catalyst. Commonly, SWNTs uses

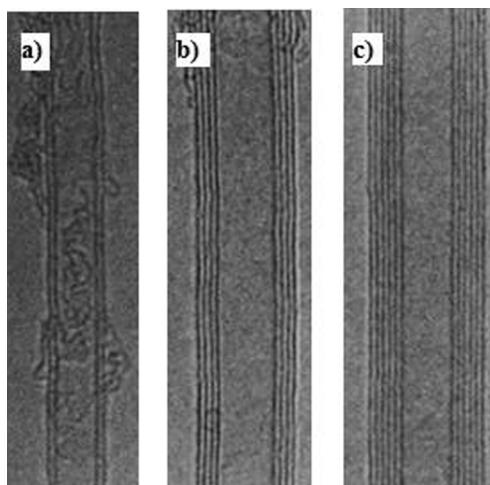


Fig. 7. CNT of 2 nm to 20 nm in diameter and length in micrometers with two or more concentric shells [3].

catalyst precursors and complex anode, prepared up of a collection of graphite and a metal, for example, Gd, Co, Ni, Fe, Ag, Pt, Pd, etc., or mixtures of Co, Ni, Fe with different components like Co-Pt, Co-Ru, Ni-Y,

Fe-Ni, Co-Ni, Co-Cu, Ni-Cu, Fe-No, Ni-Ti, Ni-Y, etc. MWNTs can be synthesis without the catalyst precursors [50]. The arc was generated between two graphite electrodes in a reactor under a helium atmosphere. The lead work of the arc-discharge technique is its capacity to create a large number of nanotubes. By this one power over the arrangement of the made nanotubes is less, leads to poor characterization and role of CNT. The presence of a metallic catalyst makes CNT to impure so purification of the product is important. Various researchers prepared the CNT via electric discharge method which is summarizing in **table 3** where an attempt had been made with details about CNT preparation parameter, characterization techniques, diameter, radius, pressure, voltage, current and time summerised in **table 4**.

2.2. Laser ablation method

The laser ablation technique is used by Thess, et. al. [87] in 1996, where the yield of CNT is decreased by 70% using a limited amount of Ni and Co at 1200 °C. The ultimate aim laser is vaporizing the graphite inside the quartz. The power of the laser pulse expands the diameter of the tubes became thinner. Laser ablation maintains constant pressure due to helium or argon.

The properties which are influenced during laser ablation methods are; structural and chemical composition of the target materials. The various laser properties like peak power, energy fullerene, oscillation

Table 3
Review CNT preparation via electric arc discharge method.

CNT Type	Diameter(mm)	Inert Gas Type	Pressure(Torr)	Characterization	Observation Parameter	Parameter	References
					Voltage(V)	Current(A)	Time
CNT	–	Air	–	FESEM	–	2.5	1.4 ms
CNT	30–80	Ar	600–675	HRTEM	20	70	15 min
MW	4.78	Ar	1034	TEM, TGA, & FESEM	–	25	60 sec
MW	50–100	Ar	525	SPM	–	50	5–10 min
SW	1.06–1.66	Ar	75	TEM, RSS, SEM & OAS	50	100	4 min
MW	20–60	Ar	760	XRD, SEM, HRTEM, RSS	380	6–20	–
MW	5–20	Ar	100	HRTEM	–	100	–
CNT	–	Open Air	–	HRTEM, SEM, & DSC	26	50	1 min
MW	–	Open Air	–	TEM, SEM, EDX, HRTEM	–	7–100	–
MW	5	Open Air	–	TEM, SEM, & EDX	–	2–25	800–1300 μs
SW	~1.62	Open Air	–	TEM & FESEM	36	100	6 min
MW	5	Open Air	760	TEM & FEG-SEM	80	2.5	1 ms
CNT	2–20	He	500	TEM	18	100	–
CNT	10–40	He	500	SEM & RSS	20	100	–
SW	–	He	400	TEM	–	85	1–2 min
MW	–	He	800	TEM	35–40	800	15–20 min
SWSW	5–201.2–20	HeHe	500100–500	SEM, HRTEM, & XRDSEM, TEM, & XRD	30–	10095–105	2 min-
SW	~1.3	He	1520	RSS, TEM, & XRD	–	70–100	1–3 min
CNT	–	He	760	SEM & RSS	20	60	2–8 sec
SW	1–3–1–5	He	375	TEM & RSS	23–25	55	20 min
SW	~1.3–1.8	He	530–550	TEM, SEM,TGA, NIR, & RSS	–	90–120	30–150 min
SW	2	He	100–1000	TEM & RSS	120	78.5	3 min
SW/HW	0.34	He	113	HRTEM & SEM	35	30	5 min
MW	30	He	140	TEM	20–30	700	–
MW	–	H ₂	50–700	TEM & HRTEM	–	90	23 min
SW	20	H ₂	200	TEM, RSS & SEM	–	150	3 min
MW	1	H ₂	10–200	TEM & SEM	–	20–100	–
MW	10–20	CH ₄	100, 300 &500	TEM, SEM, FTIR, XRD, OES, & RSS	–	90	–
CNT	30–60	N ₂	760	SEM, FTIR, & OPT	70	16–20	–
MW	–	N ₂	0–900	SEM, HRTEM, TEM, EDX, & XRD	22–25	35–44	50–120 sec
SW	0.89	NaCl	760	SEM, TEM, & EDX	26	50	60 sec
CNT	20–50	C ₃ H ₈ & Ar	760	SEM, TEM, XRD, & RSS	5–10 Kv	20	3–5 sec
SW	1.5–1.7	He & CO	225	FESEM, TEM, TGA, & RSS	50	100	–
DW	2.7–4.7	H ₂ & Ar	350	HRSEM, TEM, RSS	26–28	75–80	40 min
SW	–	He, Ar & Krypton	500	HPLC, TEM & SEM	–	22	3–30 h
SW	–	He, Ar &N ₂	50–1000	TEM & RSS	–	50–60	–

AFM – Atomic Force Microscopy, DSC – Differential Scanning Calorimeter, EDX – Energy Dispersive X-Ray Analysis, EELS – Electron Energy Loss Spectroscopy, FESEM - Field Emission Scanning Electron Microscopy, FEG-SEM- Field Emission Gun Scanning Electron Microscopy, FTIR – Fourier Transform Infrared Spectroscopy, HPLC – High-Performance Liquid Chromatography, HRTEM – High-Resolution Transmission Electron Microscopy, ND- Neutron Diffraction, NIR - Near- Infrared Spectroscopy, OAS – Optical Absorption Spectroscopy, OES – Optical Emission Spectroscopy, OPT- Optical Pyrometer, RIS – Radiation-Induced Segregation, RSS - Raman Scattering Spectroscopy, SEM – Scanning Electron Microscopy, SPM – Scanning Probe Microscopy, STEM - Scanning Transmission Electron Microscopy, TEM – Transmission Electron Microscopy, TGA – Thermal Gravimetric Analysis, XRD – X-Ray Diffraction, XPS – X-Ray Photoelectron Spectroscopy. (Abbreviation of listed characterization techniques).

Table 4
Review of CNT synthesis using the LA technique.

CNT Type	Diameter (mm)	Inert Gas Length(μm/nm)	Type	Pressure (Torr)	Characterization	Laser source	Technique Setup Temp. (°C)	Target	Catalyst	Refs.
SW	1.4	1 μm	Ar	400	SEM, TEM, RSS, & ND	CO ₂ Laser	Ambient	Graphite	Co, Co/Ni, Fe, Fe/Ni, Ni, & Ni/Y	[88]
SW	–	–	Ar	–	SEM	Pulsed Nd: YAG	1200	Graphite	Co & Ni	[89]
MW	1.5–3.5	300 nm	Ar	500	TEM	Nd:YAG Laser	1200	Graphite	No Metal	[90]
SW	1.1–1.5	–	Ar	500	TEM, SEM, XRD, TGA, & RSS	CO ₂ Laser	<1200	Carbon	Co/Ni	[91]
SW	–	–	Ar	–	TEM, SEM, & RSS	CO ₂ Laser	25–1200	Carbon	Co/Ni	[92]
SW	1.1–1.4	10–20 μm	Ar	–	HRTEM & RSS	Pulsed Nd: YAG	800–1150	Graphite	Co/Ni	[93]
SW	1–1.7	–	Ar	200–400	HRTEM & RSS	CO ₂ Laser	Ambient	Graphite	Co/Ni	[94]
SW	1.2–1.4	20–200 nm	Ar	150–760	TEM & RSS	CO ₂ Laser	Ambient	Graphite	Co/Ni	[95]
SW	1.1–1.6	20–200 nm	Ar	200–400	HRTEM & RSS	CO ₂ Laser	Ambient	Graphite	Co/Ni	[96]
SW	1.23–1.46	–	Ar	525	TEM, SEM, RSS, & AFM	CO ₂ Laser	Ambient	Graphite	Co, & Ni	[97]
SW	1.25–1.3	–	Ar	500	TEM, SEM, & RSS	Nd:YAG Laser	1000	Graphite	Ni & Co	[98]
SW	1.3–1.4	–	N ₂	500	TEM, SEM, & EELS	Nd:YAG Laser	1200	Graphite	Ni & Co	[99]
SW	1.2–1.3	–	N ₂ / Ar	750	HRTEM & RSS	CO ₂ Laser	1100	Graphite	Ni & Co	[100]
SW	10–20	1 μm	N ₂ / Ar & He	200–400	TEM, SEM, & RSS	CO ₂ Laser	Ambient	Graphite	Ni & Y	[101]
MW	50–150	1–3.5 μm	O ₂ & Ar	2	TEM, SEM, OES, & EDX	KrF Laser	Ambient	Graphite	Ni & Ni-Co	[102]
SW	30–100	–	N ₂ & B	760	STEM, RSS, TGA, XPS, & XRD	CO ₂ Laser	Ambient	Boron	Carbon	[103]

wavelength, repetition rate, flow, pressure due to buffer gas, pressure in the chamber, chemical composition, and ambient temperature. SWNTs have better purity and better-quality production in this method. From the same perspective, the arc-discharge method is the same as the laser ablation method, but in the laser method, the required force is given by a laser that heats a pure graphite pellet holding catalyst materials. Due to the use of highly purified graphite rods and laser powers, this method is economically high. The number of nanotubes synthesized every day is not much enough as arc-discharge techniques. Fig. 8a and 6b show the SWNT fibers image in 10 to 20 nm in diameter and micrometers long which was captured by SEM and TEM respectively [87].

2.3. Thermal synthesis process

Laser ablation and arc discharge methods are elementary called plasma-based synthesis. In the thermal process, thermal energy is controlled and the heat never goes beyond 1200 °C. A similar procedure

will include the

instance of plasma-enhanced CVD. The active catalyst materials like Fe, Ni, and Co. Here, CNTs depend on carbon feedstock. Sometimes active feedstock like Mo and Ru will add to form the CNTs. Synthesis of CNT by the thermal method is the easiest way for different chemical vapor deposition methods. These processes include chemical vapor deposition, monoxide synthesis, and flame synthesis.

2.4. Chemical vapor deposition (CVD)

Two major problems remain for the above synthesis techniques, for example, high temperature, large scale production, and lots of filtered purifications are needed for synthesis. In 1996, CVD was discovered for nanotube synthesis [104,105]. The method can control the development component and synthesis a huge amount of nanotubes. The presence of volatile chemicals can be changed by some reaction into the desired solid films. CVD carries out the fullerene at atmospheric pressure. Here two types of fullerene use; the horizontal and vertical configuration. Put the substrate in an oven and heated up to 700 °C–900 °C temperature and gradually add the acetylene, methane, or ethylene which are belonging to the carbon bearing gas, and nitrogen is brought into the response chamber. These carbon gases are called catalyst mixtures and carrier gases are Argon and Hydrogen. Throughout the process, nanotubes are shaped. Synthesis product yield is 90% and high purity. Due to the broken of the carbon-containing apparatus gas is being apart and the carbon becomes visible at the edge of the nanoparticles where the nanotubes start to produce. This mechanism is still under review [106]. It has mainly two major advantages; lower quantity and deposition of the catalyst over the substrate, to allow well-organized structure.

2.5. Vapor-phase growth

Vapor phase growth is an advanced and modified method of CVD. Through this method, CNT will be synthesized in the chamber with catalytic metal and without substrate [107]. In this technique, Ferrocene is acted as a catalyst with the presence of two furnaces situated in the response chamber with low temperature. All through the process, fine catalytic particles are formed in the first furnace and when they reach

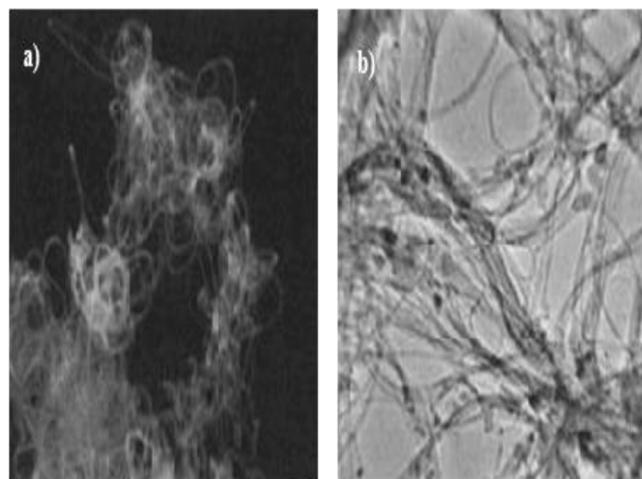


Fig. 8. a). SEM image of SWNT b). TEM image of SWNT (both are 10 to 20 nm diameter and length in micrometer range/100 nm scale bar) [87].

the second furnace, carbons are gotten up speed into the catalyst by diffusion to convert into CNTs. In some cases, argon flow was also used for catalyst and the reactant was slowly added into the chamber. Fig. 9a and 9b images of CNT which are synthesized by different gas bubbling such as Ar and C₂H₂ carrier gas respectively.

2.6. Flame synthesis method

Another method for CNTs synthesis can be possible by using a flame. Using of the flame is act as synthesis medium which provides both the energy and chemical species simultaneously a various form of carbon in nanolevel. For flame, fuel (gases like methane (CH₄), ethylene (C₂H₄) and acetylene (C₂H₂)...etc.,) with an oxidizer to produce a different gaseous mixture that involved carbon dioxide (CO₂), water vapor (H₂O), carbon monoxide (CO), hydrogen (H₂) saturated and unsaturated hydrocarbons (C₂H₂, C₂H₄, C₂H₆) and radicals [108]. Catalytic is required to provide reaction sites for the deposition of solid black carbon. While compared to another method, the flame synthesis method is an auto-thermal process where it can provide temperature to achieve the desired synthesis condition. The vaporized catalyst can be injected inside a flame. Flames are scalable and are commercially used for the production of solid carbon forms such as carbon black and printing ink. This method is useful to grow to determine the development rate and also the structure of CNTs. CNTs develop in a similar way to the CVD method.

2.7. Plasma enhanced chemical vapor deposition (PECVD)

By this synthesis method of CNTs, the temperature can be reduced. While comparing to CVD, the PECVD method is better to lessen the temperature at a low level and to control the growth mechanism. In PECVD, gas molecules are effectively dissociated by the plasmatic energy and CNTs start to form at low temperature. Its magnitude higher development rates are two orders growth. Plasma is the most significant part of the production of SWNT. In PECVD, the plasma mode of an atmospheric pressure radio-frequency discharge (APRFD) reactor, which traveled from a so-called mode (60 W) to mode (100 W) as the input power [109]. Below Fig. 10a and 10b show the TEM image of SWCNT prepared in different input power during plasma deposition technique. An electron generates when the ion hits the first electrodes and secondary electrons are created in the plasma sheet by the electric field. The growth instrument of CNTs is constrained by an outside magnetic field to steer the bearing of the ferromagnetic iron. The advantage of using the PECVD method is the built-in electric field which presents in a plasma sheath while adjusting the developing CNTs along the electric

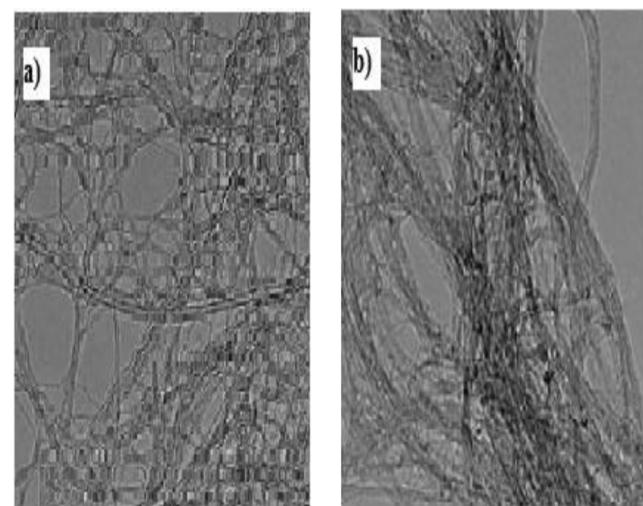


Fig. 10. a). TEM image of SWCNT at different input power 80w and b) 40w (100 nm scale bar) [109].

Table 5

Comparison of the three most common carbon nanotube synthesis methods.

Process	Arc-Discharge	Laser Ablation	CVD Method
Yield of Process [110]	Moderate (70%)	High (80–85%)	High (95–99%)
Temperature	1700 °C	1200 °C	700 °C-900 °C
Diameter	4 to 30 nm	10–20 nm	20–25 nm [111]
Purity	High	High	High
Production Rate	Low	Low	Low
Cost	High	High	Low
Process Control	Difficult	Difficult	Easy
Energy Requirement	High	High	Moderate
Advantages [112]	Simple, Inexpensive, High-Quality NT	High Purity, Synthesis in room temperature production	Simple, High purity, Large scale production
Disadvantages	High Temperature, Less purified, Tangled NT	Limited method to the lab scale	Defects in MWNTs

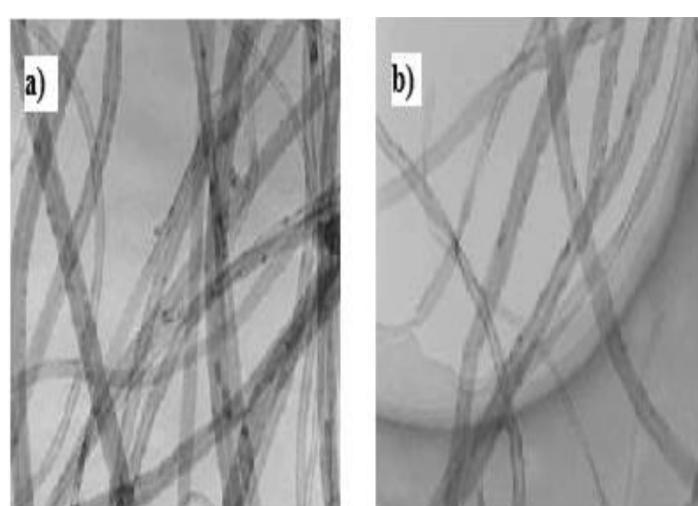


Fig. 9. a). TEM image of CNT synthesized by Ar carrier gas b) TEM image of CNT synthesized by a C₂H₂ carrier gas (in 100 nm scale bar) [107].

field lines.

Among the various synthesis method, the important synthesis methods of CNT are summarized in [Table 5](#) by comparison of their different mechanism which is important during the synthesis time and in conclusion, it shows that the CVD method is appropriate for the synthesis of CNT in which purity is high as well as the higher yield of the process (95–99%) in lowest temperature (700 °C–900 °C). The next topic of discussion is the purification of CNT which is another important aspect to get a purified form of CNT including process, arc-discharge, laser ablation and CVD method as summarised in [Table 6](#).

3. Purification of CNTs

After synthesis, the process for purification is achieved by separating from unwanted entities, such as amorphous carbon, carbon nanoparticles, residual catalyst, and other graphitic impurities. During the synthesized process, tubes are contaminated with metal nanoparticles, fullerenes, nanocrystalline graphite, and amorphous carbon which are coating with the dividers of nanotubes. Efficient and mild purification methods should be used to remove impurities where it will not harm the carbon nanotubes. This purification step involves oxidants such as HNO₃ and KMnO₄ / H₂SO₄. The raw products have impurities like aerogel, catalyst particles, amount of amorphous which is utilized to Coat on catalyst nanoparticles [133]. The process will happen in both physical and chemical where it develops three-step purification methods that

involve the selective oxidation of carbon in hydrogen peroxide (H₂O₂) at room temperature. Mesoporous silica and metal particles are removed from MWNT treatments. After implementing the purification process constitute have 95% of carbon particle. Most of the techniques are used to remove the impurities and prove the purification process at the same time. The techniques that will be discussed are liquid phase, gas phase in chemical methods and filtration, sonication, chromatography in

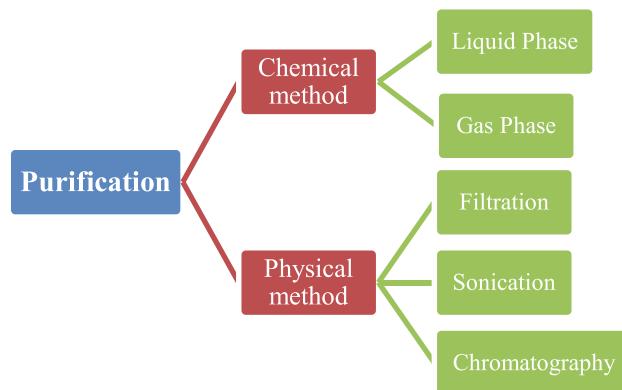


Fig. 11. Purification methods of CNT.

Table 6
Review of synthesis of CNTs employing CVD technique.

CNT Type	Diameter(mm)	Inert Gas Length (μm/mm)	Type	Pressure (Torr)	Characterization	Carbon Source	Technique Time	Setup Temp.(°C)	Catalyst	Refs.
MW SW& DW CNT	– 0.75 2–13	5–10 μm – 60 μm	Ar Ar	– –	SEM & TEM RIS & XPS	Acetylene Methane	– 30	1100 900	Ferrocene Fe, Fe/Ru, & Fe/Mo Ferrocene	[113] [114] [115]
DW & SW MW	1.1–1.42 & 1.4	–	Ar	–	TEM	Methane, butane, & acetylene Methane	10	900	Fe/Al ₂ O ₃	[116]
MW	33.8 & 37.2	–	Ar	–	TEM, SEM, AFM, TGA, & RSS	Benzene	5–240	750	Ferrocene	[117]
MW	31–36	–	Ar	–	TEM, FESEM, FTIR, & TGA	Acetylene	60	850	Ferrocene	[118]
MW	9.5–20.5	–	H ₂	–	TEM, SEM, HRTEM, RSS	Methane	10–60	1000	MgMoO ₄	[119]
MW	10–140	–	H ₂	–	TEM & AFM	Cyclohexane	5	750	Co, Fe, & Alumina	[120]
MW & SW	0.8–2	–	H ₂	–	HRTEM & RSS	Methane	10	800–1000 (MW) 1000 (SW)	Co, Fe, Ni, & Co-Fe	[121]
SW & MW CNT	10–40 20–400	Infinite 0.1–50 μm	H ₂ NH ₃	– –	HRTEM, TEM, SEM, & RSS HRTEM & SEM	Thiophene vapor & benzene Acetylene	1–30 10	1100–1200 666	Ferrocene Ni coated glass	[122] [123]
MW	10–50	–	N ₂	–	TEM, SEM, XRD, & TGA	Polypropylene	40	500–800	NiO/HZSM-5 zeolite	[124]
MW	30,40,70, & 100 at 750 °C, 800 °C, 850 °C, & 1000 °C respectively	–	N ₂	–	TEM, SEM, & RSS	Acetylene	15	750–900	NH ₃ /Co	[125]
MW	–	–	N ₂	–	TEM, SEM, RSS, FTIR & TGA	Xylene & cyclohexanol	–	750	Ferrocene	[126]
SW	1–3	–	N ₂	–	TEM, SEM, RSS, & TGA	Ethylene	10	550–750	Fe, Fe/Al, Fe/Al ₂ O ₃ , & Co/Al ₂ O ₃	[127]
SW	1–5	–	Ar & Carbon monoxide	100	TEM	Carbon monoxide	60	1200	Co-Ni & Co-Mo	[128]
SW & MW	1	–	Carbon monoxide	100	TEM & RSS	Carbon monoxide	60	700	SiO ₂ /Co-Mo	[129]
MW SW	30 0.84–1.29	12 μm ~10 μm	H ₂ –NH ₃ H ₂ –N ₂	20 –	TEM & SEM TEM, SEM, XRD, & RSS	Acetylene Coal gas	5–10 30	825 850–950	Co Ferrocene	[130] [131]
MW	100–300	50–150 nm	H ₂ –N ₂	–	TEM, SEM, & XRD	Acetylene	30	700	BaCl ₂ & CaCl ₂	[132]

physical methods. Fig. 11 shows the various method of the purification process.

3.1. Chemical Purification

For both wet and dry conditions, the for the most part utilized purification process includes the oxidation of synthesized CNTs. Oxidation for the wet condition is processed by the solution of concentrated acids or strong oxidants and for the dry condition oxidation by air, oxygen, or other gases at a controlled temperature. The idea behind this approach is a selective oxidative process, based on eliminating the amorphous carbon and carbon particles more easily than CNTs due to their higher oxidation response rate than it. Due to the availability of hanging bonds in amorphous carbon, its oxidative activity shows high with high energy meanwhile, a pentagonal carbon ring with big curvature will be attributed to the higher reactivity of the carbon nanoparticles. The reactivity and oxidizing capacity of Single-walled carbon, such as C_60 are increased with decreasing diameter [134]. Tips of the nanotubes are open due to oxidation. Pentagonal carbon rings tips have less chemically stable than the hexagonal carbon ring structure of the cylindrical tube. So at the time of the oxidation during purification, the accessibility of five-member rings in the hexagonal array turns out to be more significant of the CNT tips.

3.1.1. Liquid phase oxidation reagents

To get the most homogeneous oxidation in CNT, it should take place in solutions [135]. The common point will describe commonly used oxidation reagents and related procedures.

(a) Mineral acids

In the liquid-phase, chemical oxidation has drawn great concentration due to its simplified process and high efficiency [136]. Probably the mineral acid is the most employed treatment as compare to all methods of liquid-phase oxidation. Concentrated acid is used at the time purification process to dissolve metal particles and carbon impurity [137] from CNTs. Removing of catalyst particles depends on two factors that is oxidation duration and reflux temperature. Because of the high impact of temperatures and acid concentrations defective sites of the CNT surfaces will attack and this will tend to shorten and destruction of the CNT structure, and other perspectives for acid reflux for a short duration, low acid concentration and temperature to the introduction of CNT result from the deficient expulsion of the metal particles. Mohanapriya and Lakshmi Narayanan [138], Delpeux et. al., [139] used nitric acid for refluxing treatment for the duration of 30 min and observe that without any significant structural damages to the CNTs the metal particle dissolves, and the tips are open without any defect. By the X-ray diffraction (XRD) of CNTs showed the peak variation between metallic impurities in CNT and expulsion of the metallic impurities from it, where it shows that a very few peaks explain that the catalytic impurities diminished after the acid treatment. As for a further explanation for purification of CNT observed by Zhao and his colleagues is that shifting of XRD diffraction peak of the purified sample towards a lower angle which suggests rising in the interlayer spacing.

The oxidative etching of nitric acid on graphitic walls of CNTs is the main effective feature that was reported by researchers. During the prolonged period of purification, effective defect sites are attacked by the nitric acid and unzip the tube walls of CNTs by further oxidative etching, which increases the interlayer spacing of the tube. The carbons which were oxidatively removed through the reaction as:



Post researchers study and research show the removal of the catalyst particles in nitric reflux treatment. The carbonaceous impurities and the metal particles could be effectively dissolved and expelled from CNTs. simultaneously at the crucial conditions; some oxidative damages and

changes were induced to the walls of the nanotubes. The presence of a degree of disorder in the sample is given by D-band intensity in Raman spectra, which is mainly due to defects and carbonaceous particles of CNT [136].

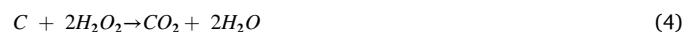
(b) Oxidants

Some other liquid oxidizing agents are also used for the purification process other than oxidants of mineral acids. Basically, the used oxidants in the treatments are hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$) [140], etc. Carbon surface will oxidize using metal cations because of sufficient high oxidation potential. The factor on which oxidation depends is the redox potential of the system and structural features of the nanotubes, where it consisting of curvature, pentagon, heptagon ring position, helicity, and many other parameters. Colomer et al., [141] and Fonseca et al., [142] have reported their research by using acidified $KMnO_4$ for the effective reflux oxidation to get control on the oxidation reaction, in low down temperatures range of around 80 °C. They detailed that the absence of amorphous carbon will get in CNT when more than 60% of carbon loss will found in it.

By the transmission electron microscopy (TEM) images of pure nanotubes obtained indicated that all aggregates of amorphous carbon have been removed by the treatment, and thus resulted in tips opening. Equation (2) represents the oxidative treatment:



Similarly, Hernadi et al., [143] got the same result by using reflux $KMnO_4$ for purification where it was reported that $KMnO_4$ was capable of creating an oxidized tube that is free from amorphous carbon. In any case at the time of oxidation extra steps are needed to extract the MnO_2 . Furthermore, it converts them into soluble or volatile products then it would be beneficial to remove carbonaceous impurities and $KMnO_4$ appears as a less suitable oxidation agent. Hernadi and co-workers have also observed that oxidation that H_2O_2 is additionally used for purification treatment since the purified product contains a low amount of impurities, and the product formed is water, as:



In the recent studies done by Suzuki et al. [144] for purification of SWCNTs by reflux of H_2O_2 solution for 6 h at 110 °C, produced using iron particles catalyst by arc plasma jet method in large quantities. By this research, the outcomes obtained that the huge amount of unwanted amorphous carbon can be successfully eliminated due to the presence of iron particles because oxygen generated by the reaction among iron and the H_2O_2 solution oxidized the amorphous carbon.

(c) Alkali

For purification of CNTs, we can also use an alkali based solution. Raymundo-Pinero and colleagues [145] have studied a technique for concurrent purification and opening of CNT using sodium hydroxide ($NaOH$). For the response to be performed 3:1 ratio of $NaOH$ with MWCNTs will be mixing physically followed by heat-treatment at around 700 °C. After the reaction, it analyzes that the Nano tubular morphology was preserved after the reaction and defects disappeared on the wall structure. This is because of the inability of metallic sodium to intercalate into well-organized materials, and it can only proceed to highly disordered carbonaceous impurities [146]. So to open the tubes, $NaOH$ treatment removed the catalytic support, amorphous carbon, and the catalyst metal particles. The mild conditions have removed the metal impurities without harm to the sidewalls [147].

(d) Mixed oxidants

To get the greater oxidative effect, mixtures of acid solutions or

strong oxidants were employed Salernitano et al., [148]. For achieving a better result he compared the effectiveness of purification between nitric acid (HNO_3) and mixtures of nitric acid and hydrochloric acid (HNO_3/HCl) at the ratio of 3:1. By the X-ray photoelectron spectroscopy (XPS) analysis for the purified CNTs showed that an expansion in C/Fe atomic ratio more than three times after HNO_3 treatment and more than eight times after immersion in HNO_3/HCl mixture, indicating the presence of synergy effect between the mixed acid solutions. They concluded that the treatment with HNO_3 dissolved the metal particles; meanwhile, HCl ensured the removal of the eventual metal oxides. Ziegler et. al. [149] have studied and shown the impact of heated and cooled piranha solution (4:1 v/v 96% H_2SO_4 /30% H_2O_2) in the oxidative cutting of nanotubes in which the readily available damaged sites on the sidewall of CNTs were removed without increasing the sidewall damage. Results demonstrated that at high temperature, the piranha is able for attacking existing harm sites and consuming the oxidized opening to cut the nanotubes, resulting in the etching of small-diameter nanotubes and In contrast, low-temperature piranha attacked the existing damage sites on the sidewall without introducing new damage sites, and therefore demonstrated minimal carbon loss and the slow etch rate preserved the original diameter distribution of nanotubes.

Another study by Zhang et al., [150] for purification of CNTs is carried out by the mixed acid treatment between sulfuric acid and nitric acid ($\text{H}_2\text{SO}_4/\text{HNO}_3$) in the ratio of 4:1 v/v. A tremendous structural modification was observed after the treatment which was suggested that after the reaction between mixed acids and CNTs some amorphous materials were formed. A lot of broken SWCNTs were observed, and the majority of these broken ends remained open. The outcome shows that mixed acid treatment is a promising method to cut CNTs into fragments with opened ends.

(e) Microwave digestion

Recently an impressive method was introduced to purify CNTs, microwave digestion [151]. Studies were showed that concentrated acid can absorb microwave rapidly by quickly dissolving the metal particles and thus preventing damages to the tubes. Researcher Chen et. al. [152] have set up a microwave digestion system that can create a homogeneous microwave field without causing incomplete digestion. Owing to the greater heat absorption without agitation, the timing of the process of microwave digestion could be reduced and the amorphous carbon together with the catalyst embedded in the tubes can be eliminated. They have also observed that the time of acid treatment will increase with the increase of purification efficiency. This finding is also reported by Ko and workers As the increased, attached impurities to the CNTs gradually began to detach and dissolve into the acid solution. Ko and workers [153] have also conducted a microwave-assisted purification without an acid solution in the presence of 20% H_2O_2 . The result shows that the oxidizing intensity of H_2O_2 toward the disintegration of amorphous carbon and metal particles is higher than that of HNO_3 over a range of temperatures, indicating that the former is a more good purification agent than the latter. This method of purification has several advantages such as low thermal budget, closed vessel, less acid consumed, and low volatile elements.

(f) Effects of liquid-phase oxidation

Purification of CNTs with liquid-phase oxidation always leads to surface chemical modification on CNTs [154]. Many elementary kinds of researches showing that, for achieving the narrow length distributions in CNTs, it should be cut into small fragments by acid modification. This modification increases with the rising time of oxidation and temperature. Moreover, for industrial applications, particularly for electronic devices production requires undamaged CNTs to place nanotubes with a specific bandgap and precise length in a well-defined location on the substrate.

Also, for other applications, it is evident that the carboxylic acids, aldehyde, alcohol, and other oxygenated functional groups would also be induced on the sidewall and finishes of CNTs [155]. This condition for requirement enables the deposition of various types of metal nanoparticles and ions or chemical attachment of different kinds of functional groups on the outside of CNTs. Because of the wide range of coupling reactions that are available on it for grafting of different types of molecules to the CNTs, carboxylic acids are the best one as a functional group. In the field of nanoelectronics, the control of fictionalization could answer the problem of reproducible and rapid placement on the nanometer scale by independent assembling. It is also worth to mention that, in certain conditions, the CNTs are functionalized as well as the amorphous carbon Rosca et al., [156] suggested that the presence of functionalized amorphous carbon may work as a surfactant for CNTs. The ease of dispersing in polar solvent indicates that there is a role played by these polar functionalized groups, where pristine CNTs are hydrophobic and remain unwanted.

3.1.2. Gas-phase oxidation reagents

In this method of purification, the gases are commonly applied for the purification like dry/wet air, carbon dioxide, and hydrogen.

(a) Air

In this air process, thermal oxidation is powerful to extract the amorphous carbon and other carbonaceous impurities at room temperature in CNTs. The result of oxygen is breaking, CNT walls, and weakening among the knotted CNT [157]. The annealing process starts from the range of 480 °C and the amorphous carbon decomposed at 480 °C-500 °C [158]. The CNT powder is oxidized in air, the configuration of the reactivity like pentagons, heptagons, and amorphous carbon is greater than that of the cylindrical wall of the CNT.Li.et.al., [159] have studied the air oxidation of CNTs in various temperature running from 480 °C to 750 °C While the result will show that temperature increases the outside area it opens the internal cavities in the shape of breaking the cylindrical walls. The annealing temperatures will rise to 750 °C about 90% of CNTs were lost and the structure gets damaged while decreasing the surface area.

(b) Other gases

To remove the selective disordered amorphous carbon will be based on mild oxidation by CO_2 [160]. Smith et al., [161] have shown mild oxidation at 600 °C and found that carbon splices were removed. 30% of the mass can be removed from the sample. The method for the response is utilized to diminish the purification.



Carbon covering on the metal catalyst particles can be removed through high temperature by treatment of hydrogen gases. The amorphous carbon is changed to carbon dioxide (CO_2) by using air oxidation and then transformed into methane (CH_4) in hydrogen treatment. Instead of using hydrogen, Wang and others [162] have developed ammonia (NH_3) to take away the carbon impurities and to repair the damaged CNT's sidewalls. It has some advantage when we compared to hydrogen in terms of safety and easy handling. NH_3 has a high temperature, a limited quantity of carbon disordered materials to cleanse the CNTs [163]. Ammonia provides strong van der Waals forces to bring about the CNTs in the characterization image of TEM and is used to form the CNTs in the method for think and entangled bundles.

(a) Effect of gas-phase oxidation

In the gas-phase amorphous carbon is useful against wet oxidation since it is more controllable [164]. Gas-phase oxidation is the more distinct procedure and it requires high activation energy for diameter

specific purification. In gas-phase oxidation, oxidizing CNTs are not introducing any sidewall impacts when compared with liquid-phase oxidation. This advantage will enable the gas phase purified nanotubes to adjust the CNT in tight bundles that are well alienated from one another and do not form any mats and clusters in acid-oxidized SWNTs. After purification, it does not need any complex equipment, and no filtration or other separation [165]. It emerged as a mild process that can resolve the dilemma of low product yield after the purification.

3.1.3. Halogenations

For some selective oxidation of carbonaceous impurities, halogen is used [166]. From the halogen family, Bromine is used for effective procedures in CNTs purification [167]. Intercalation mixes of graphene are shaped by the placing of atomic or molecular layers of a unique chemical species between layers in graphite host materials. By taking pure liquid bromine under nitrogen atmosphere Br was mixing raw CNTs. In such conditions, the configuration of the C-Br₂ complex creates on the CNT surface and defect sites by the charge transferring between Br and carbon [168]. It was interesting to observe that Br demonstrated orientation like the spoke of wheel perpendicular to the tangent of graphite layers on CNTs. According to Hou and coworkers [167], due to large amounts of defects site present on surface intercalation of Br normally takes place on. Br would be further reactive towards these regions because more defects exist on the amorphous carbon and other disorder carbonaceous materials. When brominates the CNTs were subjected to air combustion at 550 °C, the graphite layers were broken along the line in which Br accumulated, indicating that the addition of Br has influenced the reactivity of the tubes toward oxygen. The amorphous carbon can be effectively oxidized, due to the difference of oxidation between the brominate region and the normal CNTs. As a result, the catalyst particles that were initially enclosed in the tubes were exposed and displaced at that instant. During oxidation due to capillary action, Br diffused into the hollow CNTs and resulted in the breakage of interior graphite layers [168].

3.2. Physical Purification

This physical purification is used to lessen the damage caused by direct oxidation by a nonconventional technique such as ultrasonication, filtration, and chromatography to purify the CNTs.

3.2.1. Ultrasonication

The ultra-sonication techniques are performed by the separation of the particles. To apply this method high energy is applied for CNTs in the presence of the solvents like dichloromethane and O- dichlorobenzene [169]. During this process, the molecules are capable to interact with CNTs and lead to solubilization. At the time of ultra-sonication treatment, isolation of the MWCNTs is increasing simultaneously where carbon nanoparticles were observed. Lu et al., [170] have studied the result of sonication towards the CNTs structure. They observed that nanotubes show defects such as bending and buckling at very high concentrations. The external layer of the graphite was stripped to giving the thinning of the nanotubes. The outer layer will absorb the damage of the sonication and the protective the damage layer by using inner tubes. The structural damage of the tube depends upon the solvent. In this process, CNT appeared shorter and it also includes nanotube cutting, and the opening of the tip of the CNT was observed. At the same time, the functional groups should form uniformly to build the sidewalls. Ultrasonication is an effective method to functionalize the MWNTs surface [171].

3.2.2. Filtration

Filtration depends on size as far as length and diameter or particle separation. CNT is separated from impurities and also the nanotubes by a length from filtration with the membrane of the narrow pore. Some sizes and splices were not accomplished with a range of fractionating

then nanotubes and a full range of fractionating membranes were necessary for effective the nanotubes. Abatemoardo et.al., [172] has conducted filtration by membranes with different pores diameters. The sequence ranges from largest to smallest are the cross-flow system. By using this way, oxidation is not necessary. The result will be showed that way, all large aggregates were continued by the larger pore size membrane, and CNTs were continued by the smaller pore size membrane. Both larger pore and smaller pore are separated by using filtration. Here, fractionation is equal to the length of the CNTs. A type of filtration is otherwise called cross-flow filtration. This cross-flow

filtration was connected to separate water-insoluble CNTs towards the size or length. It has some cons of filtration have been revealed in leaves some undefined particles stuck to the nanopores. This technique is less effective for low quality which was generated by arc-discharge [173].

3.2.3. Chromatography

It is used for purification as well as disconnection of the length of CNTs. For length separation chromatography used two common techniques that are High-Performance Liquid Chromatography (HPLC) [174] and Size Exclusion Chromatography (SEC) [175]. In SEC length separation can be with or without the reagents to develop the CNT dispersion solvent. The outcome can be experiential that the CNT can be purified and isolated by their length.

3.2.4. Surfactants

The procedures of physical separation are based on the use of surfactant solutions to disperse the CNTs before subjecting them to separation by filtration, centrifugation, etc. [176]. In microscale aggregates, CNTs tend to self-associate so the use of surfactants was crucial to forming the individual tubes as this is called the fundamental for physical separation. Examine the solubility of CNTs is very significant for their chemical and physical properties, for its easy characterization, and facilitates their manipulation. Sodium dodecyl sulfate (SDS) [177] and dodecyl-benzene sodium sulfonate (NaDDBS) [178] were ionic surfactants used to establish to be capable and usually used to decrease CNTs' aggregative inclination in water. In the progression of dispersion, after the surfactant has been adsorbed on the nanotube surface, ultrasonication for minutes or hours the surfactant to scatter the nanotube packages by steric or electrostatic repulsion. According to Shvartzman-Cohen et al. [179] after surfactant has been included the peripheral nanotubes in a pack are dealt with more than the deepest cylinders and the nanotubes that remain transcendently packaged. Therefore, for getting individual CNTs mechanical shedding of the packs surface treatment must occur.

3.2.5. Effect of physical purification

The refinement of CNTs through chemical methods is preferable to compare to physical methods due to its mild condition which normally prompts incapable purification. However, the advantages of physical separations are the impurities such as nanocapsules, and amorphous carbon can be expelled at a time, and the CNTs are not synthetically adjusted.

3.3. Multi-Step Purification

Simultaneously, the chemical treatment and physical separation in a multi-step procedure can use; it is the purification of CNTs to effectively remove the amorphous carbon, metal particles, and multi-shell carbon nanocapsules [180]. Multi-step purification is the preferred one; as compared to single treatment when concurrently get rid of all the impurities that are present in the CNTs. By toluene, Soxhlet extraction was first done to dispose the rid of the fullerene and soluble impurities from CNTs and then followed by the liquid phase oxidation with H₂O₂ to get rid of the amorphous carbon and by treatment with the presence of SDS surfactant the metallic particles in the example were eliminated by

carrying out through acid. Finally, the graphite and ensured metallic particles are separated by physical separation in SDS solution. It resulted that these methods are proficient and apposite to get high purity CNTs with minimal wall damage [181]. The advantages and disadvantages of the methods are summarized in Table 7.

4. Characterization of CNTs

The most effective techniques for analyzing the samples are electromagnetic spectroscopy, nuclear magnetic resonance (NMR), XRD diffraction, light scattering techniques, Electron microscopy, Atomic forced microscopy (AFM) is used mainly for the general morphology of CNTs. Whereas IR spectroscopy, Raman spectroscopy, and NMR were used to confirm the presence of functional groups on CNTs.

4.1. Electromagnetic spectroscopy

Interaction between the waves and matters, in the appearance of the atoms and molecules, involves the absorption or emission of electromagnetic radiation [182]. It plotted against the wavelength or frequency. We can identify and qualify the materials by using the electromagnetic spectrum. These techniques use light beams and strongly depends upon the ambient environment and the existence of other molecules. The main techniques used in this field, name are discussed below.

4.1.1. UV-Visible Spectroscopy

Ultraviolet-visible (UV-vis) is broadly used to characterize the organic and inorganic nanosized molecules. A sample is illuminated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is analyzed to the consequential spectrum [183]. UV-visible is not only for the characterization of a sample but also for sensing applications. The principle behind the UV-vis is the absorption of photons. It is a distinctive technique for determining the electronic property of nanomaterial. The bandgap of nanosized is also determined by UV-spectroscopy. The range of wavelengths between 800 and 400 nm is visible in the photon. UV ranges are sufficient to excite molecular electrons to higher energy orbital [184]. UV radiation of a lower wavelength is hard to deal with for safety reasons and is once in a while utilized in UV-vis Spectroscopy. Fig. 12. Shows the setup for a UV-vis spectrophotometer for the study of liquid samples.

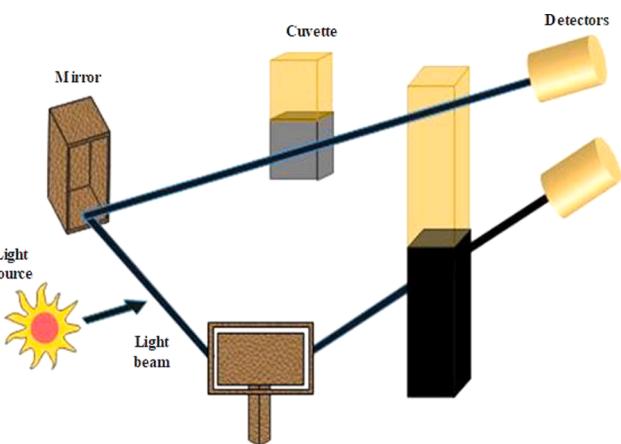


Fig. 12. A typical setup for a UV-vis spectrophotometer for liquid samples.

4.1.2. Photoluminescence (PL) spectroscopy

PL spectroscopy observes the light which emits from atoms or molecules which are absorbed photons [185]. It is apposite for the characterization of both organic and inorganic materials. The state of the samples can be either in the solid form or maybe in liquid or gaseous forms. The use of spectroscopy is in the UV and visible ranges of electromagnetic radiation. The samples can be described by the five parameters which are intensity, emission, wavelength, the bandwidth of the emission, and stability [186].

In PL, dimensions are reduced in the nanoscale range, and then the sample can alter the size and wavelength depends on the properties. Bandgap, recombination mechanism, and contamination levels are used for studying the materials in PL spectroscopy. The liquid samples are set in the quartz cuvette with a path length. In general, PL is double beam optics. The first beam enters through an excitation filter or monochromatic, then the sample is through and it will detect. Fig. 13 shows the setup of the fluorescence spectrophotometer. This impinging light causes photoluminescence which emits all the paths of the surfaces. While in the solid samples, it can be analyzed by the incident beam impinging on the materials. The emission spectrum is recorded and the sample can be monitored at the time of the function, after the flash of light. This technique is called time-resolved, fluorescence spectroscopy. PL includes brighter emission, narrower emission band, and broad UV absorption [187].

4.1.3. Infrared (IR) spectroscopy

IR is a popular characteristics technique where the sample is placed on the IR radiation path and absorbs the different frequencies [188]. All types of samples can be in many formats; like solid, liquid, and gaseous. IR photon energy in the range between 1 and 15 kcal/mol, is insufficient excites electrons to higher energy states, but transitions in vibration energy states. IR spectroscopy is used to identify the structure of bonds between two or more atoms and functional groups. It absorbs all organic compounds, but inorganic materials are less characterized, and heavy metals show vibration transitions in the IR region. Samples can be equipped in several ways for IR measurement. The covalent attachment of nanomaterial to surfaces can be confirmed and quantified using IR spectroscopy. It is useful for studying materials and surfaces of material [189]. Fig. 14 shows the block diagram of a spectrometer.

4.2. Nuclear magnetic resonance (NMR) spectroscopy

It is a complex technique to study and analyze the chemical arrangement of the organic and inorganic compounds in the form of solid or liquid [190]. Nuclei will enclose odd quantities of protons or neutrons which have an inside magnetic moment and some nuclei contain magnetic with an extremely powerful external magnetic field.

Table 7
Purification methods of nanotubes.

Medium	Purification	Description
Chemical method		
Liquid phase oxidation	Remove catalyst	
Mineral acids	Use to opening the tips	
Oxidants	Functional groups	
Alkali	Remove catalyst	
Microwave	Remove catalyst, Opening the tips, reduce the reaction temperature and acids used.	
Gas-Phase oxidation	Remove catalyst	
Air	Opening the tips	
Other gases (NH_3 , H_2 , O_2)	Less damage for CNT structure	
Halogenations	Oxidation of reactive regions of CNTs	
Physical Method		
Filtration	Separation based on their length and diameter	Oxidative treatment is not required
Sonication	The solubility of CNT is enabled in solvents	
Chromatography	CNT is separated according to the length	

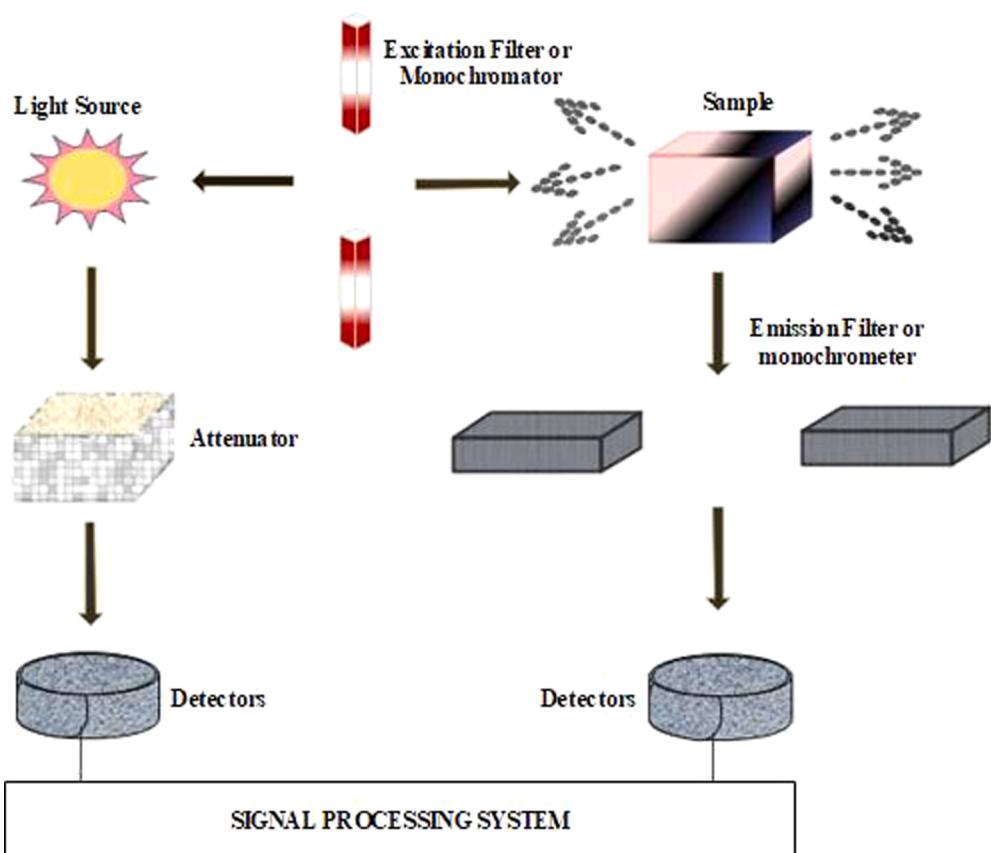


Fig. 13. Fluorescence spectrophotometer instrument setup.

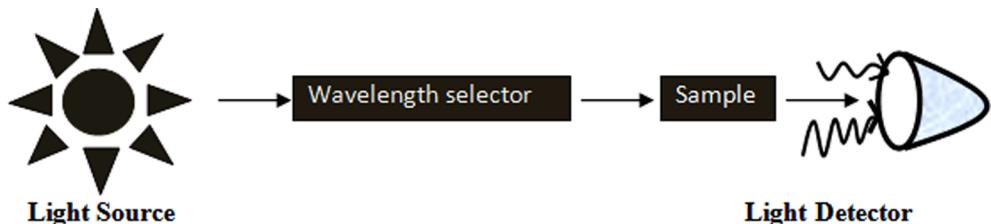


Fig. 14. Block diagram of a spectrophotometer.

Develop the novel components and to find the chemical structure of polymers and biomolecules, for example, polypeptides and proteins. It is mainly used for the structural formation of synthetic materials and explains detailed information on 3D structures and complex molecules like

protein, DNA/RNA.

4.2.1. Detection phenomena in NMR

NMR can show the resonance condition and record an NMR spectrum while using two techniques which are explained below. Fig. 15 shows the setup of NMR spectroscopy.

a) Continuous-wave NMR (CWNMR)

The different energy level can happen between the frequencies of radiation is equivalent to the energy difference between the two levels.

b) Pulsed NMR or pulsed Fourier transform NMR (FT-NMR).

It gives better resolution and sensitivity in NMR. The resonance is not measured continuously it comes one after another but all the nuclei are excited at the same time by a radio frequency pulse.

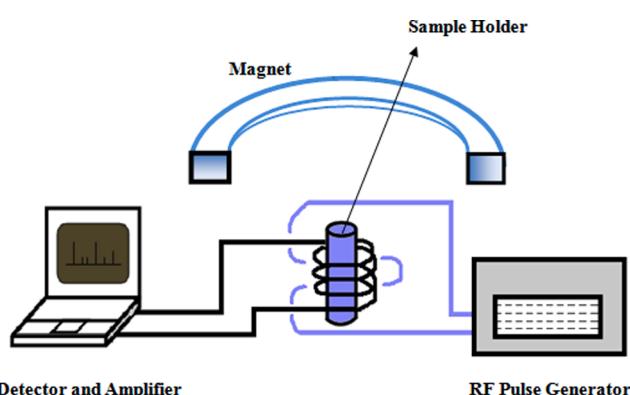


Fig. 15. NMR spectroscopy instrument setup.

4.3. X-ray diffraction (XRD)

It is a crystallographic technique used for identifying and quantifying

the samples available in the solid materials and powders [191]. The dimensional dispersion like cubic, rhombic, etc. While using powder sample on XRD it gives details about the nanocrystal structure, size, and shape of the particles. Generally, XRD is used to correlate the properties of a material to its sensing performance and to determine the structure of organic and inorganic materials [192].

4.4. Light scattering techniques

These techniques investigate the light from materials and types of light dispersing include elastic and inelastic. In elastic, light wavelength remains unchanged to the incident light and inelastic the light wavelength is different from the incident light. It depends upon the frequency of light and the types of scattering which provides initial data about the size, chemical, composition, and structure of nanomaterial. There are two types of characterization in light scattering techniques which are described in Fig. 16.

4.4.1. Dynamic light scattering (DLS)

Dynamic Light Scattering (DLS) likewise named quasi-elastic light scattering and photon correlation spectroscopy (PCS), is normally used for studying colloidal systems as it a relatively fast and straightforward technique [193]. The light beam is directed onto a sample that scatters the light elasticity. This light is scattered during the period and then analyze the particles. It has two main applications which are dynamics in real-time and absolute determination of nanoparticle size [194]. It does not have limitations and it is only suitable for particles used in Rayleigh scattering. In the case of large-size particles have a tenth of a wavelength the angle is dependent on the intensity and scattering is explained by Mie's theory. It is utilized to measure the particles from nanometers to microns. Different limitations are dilute suspension is used to minimized multiple scattering. Differentiating is difficult between tiny fluctuations and noise. A beam of monochromatic light goes through a solution containing the samples. The light dissipated in all the direction as the function of the size and shape of the molecules. The particles move about in a small random pattern at a constant temperature, large particles move slowly than smaller and the distance between the particles is constant. The number of photons can be counted by the time-dependent fluctuation while it returning to the detector after

scattering. DLS has little application are while scanning electron microscopy technique is very accurate but in DLS, estimation utilizes non-ionizing lower vitality light source is performed at room temperature. It also gives the idea about the growth of nanocrystals in solution but other techniques require the samples to be dried [195].

4.4.2. Raman spectroscopy

It is suitable for the quick and consistent screening of the nearness of SWNT. Raman spectroscopy is the method to characterize the CNTs identified with nano-objects as far as the diameter, chirality, thickness,

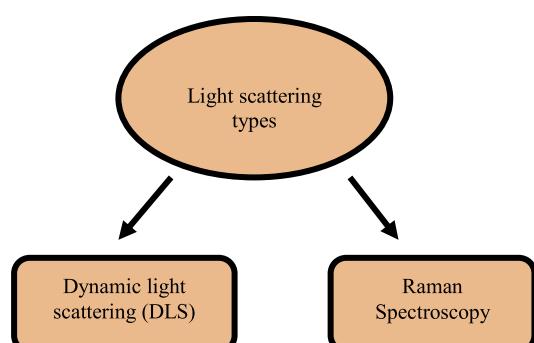


Fig. 16. Types of light scattering.

length, and imperfections. Spectroscopy was recorded in the backscattering geometry on a labram HR (Jobin -Yvon, Horiba Group, France) micro-spectrometer in conjunction with a confocal microscope. It is also a dominant analytical tool for subjectively and quantitatively of composition materials [196]. The experiments were performed out with a wavelength of 514.5 nm from tunable argon laser-concentrated on the sample by $100 \times$ Objective of 0.9 numerical apertures. The spot is around $3 \mu\text{m}$ diameter and the beam intensity is 1mW. Other laser powers and wavelengths were used in order of these parameters. The results in Raman spectroscopy is highly responsive to these materials and provides data about the structure. Even, if have capable of select the signal changes in structure. In Raman spectroscopy of SWNT have a major dilemma in impurities and these impurities have Raman features like D and G groups are identical to that of SWNTs.

4.5. Electron microscopy

Electron microscopy plays a significant role in advanced nanotechnology and nanoscience. In 1929, Ernst Ruska and Max Knoll developed the first electron microscope. Here, the sample was placed in a viewing direction by electron beam at incidence angle. Von Borries (1940) built up a Transmission Electron Microscopy (TEM) [197]. It operates similar to optical microscopes, using both illumination source and magnifying lenses. While comparing to optical, it has more resolution between electrons. nanoscale features are visible in electron microscopy but not in optical microscopes. Electron microscopy has two instruments which are scanning electron microscopy (SEM) and transmission electron microscope (TEM).

4.5.1. Scanning electron microscopy (SEM)

SEM is the most instrumentation for characterizes the nanomaterial and used to analyze the CNT morphology. It is probably going to get optional electron pictures of sample materials with nanoscale levels. The sample must be conducting or enclosed with a thin metal layer to keep away from the electric charging. Composition analyzes of material are analyzing by monitoring produced X-rays by the electron [198]. In SEM, the electron beam is ejected from a heated filament which is made from lanthanum hexaboride (LaB₆) or tungsten. By applying voltage, the filament is heated for electrons to be emitted. Sometimes, electrons can be produced by field emission (FE). Electrons are moved towards the sample after applying the electric potential and the electron beam is focused around the condenser lens. Then focused by the objective lens and raster-scanned over the sample by the scanning coils. Scan coil gets energies by the varying voltage and it creates the magnetic field. Electrons hit the sample they produce energy to electrons present in the sample and achieving in the secondary electrons. Secondary electrons have low energy and electron will collect by an Everhart-Thornley detector, which is converted to a voltage, amplified, and build the image. Low pressure will create while scanning the sample, that's why electrons will not be scattered by gas molecules

inside the chamber [199]. SEM identifies the nanostructure arrangement and development of thin films. SEM is applied for finding the morphology and topography because the researchers understand the connection between the sensing layers or media and the analyses. The basic Setup of the SEM instrument is shown in Fig. 17.

4.5.2. Transmission electron microscope (TEM)

Application on TEM will give the information about morphology, crystallography, and particle size. TEM focused on a beam of high energy electron passed through a thin film and it is capable to provide atomic resolution for lattice images and chemical information at a goal of 1 nm. It is applied for single nanoparticles in a sample and directly identifies the structure. TEM does not identify the metallic impurities. The electron beam passes through the sample, certain parts are transmitted and making an amplitude of contract image. The electron gun looks like a pin shape cathode and the heating process is applied by a

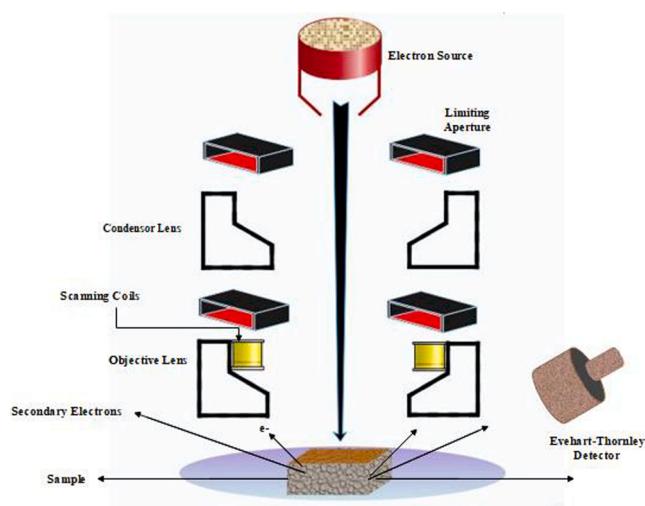


Fig. 17. Schematic diagram of an SEM setup.

large current which creates a stream of monochromatic electrons. The condenser lens focused on the beam and the coherent cylinder remove the electrons at large angles [200]. It was capable to create electron microscope images and diffraction design for their similar material by varying the magnetic lenses. TEM can provide individually nanoparticle can be selected and characterize by the diffraction pattern, lattice constants, nanostructured materials, and particle size. It is additionally utilized for picture cell take-up of CNT medicate composites.

4.6. Atomic Force Microscope (AFM)

AFM is used to measure attractive or repulsive forces of scanning probe tips with the sample surface. It was created by Binnig, Quate, and Gerber in 1986 [201]. The images are measured in atomic-scale images. The AFM tip and the sample's surface are bringing within a few nanometers and the force between atoms in the tip and sample cause to detect. The forces generally measured are van der Waals, electrostatic, magnetic, capillary, casimir, and solvation forces. AFM is not only for characterization tool for force and for particular sensor applications like the current, chemical, physical, and biosensor [202]. It has drawbacks as

just having the option to take an image of maximum height in a range of micrometers with a limited scan area. AFM consist of a cantilever made up of silicon or silicon nitride. Cantilever deflection is responsible for measure nanoparticle's morphological structure.

The cantilever redirection can recognize a few different ways, where laser light that is reflected from the apex of the cantilever onto a position sensitive. For delicate samples, constant force or tapping modes are utilized. The sensitivity of force measurement depends on the size and stiffness of the cantilever. The minimum force for the AFM tip is approximately 5pN. Several modes of operation are possible for AFM. The first mode is contact mode, where the tip and surface are in contact to scan across the surface and deflected the surface of the counters. Another mode is a constant force, where distance is maintained between the tip and surface, so it maintains the constant deflection and height above the surface. Tapping mode or dynamic force mode (DFM) is the third method where the cantilever is brought with the closer the closeness of the surface and then oscillates and changes in the resonant frequency or amplitude of the cantilever are measured during the scan [203]. Below Fig. 18 summarize the all characterization techniques based on their application perspective. By this figure one can aware the basic understanding of characterization device used for different studies of synthesized CNT. Before moved to application of CNT, researcher must aware the below characterization devices.

5. Properties of CNTs

Availability of higher strength in CNTs than steel and Kevlar because of the stronger bond is gain by sp^2 rather than the sp^3 bond which found in the diamond. CNTs are quality well in strength but also inelastic for which CNTs perform well in different polymers and ceramics for desired consumer products. The important properties of CNTs are stated below.

5.1. Mechanical properties of CNT

CNTs are considering the strongest materials in nature at this point. It is the most grounded and most adaptable molecular material because of the presence of a C–C covalent bond and seamless hexagonal network architecture. This property is helpful for Young's modulus. Covalent sp^2 bonds are made between the single and different carbon atoms to form the strength. The estimated for SWNT value in young modulus up to 1Tpa to 1.8Tpa. These high values of modulus make many applications

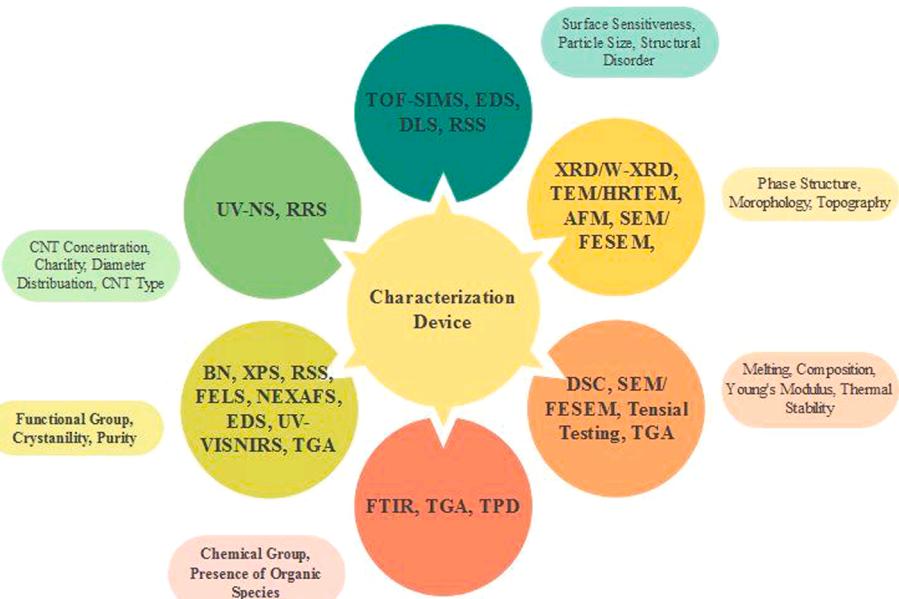


Fig. 18. Characterization devices used for various studies of CNT.

like probe tips of scanning microscopy. In SWNT will depend upon the diameter and chirality but in MWNT, it coordinates to the quantity of the sidewalls.

The outer graphite shell indicates the experiments which can support stress in the tubes are diffuse in an epoxy matrix value like 1,3, and for SWNT inner tube cohesion gives significantly and it gets reduced when compared to individual bonds [204]. Mechanical property combined with the lightness of CNT to give extraordinary potential in aerospace. The carbon nanotube is used in the “space elevator”, an Earth-to-space cable suggests by Arthur C. Clarke. CNT structure depends upon the metallic or semiconducting materials. While compared to silicon, copper has higher conductivities. Carbon nanotubes include flat board displays, scanning probe microscope, and detecting devices [205]. Due to the remarkable properties of carbon nanotubes, it can use for many applications [206].

5.2. Electronic properties of CNT

The electronic band structure is determined by symmetry where,

$n = m$; is metal

$n - m = 3j$ (j is a non-zero integer) – tiny bandgap semiconductor
large bandgap semiconductor

The bandgap depends upon n and m value and by the diameter of the tube [207]. CNTs are highly flexible and Young's modulus is used to measure the elasticity. The modulus of carbon nanotubes is about 1800 Gpa where it is about 210 Gpa for steel. CNT shows large strength in tension as compared to steel 20 times more than steel strength. The yield stress is for measuring the length. CNTs can withstand bigger strains without breaking than steel. It carries an electrical current flow density of $4 \times 10^9 \text{ A/cm}^2$ which is bigger than metals current flow density such as copper [208]. Electrical property affected the CNTs by scattering and deflect the inner wall by lattice vibrations and is leads to a change in the resistance, capacitance, and inductance which is similar for bulk materials. Anisotropic properties are needed in composite materials that are suitable for potential applications [209].

5.3. Thermal properties of CNT

Nanotubes have superior thermal conductivity; exhibit a property known as “ballistic conduction”. CNT exhibits superconductivity below (20 K) approximately -253°C due to the strong in-plane C-C bonds of graphene. The C-C bonds give quality and stiffness against axial strains. The outcome is high adaptability against non-axial strains. It will able to transmit up to $6000 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature while comparing to the copper [210]. Specific heat differs between single-walled nanotubes, 2D graphene, and 3D graphite at low temperatures, where the 1D quantum of the phonon band structure is also observed [211]. The thermal conductivity of nanotube is huge, even in mass examples. The thermal conductivity of pyrolytic graphite is high. Diamond has the highest measured thermal conductivity and not at all like materials, for example, has mica, an amazingly enormous size gem graphite not developed in exceedingly arranged pyrolytic graphite. Metal is a good thermal conductivity, which transmits $385 \text{ W m}^{-1} \text{ K}^{-1}$ and the temperature for carbon nanotubes is up to 2800°C in a vacuum and about 750°C in air. The thermal property of CNTs will be basically isotropic and is not quite the same as conventional graphite fibers, and strongly anisotropic [212]. The thermal conductivity of nanotubes is dependent on the temperature and environment.

5.4. Optical properties of CNT

CNT plays an important role in optics. This is interrelated to their one-dimensional [213]. In theoretical studies have disclosed the optical action of the chiral nanotube disappears if the nanotube becomes larger. The π - tight-binding model, within one-third of the nanotubes, relies on the metallic, and two-third of the nanotubes are semiconducting which

depends on the indices (n, m) [214]. Band hole is contrarily corresponding to the cylinder measurement with the range between 1 nm and 2 nm. Which prompts an optical absorption which that overlaps the 1550 nm windows. Optical properties are commonly used for fiber optic technologies. The optical action may bring about optical gadgets [215].

5.5. Chemical properties of CNT

CNT is in the form of graphene, the chemical enhancement is acquiring at the time of chemical synthesis. Response in CNT is straightforwardly identified with pi - orbital difference caused because of the increased curve [216]. Due to this difference came between the sidewall and the end cap of CNTs. Less the diameter, the more the reactivity. The reaction is done for both sidewall and end top of CNT. For instance, we can control the dissolvability and reactivity of CNTs in the diverse dissolvable can be controlled. Though it is very difficult to investigate the chemical modification on nanotube because it is yet not pure.

6. Functionalization of CNTs

In aqueous media, carbon nanotubes have been a major disadvantage in natural and biomedical applications. To conquer this problem, functionalization is used as a solution because it is achieved by using different molecules, absorption, electrostatic interaction, or covalent bonding [217]. In such changes, the solvency of water is improved and their biocompatibility profile is completely transformed. According to Vander Waals force, Individual tubes are reduced through the functionalization of the surface. The chemical modifies and functionalizes carbon nanotubes have made it conceivable to soluble in water. In natural and bioactive species, for example, protein, carbon hydrates, and nucleic acids can be conjugated with the carbon nanotubes [218]. This functionalization plays the main role in biomedical applications of carbon nanotubes. SWNT functionalized by the covalent method with Phenyl-SO₃4 or phenyl - (COOH)₂ groups which will deliver less cytotoxic impact. SWNT has been reported to be further decreased with increasing the stage of sidewall functionalization [219]. In CNT, any number of approaches are used for HNO₃ oxidation is a common impart for -COOH functionalization but the common approaches are covalent and Non- covalent functionalization.

6.1. Covalent functionalization

The function of carbon nanotube can be developed by using the oxidation method and covalent reactions. The oxidation method is done by utilizing oxidizing agents such as nitric acid, oxygen air, concentrated sulfuric acid, aqueous hydrogen peroxide [220]. During the covalent process, Carboxyl groups are formed towards the end of the tube to defect the sidewalls. The oxidation procedures and the oxidizing agent depend upon the function of carboxyl groups [221]. CNT allows the various types of functional groups on the nanotube. For medical, biological, and industrial applications is used to modify adjust the outside of CNTs. Surface function groups can adjust the surface charge, the reactivity of the surface, functionality, stability, and dispensability of CNTs.

The expansion of carboxyl gatherings to MWCNTs can diminish or take out the bioactivity of CNTs in Vitro macrophages. Hydrochloride (HCl) refluxing treatment and MWCNTs well functionalized with the -COOH by nitric acid to remove the surface amorphous carbon and residual metals in MWCNTs [222]. Metal catalysts can respond with HCl to shape metal chloride. HCl is a non-oxidative acid and cannot present oxygen-containing groups, and upgrade the introduction of undefined carbon joined onto the scattered carbon which prompting the water dispersibility. The MWCNT store the hydroxylated amorphous carbon and nickel chloride in the liquid phase. It can be separated from MWCNTs by centrifugation and decantation process [223]. Functional

groups on to the MWCNTs because of simplicity and efficiency. HCl purified the MWCNTs have poor water solubility after oxidation of MWCNTs shows good water solubility [224]. Functionalized MWCNTs are less toxic when compared to the unfunctionalized MWCNTs or purified MWCNTs. Functional MWCNTs with -COOH had effects on both properties and bioactivity of CNTs. Unfunctionalized or raw MWCNTs are very poor and form large groups. The bioactivity like groups was taken by the macrophages rather than any single MWCNTs. The functionalized MWCNTs are well dispersed in water and shape a stable state. Functionalization of the MWCNTs is decreased in bioactivity because of the mechanism of surface properties and better dispersion [225]. In the covalent function, it explains clearly the changes in surface properties had a significant impact on dispersion. Two main categories are used to attach functional groups to CNTs. Fig. 19. Shows the covalent functionalization of CNT.

6.1.1. Oxidative treatment using strong acid solutions

The difference in acid is varied in concentration and the reaction conditions where temperature and sonication generated carbon nanotubes by carboxyl functions at their tips and defect points. The carboxyl was used to get better CNT solubility. Oxidized CNT was solubilized by heating with the presence of amino polymers [226].

6.1.2. Addition reactions for CNTs

To employ the CNT by using the chemistry of fullerenes, the 1–3 dipolar cycloaddition of azomethine ylides, aryl diazonium salt addition, or reductive alkylation using lithium and alkyl halides done successfully. The further determinations demonstrate that the sidewall change of CNT permitted the incorporation of an alternate functional group on the nanotube. When contrasted with non-covalent dispersion, the covalent bond shows the advantage for manipulation and processing the CNTs [226].

6.2. Non-covalent functionalization

In CNTs coating of surfactant molecules or polymers is done by non-covalent functionalization rather than covalent functionalizations. Physical properties of CNTs are effectively conserved by the non-covalent approach and the chemical structure of the π - π network of CNTs, is not disrupted, apart from limitation of length because of the Sonication utilized in the functionalization procedure [227]. It mainly contains surfactants, biomacromolecules, or wrapping with polymers. Forming supramolecular complexes on the CNTs, there should be an enclosing of hydrophobic components of the related micelles and polymer [228]. Soluble CNT preserves its aromatic structure also electronic characteristics because of the presence of non-covalent dispersion. The gifted materials for modifying the surfaces of CNTs are polyaniline, polypyrrole, polythiophene, and their derivatives and due to the presence of different oxidation structures [229]. Fig. 20. Shows the non-covalent functionalization of CNT.

For bio-related applications, Polyethylene glycol (PEG) has been one of the most favored synthetic molecular because of its non-toxicity just as its better dissolvability under various physiological conditions. By amphiphilic molecules to functionalize CNT surfaces has been recognized most helpful approaches to develop the dispersion of CNTs in aqueous media. By utilizing amphiphilic diblock copolymer, comprising of hydrophilic and hydrophobic surfaces with a non-covalent procedure for surface functionalization of SWCNTs which is remarkably enhanced solvency especially in watery media, portrayed by Park and his collaborators [230]. Developing polymer chains to 'wrap' CNTs is an imperative and efficient path for CNT functionalization. Sometimes block copolymers (BCPs) may use as a sequence for appealing non-covalent wrapping for the functionalization of CNTs [231]. These applications are approaches to deal with the connection between CNTs and polymers. Zhang and his colleagues have studied the effect of melt mixing on the connection between MWCNTs and polystyrene (PS) matrix. They observe that the interaction between pristine MWCNTs and PS in solution did exist yet not sufficiently able to permit MWCNTs to be dissolvable in dissolvable [232]. Among the non-covalent functionalization, in the functionalized CNTs are nonappearance of reactive gatherings leads to weak interfacial interaction between CNTs and epoxy. Within the sight of sodium hydroxide, the non-covalent functionalization of MWCNTs by utilizing 2-amino ethanol ($H_2NCH_2CH_2OH$) was readied and the application for conductive composites with higher conductivity was described by Li and his groups. The used amine group is predicted to react with the epoxide group from epoxy prepolymer to get better the interfacial interaction between MWCNTs and epoxy matrix leading to efficient MWCNTs dispersion. By surface adjustment with various homopolymers and block copolymers, either covalently, for example, surface focused on grafting or in situ polymerization, or non-covalent a better dissolvability of intrinsically insoluble CNTs in natural solvents has been achieved. Another advantage of Non-covalent functionalization to the CNT compared with covalent functionalization is preserving the nanotube's sp^2 structure, as such the electronic properties [233].

Because of the functionalization of CNTs with natural macromolecules, for example, proteins and oligosaccharide, the potential utilization of CNTs in bio-related regions have supported by many researchers. Non-covalent functionalization of CNTs with biomacromolecules, for example, DNA and proteins is an extra potential system to get ready new bioelectronics nanomaterial, which could take advantage of the molecular acknowledgment properties of the bound biomolecules. By hydrophobic protein called polycyclic aromatic nitrogen heterocycle molecules (PANHS) can be used for controlled non-covalent functionalization of MWCNTs and in the meantime can be used to manage the assembly of Gold nanoparticle (AuNPs) after binding AuNPs onto the proteins was studied by Wei and his co-workers [234]. They additionally investigate the improvement of MWCNT-AuNP hybrids by incubating protein-protected AuNPs with PANHS functionalized MWCNTs. They establish that proteins, as a transitional that can respond with both

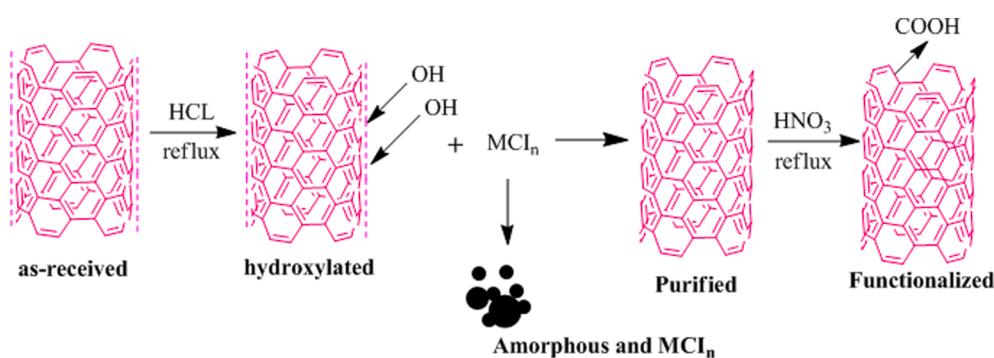


Fig. 19. Covalent Functionalization.

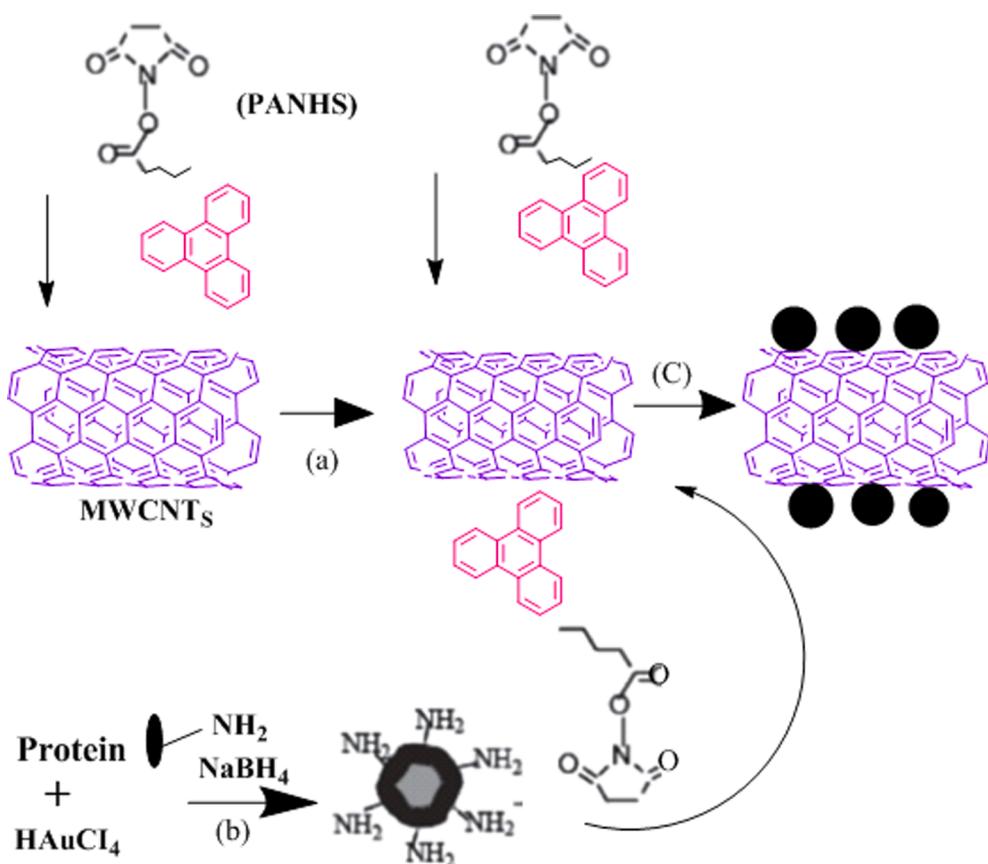


Fig. 20. Non-Covalent Functionalization.

MWCNTs and AuNPs, play a major role for mediate the assembly of AuNPs and the development of various hybrids based on MWCNTs.

6.2.1. Surfactants

A sequence of attempts has been attempted to disperse nanotubes with anionic, cationic, and nonionic surfactants. Two surfactants sodium dodecyl sulfate (SDS) and Triton X-100 utilized to get CNT suspensions up to 0.1 and 0.5 mg/mL, individually. The strength of this suspension was no longer than one week. To get a better result, another attempt was obtained by using sodium dodecylbenzene sulfonate (SDBS), which was able to grant better stability over one month reaching 10 mg/mL concentration of the suspension. The grouping of the k-k combination of aromatic moieties between CNT and SDBS and the long lipid chains of the SDBS enhances the power of the complex. By atomic force microscopy (AFM) and electronic transmission microscopy (TEM) investigations of SDS/CNT scatterings delighted that surfactant is consistently secured by cylinders where individual CNTs are introduced [235]. A long lipid chain with is amphiphilic molecules formed by a chamber opposite or tilted around the cylinders in a micelle-like course of action. Another methodology for the adsorption/dispersion of CNT via k connection lives on the use of 1-pyrene butanoic acid with a succinimidyl ester, which promptly responds with the amino groups available in the proteins like ferritin or streptavidin. The dissolubility of CNT was someplace in the scope of 0.1 and 0.7 Mg/mL which is quite low but suitable for biological use. Although surfactants might be skilled in the solubilization of CNT, they are known to permeabilize plasma membranes and have toxicity data of their own, so the implications stemming from the utilization of surfactants interacting with biological systems have a limit in the biomedical applications.

6.2.2. Polymers

Polymers are generally utilized as molecular carriers for drug

delivery. In the solubilization of CNT they do not have better scattering adequacy additionally they speak to a decent substitute to surfactants. Wrapping of the polymer around the cylinders is because of the reason for scattering. On account of nonionic polymers, the efficiency of the scattering is because of their hydrophilic part, which depends on poly (oxyethylene) copolymers. The nanotubes were enclosed by the hydrophobic backbone of the polymer while the positive tetra alkyl ammonium groups were exposed at the surface to show water solubility [235]. These types of fluorescent polymers have also been used to think about the interaction with mammalian cells. Poly (vinyl pyrrolidone) was conjugated with various fluorescent dyes. CNT was suspended in 1% SDS and blended with the fluorescent polymers to frame supramolecular edifices, which were found to have potential applications as new molecular probes.

6.2.3. Biopolymers

A self-assembling method similar to k-k interactions typical of double-stranded DNA can be connected to a scattering of nanotubes. Nucleic acids are a perfect component to form supramolecular complexes based on k-stacking between the aromatic bases and the CNT surface. The DNA-nanotube dissolvability in the scope of mg/ml and their complexes showed good stability permitted the purification using ion-exchange chromatography. Amphiphilic peptides have a place with another class of biopolymers that proficiently scatter CNTs. For the solubilization procedure in water, the nearness of amino acids like tryptophan, phenylalanine, tyrosine, and histidine into the peptide arrangement assumes a major role. The structure of very explicit peptides ready to overlap over the nanotubes speak to an alluring method to guarantee dissolvability and may even give a valuable apparatus to estimate partition for better task and application. Newly, cyclic peptides were also proven to have similar capabilities [235].

6.3. Pharmacology of CNTs

Depends upon the CNT's physicochemical qualities such as size, shape, aggregation chemical composition, surface functionalization, and solubility, it's used for the biodistribution and pharmacokinetics of nanoparticles to large extent [236]. Wang et al. [237] used iodine-labeled multiply hydroxylated (SWNT) were functionalized by oxidation and radiotracer by intraperitoneal. Other routes were compared with intraperitoneal for example subcutaneous, oral (by stomach incubation). By utilizing this CNT biodistribution was not by organization course and that the I-SWNT-OH appropriate all through the entire body. Preferred Organs like kidney, stomach, and bone [238]. In the safety view, 94% of the nanotubes were released into the urine and 6% in the feces as observed. Using this study we observed that the tissues do not get any damaged or distress. Secondly, Wang et al. studied the intravenous course of the organization and functionalized using SWNT & MWNT following a different surface chemistry (by 1, 3- dipolar cyclo-addition reaction) which compared to the SWNT. Diethylenetriaminepena acetate (DTPA) and radiolabel with indium are used to functionalize the CNT. In this investigation, the consequence of biodistribution and blood flow of degree surface with DTPA. The biodistribution indicates both sorts of functionalized DTPA-SWNT for kidneys, muscle, skin, bone, and blood. Tissue and maximum blood circulation were cleared in all types of nanotubes [239]. Both SWNT and MWNT were functionalized in DTPA which was seen to be discharged through the renal route into the bladder and urine intravenous administration. The DTPA CNT was watched flawless in the discharged urine by transmission electron microscopy.

6.4. Toxicity of CNTs

Toxicity is a huge piece of CNTs where it's controlled and application depends. As CNTs have extraordinary physical and chemical properties, their usage in the industrial sector has been seriously considered, but there are certain restrictions associated with their application, especially problems related to their toxicity. Human health is also adversely affected by CNTs, especially in the human pulmonary system, which is an essential source of presentation [240]. So it's important to takes steps to minimize the toxicity of CNTs. By exposing to CNT dust also causes inflammation and oxidative stress. Recent research of CNTs showed that change in length and rigidity of the nanotubes has greatly influenced the pro-inflammatory effect of CNTs [241]. For getting a better idea to control over toxicity, further study is needed to discover the possible influence of other physicochemical properties on account of their surface influence characteristics to the pro-inflammatory effect of spherical nanoparticles, it can be expected for modification of their toxicity without influencing their particular properties and potential for use in future applications, which is incorporating CNTs in polymeric materials. From the enormous investigation of the toxicity of CNTs, it is concluded that surface changes are an important factor to limit CNT toxicity [242]. A process called covering could be a helpful and significant device, as it allows modification of the outside surface of CNTs without affecting their intrinsic structure or basic properties. The harmful impact of nanoparticles arises because of the combination of different particles; out of these two are particularly significant [243]. The toxicity of the morphological arrangement (surface) and the high exterior area.

In comparison with conventional nanoparticles of larger diameter, nanoparticles that have under 100 nm can conceivably be more toxic to the lung, can distribute from their place of deposition, can remove from the typical phagocytic defenses, and can change the structure of proteins. Therefore, this above may affect normal tissue function and activate inflammatory and immunological responses [244]. With regards to toxicology, CNTs can be named 'nanoparticles' due to their nanoscale measurements, so unforeseen toxicological impacts upon contact with biological systems might be initiated. The nanometer-scale measurements of CNT may have amounts of milligrams of a large number of

round and hollow, fiber-like particles, with a simultaneous exceptionally high absolute surface zone. The level of packaging and aggregation of nanotubes in solution is another factor of the complete surface zone. Surface functionalization and the different toxicity of functional groups are affecting the intrinsic toxicity of CNTs. After the synthesis CNT (non-purified and/or not functionalized) promptly hold polluting influences such as amorphous carbon and metallic nanoparticles), which can also be the source of severe toxic effects. The auxiliary qualities of nano-material's for example, the fiber shape, the length and the aggregation status of the CNT, can also affect their initial deposition in the lungs and the immunological response [245]. Body for metabolism, degradation, clearance, and bioaccumulation for the body requires more consideration and study on CNT to acquire a suggestion of the limitations of such nanomaterial as apparatus of pharmaceuticals [246]. So far most far reports accessible and contemplate on the organization of CNT are principally concerned and centered with the toxicology of CNT, addressing and analyzing the possibility of negative side effects of this nanomaterial on human health, environment [247]. As enormous scale fabricating step by step winds up routine for the generation of CNT with taking care of and presentation of laborers to CNT brings introduction hazard issues to the surface.

7. Application of CNTs

Benefits for new materials and the main advantages of the latest and most developed technology are through nanotechnology. Different applications can be applied in different fields includes nanomedicine, energy, environment, and sensors [248]. The area of nanotechnology materials is vast and comes into regular use. In nanotechnology, CNTs are the most growing nanomaterial due to various applications. A lot of them have developed several applications in diverse fields, electronics, material science and energy storage with many studies focus on nanotechnology. CNT require conductivity and a high adsorption capacity and high-quality composites, energy conversion gadgets, field emission devices, hydrogen storage devices, and semiconductor devices [249]. The foremost dilemma in CNTs is their high cost and non-renewable characteristics. Recently, to develop certain preparation process for CNTs is used to reduce their cost. A few of the important and applications of CNTs are discussed below in detail.

7.1. CNTs as fillers

Fillers are used in various materials to form composites. Many researchers are working in the basic ground of nanocomposites to use CNTs as filler. To improve the properties of the CNTs is fusing into different polymers and other materials. The mechanical, electrical, and thermal properties are improved to an ideal range. Garcia-Gutierrez et al. [250] arranged to dissolve prepared infused shaped polybutylene terephthalate (PBT) and nanocomposites and the effect of SWNT polymers are shearing and the crystallization of PBT behavior. Siochia et al [251] founded that the SWNTs/Polyimide nanocomposite with the tensile modulus and yield quality expanded with the expansion of SWNT. They proved that the mechanical properties of polyimide were enhanced with good dispersion. Bhattercharaya et.al., [252]. Synthesized melt-mixed styrene-maleic anhydride (SMA) SWNT's with a polyamide-12 (PA 12) framework in a funnel-shaped twin-screw extruder. The SMA copolymer drives an incredible scattering of SWNT and improves the interfacial bond between the PA 12 and SMA with changed SWNT. Saeed and Park [253] Prepared MWNT/Nylon composites in situ mass polymerization. They utilized pristine MWNTs (P-MWNTs) and purified acid-treated MWNTs (A-MWNTs) as a material, the properties and also structural morphology and crystallization temperature. It can vary the techniques by comparing the properties of both P-MWNT and A-MWNT nylon nanocomposites. By comparing the functional group as A-MWNT get better dispersion than P-MWNT. The ratio of MWNTs in nylon is increased with the crystallization temperature. Prashantha.Et.al [254]

prepared MWNTs and polypropylene grafted maleic anhydride (MWNT/PP-g-ma) and MWNTs and polypropylene (MWNT/PP) nanocomposites were studied about the rheological, mechanical, and morphological properties of these composites with various ranges of techniques using in MWNTs compositions. The pp-g-ma has good adhesion and strong interfacial strength because it has high mechanical properties. The use of fibrous Nano carbons in intrinsic properties in polymers could be attained by the interface interaction between surfaces and polymers. The polymers or epoxy could be applied to improve the adhesion properties among filler and matrix. The result in the polymer is transferred from the nanotubes [255]. In the industrial view, ozone treatment is a very impressive technique. The dispersion of nanotubes or nano-fibers in the polymers should be in the uniform matrix.

7.2. Sensors

Nanomaterials are unique materials for chemical sensors and bio-sensors due to their dimensional decrease and large surface-to-volume ratio. Greatly, encourage the CNTs about the exploration and growth of a wide scope of chemical, molecular and biological sensors with the advantages of the century-old wealth of knowledge about the carbon structures. The main operating principle for CNTs sensors are pristine, high-quality nanotubes are chemically applied by a suitable coating or attaching a Specific functional group for their selectivity and sensitivity. Wong et.al [256] was the first to utilize that the conceivable to detect the practical synthetic gatherings where it joined as far as possible of the CNTs. In other cases, CNTs are used as an electrode for the capacitance-based sensor to generate the high electric fields at their tips to ionize a gas [257]. For non-nanotube sensors, selectivity and sensitivity are never-ending themes of sensor research and development. The nanotube-based sensors are developed for two-terminal CNT gadgets or three-terminal transistors like a structure. In the CNTs, the little Nano-scale measurement is perfect for interacting with bio-molecules. The nanotubes are treated for a variety of reasons including the biological environment or to monitor/sense that protein to convey pass on data about the biological event and processes [258]. Nanosensors are a growing trend to integrate them with silicon electronics for calibrated, improved, and robust sensor performance. Behavior is significant for analysis of the high performance of CNT which relates to the chemical and biological sensors. Fig. 20 shows a sensor chip develop for chemical sensing.

In bio applications, CNTs are widely active for cancer treatment and as a nano-vehicle for drug delivery [259]. CNT chemical sensors and the interface chip are integrated on a PCB level, and the functionality of the system is tested by exposing the CNT sensors of NO₂. The gas was introduced to the CNT sensors that sit in a gas chamber, and the measurement taken by the fabricated chip is acquired by a logic analyzer. The real-time sensing operation of the CNTs as well as the proper functionality of the CMOS interface can be seen in Fig. 21.

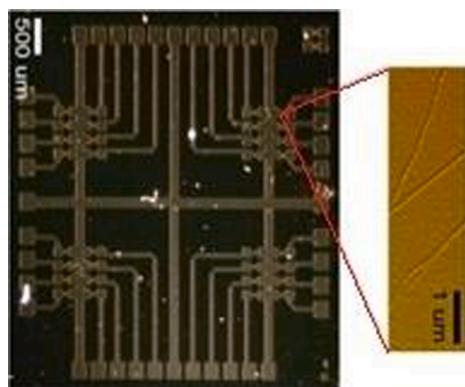


Fig. 21. CNT chemical sensor chip [260].

7.3. Scanning probe tips

Scanning probe is to get the image with a better higher resolution. Instead of using a normal probe, MWNTs using the scanning probe tips and it gives a better result. It includes AFM and STM has become a necessary part and routine imaging technique is utilized to understand the surface topology, surface physics, and surface chemistry [261]. The essential component of all Scanning probe is the probe tips, the tip is fixed to the cantilever and accurately moved the sample surface to measure the surface properties. The spatial resolution determines the lateral dimension of the probe tip and vertical lengths can decide the image of deep trenches. The distance across of the CNTs structure in the request of nanometers and length of the micrometers coupled with their axial stiffness to make ideal probe tips [262]. To functionalizes the tip of the nanotube with chemical groups to include the high-resolution imaging of surface with potential applications. The nature of the CNT has a trade-off between the lateral resolution and the depth resolution. The maximum lateral resolution with a nanotube of about 1 nm diameter and the length needs to short with ~ 10 nm to maintain stiffness for reliable usage and imaging of micrometer will require CNTs diameter greater than 10 nm [263]. While coating the nanotube to extract some conical structure, fine lateral and depth resolution on flat and corrugated surfaces can be removed as shown in Fig. 22. In several, probe manufacturers are already offered nanotube probe tips as their catalog, and a premium price. It can be continued that to controllable large scale synthesis on microfabricated cantilevers will be done a way in making nanotube probe tips which is more affordable and routine usage.

7.4. CNTs in Supercapacitors and actuators

CNTs are superior materials for electrochemical devices because of their surface area also for their high electrical conductivity. Niu et al., [264] were the first to prepare that sheet cathode of pyrolytically developed MWNTs and it is possible to produce very high specific capacitances in individual cells in devices containing 38 wt% of H₂SO₄ as the electrolyte. Each cell could reach 8000 W/Kg power densities. CNT supercapacitors are used in applications to store high capacity and high power. In the CNTs, the power thickness is up to 20 KW/Kg when the energy density is 7 Wh/Kg [265]. In embedded, CNT supercapacitors can be connected to give quick speeding up and to store data about braking energy electrically for hybrid electric vehicles. Actuators are key devices, but the difficulty is their efficiency decrease with a temperature increase. Nowadays actuators are prepared by using CNTs with low voltage and temperatures as high as 350 °C [266].

7.5. Nanoelectromechanical system (NEMS)

NEMS is a device that shows electrical and mechanical usefulness at

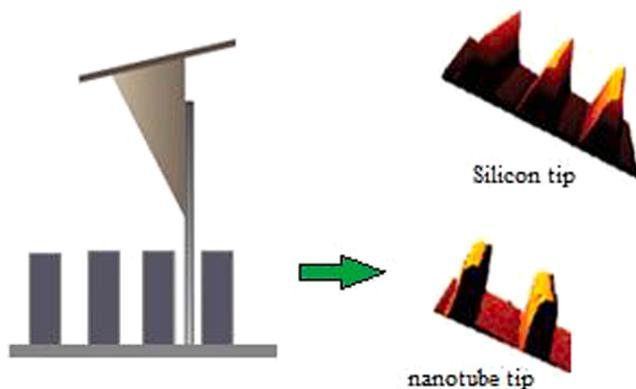


Fig. 22. Silicon probe tip with Multi-walled CNT [263].

the Nanoscale dimension. The cantilever is normally utilized as a physical sensor, where its position or motion in environmental conditions or actuators can be controlled electrically. Naturally, CNTs can be suitable for cantilever which is used to design the NEMS slender structure, high stiffness, low mass, chemical inertness, and attractive electrical and thermal properties. Cantilever capacity to accomplish large strains without any breaking [267]. NEMS showed high performance in the experimental system which includes sensitive pressure sensors, nanotweezers, high-speed nanorelays, non-volatile memory, tunable oscillators, and a multifunctional single nanotube-NEMS radio. Recently, the CNT cantilever is performed as an atomic resolution of the mass sensor [268]. In the NEMS relay, this currently uses the nanoscale switching devices that offer virtually zero leakage current. NEMS nanotube will go a long way in optimizing the device's working performance and in developing technology to commercial. Rueckes et al. [269] investigated a nanotube-based non-volatile random access memory by considering a bistable nanoswitch based on electrostatic and van der Waals forces which in a high level of integrated nano switches with 1012 elements and operating frequency with 100 GHz. The idea suitability was demonstrated by the trial acknowledgment of a reversible bistable nanotube-based piece. The main nanotube was as of late dependent on integrating electronic control and the mechanical reaction was grown uniquely by Fennimore et.al. [270]. To build up the NEMS structure, the entirety of trial information is constrained because of the multifaceted nature worried in nanodevices. Accurate and formulas are as yet missing to design the NEMS devices. Pressure sensor consist of a pressure sensor consists of an ultrathin atomic layer deposited (ALD) alumina (Al_2O_3) membrane with the radius $r_0 = d/2$ which integrated electrically contacted SWNT as the strain gauge. The SWNTs to the alumina surface by van der Waals forces and are also clamped in place by two metal electrodes. It is assumed that the SWNTs experience the same stretching as the membrane, similar to the doped-silicon strain gauges used in the MEMS pressure sensors.

7.6. Field emission of electrons

The electron gun is performed on the field emission of electrons from the tip of vertical alignment of the earliest properties of the CNTs. It generates a wave of the potential use of industrial and scientific explorations which include vacuum electronics, cold cathodes, electron microscopes, field emission displays, and X-ray sources for medical applications [271]. Electrons work by the use of a high electric field to the tip of the nanotube to emit electrons. Electrons are effectively radiated from their tips because of curvature which presents in the CNTs in the form of pentagons or because of their presence of oxidized tips. The mechanical firm structure of nanotubes combined with the thermal conductivity and chemical stability are the desired quantities of field emitter and the small radius affords the high field upgrade factors. The continuous electron emission is achieved by applying a high electric field between the anode and cathode. From the theory, there is a common metal that can be portrayed by Fowler-Nordheim [272]. The electron discharge procedure of nanotube like a metallic sharp tip and has been validated in several experiments. CNTs are good in emitters and composites with surface vacuum stability. Many advantages can be achieved by field emission electrons which include a long lifetime of the parts, stable field emission over delayed periods, low emission threshold potential, ultra-high vacuum, and high current densities. It has been reported that a large current density of $4\text{A}/\text{cm}^2$ can be achieved [273].

7.7. Integrated electronics on flexible substrates

The past 15 years show the combination of transistors and passive components on plastic flexible substrates for large-area electronics that are conformal, lightweight, and shock-resistant at a minimal cost [274]. The range of applications is constant which includes large-area flexible displays, electronic paper, low-cost photovoltaic, wearable electronics,

and structure for mobile systems or moving vehicles. Using integrated electronics are difficult to achieve on inflexible substrates like silicon wafers. On large scale, the area would be extremely cost prohibitive on semiconductor substrates with conventional semiconductor fabrication techniques using vacuum deposition and etching, which are geared to deliver micro-scale electronic chips. Fabrication of passive components, such as inductors, capacitors and interconnect wires, variety of plastic and ceramics substrates using inexpensive printing techniques for a long time, and printed circuit board.

The evolution of printed electronics is the monolithic integration of a suitable semiconductor with acceptable performance to serve as the active component. The printed or in by and large vanished, the semiconductor is used commonly for organic semiconductors, such as pentacene [275]. For integration on flexible substrates for semiconductors identified the semiconductors for aligned arrays or networks of interconnected nanotubes. The objective of the CNTs is high mobility, high current densities, high optical transmittance, flexible platform, and robust mechanical properties. To integrate the transistor in plastic requires deposition techniques for gate electrodes, gate dielectrics, a semiconducting material, and source/drain electrodes. Fig. 23 shows a thin plastic (polyimide) sheet where CNT transistors and circuits implement designed on it.

The conventional vacuum deposition techniques lead to evaporate the conductors, dielectrics, and pentacene. Printing techniques employ the solution to process the conductors, dielectrics, and semiconductors. By transferring the CNTs grown on an oxidized silicon wafer to a plastic substrate and using photolithography with conventional deposition techniques, high-performance nanotube transistors and circuits have been realized on a flexible platform as shown in Fig. 18. Research is geared towards further increases in device mobility while developing the technology infrastructure such as characterized the process recipes, standard design guidelines, and device or circuit modeling, for high yield fabrication of integrated electronics on flexible or low-cost substrates for a range of applications [276].

7.8. Hydrogen storage

The increasing awareness of the adverse effects of environmental pollution has led to great efforts to develop green technologies. Their major problem of pollution comes about by-products from the burning of crude oil or hydrocarbons to provide energy to move vehicles for the transportation of people and goods [278]. To provide energy for a cleaner method for transportation is much technology with global ramifications. To employ the electrical energy released in the hydrogen to move the powerful vehicles.

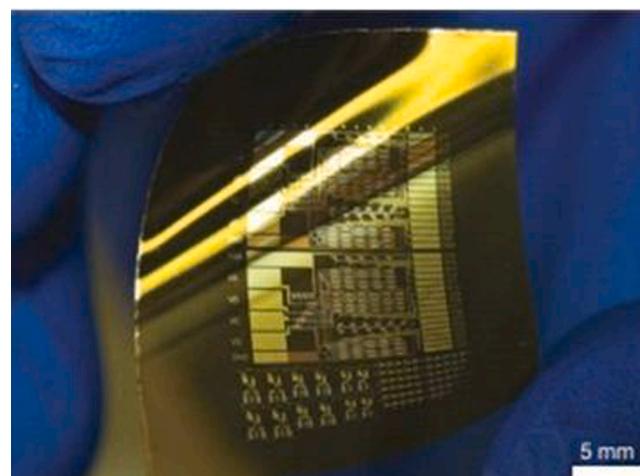


Fig. 23. CNT transistors and circuits on a thin plastic (polyimide) sheet [277].

The motive of hydrogen gas with several reasons are [279],

- High energy content
- Hydrogen is the amplest element in the world
- Product or oxidation product associated with energy generation in water to begin environmentally.

To create the hydrogen undoubtedly is to harvest the energy present in sunlight for the electrolysis of water into hydrogen and oxygen in a photoelectrochemical cell. It is known as “water splitting”. The hydrogen-powered transportation system involves the distribution and storage of hydrogen. Dillon et.al.[280]. Single-walled CNTs are predominantly attractive for hydrogen storage for their light mass and fully exposed atomic structure. Hydrogen will adsorb due to the presence of the carbon atoms. The use of single-walled nanotubes for hydrogen storage is a promising realistic technology. The challenges can be overcome in volumetric capacities. Research is ongoing and the considerable rewards waiting at the end of the journey while continuing to inspire further explorations. Fabrication of composites by CuO nanoplates with support of TiO₂ nanosheets are used for water splitting application where the CuO nanoplates form three-dimensional (3D) structures by intersecting with each other and the TiO₂ sheet place on the CuO nanosheet without any aggregation. The advancement of this type of composites is used as an anode in Li-ion batteries (LiBs) [281]. Gaining the stability of a Li anode by “two-pronged approach”, where the approach is formed by a combination of SnO_x designed on N-doped carbon fiber (CNF) with a plate-shell of Sn on the Li substrate for better output current density of value of 3 mA/cm² and 5 mA/cm² [282].

7.9. Composites

These materials are loaded with carbon matter were one of the initial applications of tubular carbon in their modern history, with the 19th century. Carbon fibers were used as high- temperature conductive filaments in the lighting industry. The work was spearheaded by Roger Bacon, a physicist taking a shot at carbon fiber combination. In 1900, there was an interest in carbon fiber for high- temperature lightweight composites for aircraft and satellites [283].

The same attractive thermal, mechanical, and electrical properties of carbon fibers are even more pronounced in CNTs and this is the reason for the current renaissance in CNT composites. Currently, the CNTs are the strongest, most resilient materials and at the same time of prevalent electrical and thermal conductivities exceeding those silver and diamond respectively [284]. The physical properties of CNT are to composite the materials to achieve the overall performance that can be customized for the particular applications at hand. In such cases, the composites are ordinarily processed or loaded with 5–10 wt% of CNTs. The wide scope of application has evolved beyond the traditional base and is more or less limited by the imagination of the moment.

Applications are included with lightweight, high-temperature composites with strength, more prominent than steel, and which in some cases it can be synthesized to the comparison of the spider silk are the obvious applications [285]. Novel applications like sensors, supercapacitors, polymers for photovoltaic, copper for high reliability interconnect in Nanoscale technology. CNT composite fibers for electronic textiles and CNT coated electrodes are used for probing neurons in the cerebrum and bio-compatible materials for scaffolding in tissue engineering are included in the applications [286]. The space elevator is perhaps the most widely reported example of the very inspired use of nanotube composites. Already the products are accessible in the market place such as premium-quality tennis rackets and bikes.

7.10. Genetic engineering

In genetic, the CNTs and CNHs are utilized to control atoms and genes to develop biomedical genomes, proteomics, and tissue

engineering. SWNT around the unwound DNA by connecting the specific particular and causes change its electrostatic property. The potential application makes the diagnostics and therapeutics. For analyzing the DNA, the wrapping of carbon nanotube by single-stranded DNA was seen to be succession subordinate [287]. As the structure of the Nanotube is in the form of the chamber for which it carried various properties for genes to treat genetic disorders and cancer. Gene therapy has demonstrated the tabular nature of vectors. Nanotubes complexes with the DNA began to discharge the DNA before it destroys the cells in the defense system and boosting transfection significantly. Nanostructures have shown an antiviral effect in respiratory syncytial virus (RSV), and a virus with severe bronchitis and asthma.

By combining nanoparticles and gene slicing technologies are done by using the treatment. Here a piece of RNA is capable of inhibiting a protein is typified inside nanotubes and controlled which in the form of nasal spray or drops. The result has been noted in the rapid increase of virus. Nanotubes are redesigned in the form of helical crystallization of protein and develop of embryonic rat brain neurons. CNT via 1-pyrene butanoic acid and succinimidyl ester 32 were immobilized successfully in the streptavidin protein. Here, nanotubes and Nano horns can have different antigens on their surface and also perform as a source of antigen in vaccines. By apply of CNT, the dead bacteria as a basis for antigen and sometimes dangerous can be controlled [288].

7.11. Biomedical application

CNT had soluble and peptides linked with biological activities were prepared by Bianco et. al. [289]. This was explained by viral protein VPI of foot mouth disease virus (FMDV) showing immunogenicity antibody response. A Drug that is embedded with nanotubes will attack viral ulcers and destroy the presence of viruses in the chemotherapy. Non-availability of antibodies and no intrinsic immunogenicity can be created at the time of the CNT backbone. The properties of a vaccine system where the fact is that prolong capacity of the anti-peptide antibody to neutralize FMDV has enhanced in the CNT have an important role in the development of the novel and effective vaccines. In the vitro studies [290] it showed the selective cancer cell killing obtained by hyperthermia due to the thermal conductivity of CNT internalized into those cells. CNT makes use of gene therapy vectors that show the structure of genes and drugs inside the mammalian cells. The genetic material of the CNT has conserved the possibility to express the protein.

In the early stage, the identification of cancer is very censorious to improving cancer treatment. At present, detection and analysis of cancer typically depend on changes in cells and tissues that are controlled by the doctor's physical touch or imaging expertise. The ideal potential nanostructures are entered and analyzed by the single cells [291].

8. Summary

Elucidation of the CNT synthesis, structure, synthesis method, purification, characterization, properties, functionalization, and application in detail has been reported in this review article. Preparation of the CNT with better quality, fewer impurities, fewer costs, and apposite application has been significant for researchers during the synthesis of it. During the literature review, the researcher has been synthesized the CNT with the observation of fewer defects and proper growth rate which was employing different characterization techniques. Investigation of the CNT by different techniques has been proved the best structural result of the CNT with superior quality but hitherto need to explore the quantitative part of the CNT such as morphology, defect type, growth rate, etc.

Discussion of graphite and graphene with their evolution has been implanted in this review in a summarizing manner via a table. It is easy to understand the CNT if we are well known to graphene, so a proper explanation of graphite and graphene has been discussed in the earlier part of the review. To get better knowledge about carbon-related

material (graphite, graphene, and graphene oxide) another table also added with their evolution. Afterward, an explanation of different CNT structures with various images also has been implanted in this review profoundly. The images are very clear and easy to find out the different types of CNT based on the n and m. The explained images are the basic understanding of the SWNT, DWNT, and MWNT with apt leveling. Fig. 4 is the one-layer graphene sheet where all information regarding the graphene sheet has been shown. One-layer graphene sheet when rolled-up as result the CNT is formed which has been shown in Fig. 5. Different chirality of CNT (zigzag, armchair, and chiral) have been explained with the respective diagram.

The techniques of CNT synthesis have been described by inserting various characterization images. The oldest synthesis technique of the CNT is the arc discharge method which was used by Iijima in 1991. The specialty of this technique is the high yield rate at high temperatures. Various researchers synthesized the CNT by arc discharge methods which are shown in table 3 where proper information has been inserted for better understanding. Nearly seven different synthesis technique has been discussed in this review paper and it came to conclude that chemical vapor deposition (CVD) is the best techniques among all because of various properties such as synthesis in moderate temperature, not required any filtered purification, high yield rate processing, produce high purity CNT, operation cost is viable, the requirement of energy is also moderate, and have a large scale production. In comparison to table 5, it has been noticeably distinguished between all important synthesis techniques with their pros and cons. More information about different techniques has been added in different tables in shorten format.

Purification of the CNT is carried after the synthesis to get a pure CNT for different applications. Different unwanted entities such as carbon nanoparticles, graphitic impurities, residual catalyst, metal nanoparticles, amorphous carbon, and fullerenes are occupying the CNT surface during the synthesis of it. To eliminate the various impurities, the purification process is carried out. Different purification techniques have been discussed in the review with various examples. In chemical purification, concetration acids and air or other gases are used for purification via the wet condition and dry condition respectively. Different purification agents such as mineral acids, oxidants, alkali, mixed oxidants under chemical purification techniques have been discussed broadly in the review. In the physical purification process, the CNT exhibits less damage during purification techniques. Different purification techniques such as filtration, ultra-sonication, and chromatography have been discussed thoroughly.

Characterization of the CNT is very important to know the structure, radius, morphology, etc. after synthesis. Different techniques have been analyzed in the review with their application for the characterization of CNT. The discussed characterization techniques are IR spectroscopy, Dynamic light scattering (DLS), Raman spectroscopy, XRD diffraction, light scattering techniques, electron microscopy, atomic forced microscopy (AFM), and nuclear magnetic resonance (NMR). All the techniques are different from each other with their principle of operation and working condition. Different techniques figure been added in the review based on their working principle. The inserted images are added for a better understanding of the technical set-up. TEM is used to investigate the morphology of the CNT where we can find the exact dimensions, calculation of tubular morphology, presence of impurities, and defect calculation. Another technique Raman spectroscopy is employed to detect the crystallinity and structural disorder such as tube alignment and defects.

The most important things of the CNT are various inbuilt properties such as mechanical, electronic, thermal, optical, and chemical. All properties of the CNT have been explained with their related perception and importance during synthesis as well as application perspective. The mechanical properties explicate the strength of the CNT, Young's modulus, cohesion, etc. The electronics property of CNT describes the electronic configuration, bandgap, electrical properties, lattice, etc. The

chirality of CNT and diameter of it defined the bandgap of CNT. The thermal conductivity of the CNT is at a high peak at -253°C due to its strong bond between carbons. Other qualities of the thermal properties have a great impact on the application been discussed in the review. The optical also have a greater effect during the synthesis of the CNT. From an application perspective, optical properties are more important during fiber optic technology. Another essential property of the CNT is chemical properties which arise during the chemical synthesis. All the above properties play a vital role during the application of the CNT, so researchers need to look after all properties attentively and make it an important study during the CNT synthesis.

To overcome some problems, functionalization to the CNT is very important. During biomedical application functionalization to the CNT enhance the selectivity towards proper application. Functionalization to the CNT by absorption, different molecules, electrostatic interaction, and bonding achieved for different applications. Functionalization enhances the solvency in water and biocompatibility. Surface modification techniques are used to enhance the dispersion uniformity and improve the interaction with milieu material. Different functionalization such as covalent functionalization and non-covalent functionalization have been explained in review with various examples. The toxicity of CNT has also been conferred in the review with its effect on the eco-system. In the end, various applications of CNT have been discussed by inserting some figures by referring to different references. The CNT has been used in diverse fields such as biomedical, composites application, integrated electronic device, energy storage, hydrogen storage, sensor, scanning probe, and many more. As the application of CNT is diverse so only some of the important application has been accentuated during the discussion in this review. Overall this review emphasized the CNT from its history to its recent application broadly which can give confidence and create a strong concept related to CNT after referring this review by a reader.

9. Conclusion

The presented review is the overview of synthesis, structure, properties as well as the application of CNTs. Many methods were explained briefly for synthesizing the CNTs (SWNTs and MWNTs). Some of the properties of CNTs were also reviewed with a common set of Nanotubes. In greater potentials, it is clear that the novel technology will emerge in the future in CNT. The problem that arises in technology is the quantity and cost of CNTs. It was also explained that the nanotube functionalization method with less toxic CNTs than pristine CNTs. Different important massages have been inserted in this review which result makes an easier communication with a reader for a better understanding of the CNT. Preparation of the CNT can be achieved in both semiconductive and metallic forms which lead to making mixt junctions between metal and semiconductor.

By referring to various research works, it has been concluded that CNT has many potential applications but still need to reconnoiter further. During the elucidation of structure, synthesis, and functionalization it concludes that the results obtained from the above studies have momentously devoted to the auspicious development in the sundry field. Different techniques have been used for the synthesis of the CNT but in every technique yield, purity, and structure of CNT are not up to par, so the researcher needs to revolutionize the new techniques to synthesis for CNT with advanced features. Different working agents affect the structure, diameter, purity, etc. of the CNT, for instance, catalyst size has a control on the diameter of the CNT. The most important thing to look after is the cost-effectiveness of the carbon source used in CVD techniques. The carbon source is used for the preparation of CNT so the price of the CNT is mainly based on carbon source price, so endeavors should be through to find out a novel carbon source.

From an application point of view, every researcher wants to develop the device in miniature level (size and shape) and this can be achieved by the properties of CNTs. The various unusual properties of the different CNT (SWNT, DWNT, and MWNT) lead to the development of

any device in the range of nanometers. Fast-growing application of the CNT can lead to us portable machines such as in an airport, ambulances, etc., heat management for interconnect application, used in transistor for biosensor because its higher resistance nature towards to electromigration, in composition with Si used in nanoelectronics, automatic sensing due to thermoelectric effect, and many more. Also, the non-toxic vehicles will increase the solubility of the drug attached and resulting in greater efficiency and safety. CNT has the advantages of prospective nanodevices for controlling drug delivery. The scientist has begun the structures with the possibility of gene therapy, cancer treatments, and innovative new devices. The properties and characteristics of CNTs are still being researched profoundly. Carbon nanotubes will play a major role in a range of applications in the future. This also helps to solve the problems in the world's energy.

The fast in researching and innovating innumerable newer techniques make the CNT a frontier agent for every field of application. Researchers should give more effort to make a purified CNT with less defect by which CNT will deploy its importance in the arena of industrial as well as commercial also. Implementing the various technologies such as silicon technologies, with CNT will make the process more efficient, rapid production, and lessen defects in the application of the electronic field. Hope in near future some techniques will emerge and make the CNT to more affordable and viable in various field of applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] K.S. Ibrahim, Carbon nanotube - Properties and Applications: a Review, *Carbon* 14 (2013) 131–144.
- [2] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *C₆₀: Buckminsterfullerene*, *Nature* 318 (1985) 162.
- [3] S. Iijima, Helical Microtubules of Graphite Carbon, *Nature* 354 (1991) 56–58.
- [4] T. Yamaguchi, S. Bandow, S. Iijima, Synthesis of Carbon Nanohorn Particles by Simple Pulsed Arc Discharge, *Chem. Phys. Letters.* 389 (2004) 181–185.
- [5] S. Iijima, T. Ichihashi, Single-Shell Carbon Nanotubes of 1-nm Diameter, *Nature* 363 (1993) 603–605.
- [6] D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Cobalt-Catalyzed Growth of Carbon Nanotubes with Single-Atomic-Layer Walls, *Nature* 363 (1993) 605.
- [7] Dresselhaus, M.S., Dresselhaus, G., Charlier, J.C., Hernandez, E., Electronic, Thermal, and Mechanical Properties of Carbon Nanotubes. *Philos Transact A Math Phys. Eng. Sci.* 362 (2004) 065–2098.
- [8] R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998.
- [9] S. Iijima, *Challenge of Carbon Nanotubes*, Iwanami-Shoten, Tokyo, 1999.
- [10] M.S. Dresselhaus, P. Avouris, Introduction to Carbon Material Research, *Appl. Phys.* 80 (2001) 1–9.
- [11] Zhong Lin Wang and Chun Hui, *Electron Microscopy of Nanotubes*, Kluwer Academic Publishers, Boston, 2003.
- [12] D. Tománek, R.J. Enbody, *Science and Application of Nanotubes*, Kluwer Academic/Plenum Publishers, New York, 2000.
- [13] Y. Saito, S. Bandow, *Basis of Carbon Nanotubes*, Corona-Shya, Tokyo, 1998.
- [14] Y. Ando, X. Zhao, T. Sugai, M. Kumar, Growing Carbon Nanotubes, *Mater. Today* 7 (2004) 22–29.
- [15] Y. Ando, X. Zhao, Synthesis of Carbon Nanotubes by Arc-Discharge Method, *New Diamond Front. Carbon Tech.* 16 (2006) 123–137.
- [16] T.W. Ebbesen, Carbon Nanotubes, *Phys. Today* 49 (1996) 26–32.
- [17] M. Terrones, Carbon Nanotubes: Synthesis and Properties, *Electronic Devices, and Other Emerging Applications*, *Int. Mater. Rev.* 49 (2004) 325–377.
- [18] Y. Ando, Encyclopedia of Nanoscience and Nanotechnology, Edited by H. S. Nalwa, American Scientific Publishers, 1 (2004) 603.
- [19] W. Krätschmer, K. Fostiropoulos, Donald R. Huffman, The Infrared and Ultraviolet absorption spectra of Laboratory-Produced Carbon Dust: Evidence for the Presence of the C₆₀ Molecule, *Chem. Phys. Lett.* 170 (1990) 167–170.
- [20] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, Soild C₆₀: A New Form of Carbon, *Nature* 347 (1990) 354–358.
- [21] T. Guo, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Catalytic Growth Of Single-Walled Nanotubes by Laser Vaporization, *Chem. Phys. Lett.* 243 (1995) 49–54.
- [22] D.D.L. Chung, Review graphite, *J. Mater. Sci.* 37 (2002) 1475–1489.
- [23] R. Dweiri, J. Sahari, Computer Simulation of Electrical Conductivity of Graphite-based Polypropylene Composites based on Digital Image Analysis, *J. Mater. Sci.* 42 (2007) 10098–10102.
- [24] T. Ndlovu, O.A. Arotiba, S. Sampath, R.W. Krause, B.B. Mamba, Reactivities of Modified and Unmodified Exfoliated Graphite Electrodes in Selected Redox Systems, *Int. J. Electrochem. Sci.* 7 (2012) 9441–9453.
- [25] H.P. Boehm, R. Setton, E. Stumm, Nomenclature and Terminology of Graphite Intercalation Compounds, *Pure Appl. Chem.* 66 (1994) 1893–1901.
- [26] Matthew J. Allen, Vincent C. Tung, Richard B. Kaner, Honeycomb Carbon: A Review of Graphene, *Chem. Rev.* 110 (2010) 132–145.
- [27] D.A. Brownson, C.E. Banks, Graphene electrochemistry: an overview of potential applications, *Analyst* 135 (2010) 2768–2778.
- [28] H. Kim, A.A. Abdala, C.W. Macosko, Graphene/polymer nanocomposites, *Macromolecules* 43 (2010) 6515–6530.
- [29] X.-M. Chen, G.-H. Wu, Y.-Q. Jiang, Y. Wang, X. Chen, Graphene and Graphene-Based Nanomaterials: The Promising Materials for Bright Future of Electroanalytical Chemistry, *Analyst* 136 (2011) 4631–4640.
- [30] D. Chen, L. Tang, J. Li, Graphene-Based Materials in Electrochemistry, *Chem. Soc. Rev.* 39 (2010) 3157–3180.
- [31] J.Y. Jang, M.S. Kim, H.M. Jeong, C.M. Shin, Graphite oxide/poly (methyl methacrylate) Nanocomposites Prepared by a Novel Method Utilizing Macroazoinitiator, *Compos. Sci. Technol.* 69 (2009) 186–191.
- [32] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The Chemistry of Graphene Oxide, *Chem. Soc. Rev.* 39 (2010) 228–240.
- [33] S. Park, J. An, J.R. Potts, A. Velamakanni, S. Murali, R.S. Ruoff, Hydrazine – Reduction of Graphite and Graphene Oxide, *Carbon* 49 (2011) 3019.
- [34] B.C. Brodie, On the Atomic Weight of Graphite, *Philos. Trans. Royal. Soc. London* 149 (1859) 249–259.
- [35] Poh, H.L., Sanek, F., Ambrosi, A, A, Zhao, G., Sofer, Z., and Pumera, M., Graphenes prepared by Staudenmaier, Hofmann and Hummers Methods with Consequent Thermal Exfoliation Exhibit Very Different Electrochemical Properties, *Nanoscale* 4 (2012) 3515–3522.
- [36] A.V. Talyzin, G. Mercier, A. Klechikov, M. Hedenstrom, D. Johnels, D. Wei, E. Moons, Brodie Vs Hummers Graphite Oxides for Preparation of Multi-Layered Materials, *Carbon* 115 (2017) 430–440.
- [37] S. Park, R.S. Ruoff, Chemical Methods for the Production of Graphenes, *Nat. Nanotechnol.* 4 (2009) 217–224.
- [38] U. Hofmann, A. Ragoss, R. Gerda Rudorff, W. Holst, A. Ruston, G. Ruess Russ, The Structure and Graphitization of Carbon, *J. Inorgan. Chem.* 255 (1947) 195–211.
- [39] T. Nakajima, Y. Matsuo, Formation Process and Structure of Graphite oxide, *Carbon* 32 (3) (1994) 469–475.
- [40] H. He, T. Riedl, A. Lerf, J. Klinowski, Solid-State NMR Studies of the Structure of Graphite oxide, *J. Phys. Chem.* 100 (1996) 19954–19958.
- [41] W. Scholz, H.P. Boehm, Investigations on Graphite Oxide. VI. Considerations on the Structure of Graphite Oxide, *Zeitschrift für anorganische und allgemeine Chemie* 369 (1969) 327–340.
- [42] L.V. Radushkevich, V.M. Lukyanovich, The Structure of Carbon Forming in Thermal Decomposition of Carbon Monoxide on an Iron Catalyst, *Russian J. of Phys. Chem.* Russia 26 (1952) 88–95.
- [43] Boehm, H.P. Carbon from Carbon Monoxide Disproportionation on Nickel and Iron Catalysts: Morphological Studies and Possible Growth Mechanisms, *Carbon* 11 (1973) 583–586, IN1–IN5 587–590.
- [44] L. Staudenmaier, Verfahren zur Darstellung der graphitsäure, *Ber. Dtsch. Chem. Ges.* 31 (1898) 1481–1487.
- [45] Hummers Jr, W.S., and Offeman, R.E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* 80, (1958), 1339–1339.
- [46] Rues, G.,Über das Graphitoxyhydroxyd (Graphitoxyd), *Monatshefte für Chemie und Verwandte Teileanderer Wissenschaften*, 76, (1947), 381–417.
- [47] Prasher, R.S., X. J. Hu, Chalopin, Y., Mingo, N., Lofgreen, K., Volz, S., Cleri, F., and Kebinski, P. Turning Carbon Nanotubes from Exceptional Heat Conductors into Insulators, *Physical. Rev. Lett.* 102 (2009) 105901–1 – 105901–4.
- [48] Vander Wal, R.L., Berger, G.M., and Ticich, T.M. Carbon Nanotube Synthesis in a Flame using Laser Ablation for in Situ Catalyst Generation, *Appl. Phys. A.77* (2003) 885–889.
- [49] T.W. Ebbesen, P.M. Ajaya, Large Scale Synthesis of Carbon Nanotubes, *Nature* 358 (1992) 220–222.
- [50] R.A. Donald, P. Prabhakar, The science and emerging of materials, Thomson/ Brooks – Cole, Australia, 4th Edition., 2003.
- [51] J.S. Su, Investigation on Carbon Nanotube Growth using One-Pulse Discharge with Shield, *Proc. Inst. Mech. Eng. Part N: Journal of Nanomaterials, Nanoeng and Nanosys.* 226 (2012) 175–180.
- [52] Z. Wang, Z. Zhao, J. Qiu, In Situ Synthesis of Super-Long Cu Nanowires Inside Carbon Nanotubes with Coal as Carbon Source, *Carbon* 44 (2006) 1845–1847.
- [53] N. Arora, N.N. Sharma, Sustained Arc Temperature: Better Marker for Phase Transformation of Carbon Black to Multiwalled Carbon Nanotubes in Arc Discharge Method, *Mater. Res. Express* 3 (2016) 1–9.
- [54] K. Kazemi Kai, F. Bonabi, Using Hydrocarbon as a Carbon Source for Synthesis of Carbon Nanotube by Electric Field Induced Needle-Pulsed Plasma, *Thin Solid Films* 534 (2013) 162–167.
- [55] A. Roch, O. Jost, B. Schultrich, E. Beyer, High-Yield Synthesis of Single-Walled Carbon Nanotubes with a Pulsed Arc-Discharge Technique, *Phys. Status Solidi Basic Res.* 244 (2007) 3907–3910.
- [56] S. Zhao, R. Hong, Z. Luo, H. Lu, B. Yan, Carbon Nanostructures Production by AC Arc Discharge Plasma Process at Atmospheric Pressure, *J. Nanomater.* 2011 (2011) 1–6.

- [57] S.-D. Wang, M.-H. Chang, J.-J. Cheng, H.-K. Chang, K.M.-D. Lan, Unusual Morphologies of Carbon Nanoparticles Obtained by Arc Discharge in Deionized Water, *Carbon* 43 (2005) 1322–1325.
- [58] N. Parkansky, R.L. Boxman, B. Alterkop, I. Zontag, Y. Lereah, Z. Barkay, Single Pulse Arc Production of Carbon Nanotubes in Ambient Air, *J. Phys. D Appl. Phys.* 37 (2004) 2715–2719.
- [59] Y.Y. Tsai, J.S. Su, C.Y. Su, A Novel Method to Produce Carbon Nanotubes using EDM Process, *Int. J. Mach. Tools Manuf.* 48 (2008) 1653–1657.
- [60] A.J. Berkmans, M. Jagannatham, D.R. Reddy, P. Haridoss, Synthesis of Thin Bundled Single Walled Carbon Nanotubes and Nanohorn Hybrids by Arc Discharge Technique in Open Air Atmosphere, *Diam. Relat. Mater.* 55 (2015) 12–15.
- [61] Y.Y. Tsai, J.S. Su, C.Y. Su, W.H. He, Production of carbon nanotubes by single-pulse discharge in air, *J. of Materials Processing Technology* 209 (2009) 4413–4416.
- [62] T.W. Ebbesen, P.M. Ajayan, Large-scale Synthesis of Carbon Nanotubes, *Nat. Publ. Gr.* 358 (1992) 220–222.
- [63] B.H. Chang, S.S. Xie, W.Y. Zhou, L.X. Qian, Z.W. Pan, J.M. Mao, W.Z. Li, Loosely-Entangled Carbon Nanotubes Prepared in Modified Arc-Discharge, *J. Mater. Sci. Lett.* 17 (1998) 1015–1017.
- [64] M. Ohkochi, X. Zhao, S. Inoue, Y. Ando, Synthesis and Purification of Singlewalled Carbon Nanotubes by AC Arc Discharge, *Japan Soc. Appl. Phys.* 43 (2004) 8365–8368.
- [65] P.K. Jain, Y.R. Mahajan, G. Sundararajan, A.V. Okotrub, N.F. Yudanov, A. I. Romanenko, Development of Carbon Nanotubes and Polymer Composites Therefrom, *Carbon Sci.* 3 (2002) 142–145.
- [66] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, Large-scale Production of Single-Walled Carbon Nanotubes by the Electric-Arc Technique, *Nature* 388 (1997) 756–758.
- [67] D.S. Bethune, C.H. Kiang, M.S. De Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Cobalt-Catalysed Growth of Carbon Nanotubes with Single-Atomic-Layer Walls, *Nature* 363 (1993) 605–607.
- [68] Y. Saito, Y. Tani, N. Miyagawa, K. Mitsushima, A. Kasuya, Y. Nishina, High Yield of Single-Wall Carbon Nanotubes by Arc Discharge Using Rh – Pt Mixed Catalysts, *Chem. Phys. Lett.* 294 (1998) 593–598.
- [69] M. Nishio, S. Akita, Y. Nakayama, Cooling Effect on the Growth of Carbon Nanotubes and Optical Emission Spectroscopy in Short-Period Arc-Discharge, *Thin Solid Films* 464–465 (2004) 304–307.
- [70] K.H. Maria, T. Mieno, Synthesis of Single-Walled Carbon Nanotubes by Low-Frequency Bipolar Pulsed Arc Discharge Method, *Vaccum* 113 (2015) 11–18.
- [71] X. Lv, F. Du, Y. Ma, Q. Wu, Y. Chen, Synthesis of High Quality Single-Walled Carbon Nanotubes at Large Scale by Electric Arc Using Metal Compounds, *Carbon* 43 (2005) 2020–2022.
- [72] E.I. Waldford, A.M. Waas, P.P. Friedmann, M. Keidar, Characterization of Carbon Nanotubes Produced by Arc Discharge: Effect of the Background Pressure, *J. Appl. Phys.* 95 (2004) 2749–2754.
- [73] Y. Li, S. Xie, W. Zhou, D. Tang, Z. Liu, X. Zou, G. Wang, Small Diameter Carbon Nanotubes Synthesized in an Arc-Discharge, *Carbon* 39 (2001) 1429–1431.
- [74] H. Zeng, L. Zhu, G. Hao, R. Sheng, Synthesis of Various Forms of Carbon Nanotubes by AC Arc Discharge, *Carbon* 36 (1998) 259–261.
- [75] X.K. Wang, X.W. Lin, V.P. Dravid, J.B. Ketterson, R.P.H. Chang, Carbon Nanotubes Synthesized in a Hydrogen Arc Discharge, *Appl. Phys. Lett.* 66 (1995) 2430–2432.
- [76] C. Liu, H.T. Cong, F. Li, P.H. Tan, H.M. Cheng, K. Lu, B.L. Zhou, Semi-Continuous Synthesis of Single-Walled Carbon Nanotubes by a Hydrogen Arc Discharge Method, *Carbon* 37 (1999) 1865–1868.
- [77] X. Zhao, M. Ohkochi, M. Wang, S. Iijima, T. Ichihashi, Y. Ando, Preparation of High-Grade Carbon Nanotubes by Hydrogen Arc Discharge, *Carbon* 35 (1997) 775–781.
- [78] Chaudhary, K.T., Ali, J., and Yupapin, P.P. Growth of Small Diameter Multi-Walled Carbon Nanotubes by Arc Discharge Process, *Chinese Phys. B* 23 (2014) 035203-6.
- [79] H.M. Yusoff, R. Shastry, T. Querrioux, J. Abrahamson, Nanotube Deposition in a Continuous Arc Reactor for Varying Arc Gap and Substrate Temperature, *Curr. Appl. Phys.* 6 (2006) 422–426.
- [80] S. Cui, P. Scharff, C. Siegmund, D. Schneider, K. Risch, S. Klötzer, L. Spiess, H. Romanus, C. Schwöhl, Investigation on Preparation of Multiwalled Carbon Nanotubes by DC Arc Discharge under N₂ Atmosphere, *Carbon* 42 (2004) 931–939.
- [81] S.-D. Wang, M.-H. Chang, K.M.-D. Lan, C.-C. Wu, J.-J. Cheng, H.-K. Chang, Synthesis of Carbon Nanotubes by Arc Discharge in Sodium Chloride Solution, *Carbon* 43 (2005) 1792–1795.
- [82] D.L. Sun, R.Y. Hong, F. Wang, J.Y. Liu, M. Rajesh Kumar, Synthesis and Modification of Carbon Nanomaterials via AC Arc and Dielectric Barrier Discharge Plasma, *Chem. Eng. J.* 283 (2016) 9–20.
- [83] Y. Su, Z. Yang, H. Wei, E.S.-W. Kong, Y. Zhang, Synthesis of Single-Walled Carbon Nanotubes with Selective Diameter Distributions using DC Arc Discharge Under CO Mixed Atmosphere, *Appl. Surf. Sci.* 257 (2011) 3123–3127.
- [84] J.L. Hutchison, N.A. Kiselev, E.P. Krinichnaya, A.V. Krestinin, R.O. Loutfy, A. P. Morawsky, V.E. Muradyan, E.D. Obratzsova, J. Sloan, S.V. Terekhov, D. N. Zakharov, Double-Walled Carbon Nanotubes Fabricated by a Hydrogen Arc Discharge Method, *Carbon* 39 (2001) 761–770.
- [85] T. Sugai, H. Omote, S. Bandow, N. Tanaka, H. Shinohara, Production of Fullerenes and Single-Wall Carbon Nanotubes by High-Temperature Pulsed Arc Discharge, *J. Chem. Phys.* 112 (2000) 6000–6005.
- [86] Y. Makita, S. Suzuki, H. Kataura, Y. Achiba, Synthesis of Single Wall Carbon Nanotubes by using Arc Discharge Technique in Nitrogen Atmosphere, *Eur. Phys. J. D* 34 (2005) 287–289.
- [87] Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y. H., Kim, S., Rinzler, A.G., Colbert, D.T., G.E., Tomanek, D., Fischer, J.E., and Smalley, R.E. Crystalline Ropes of Metallic Carbon Nanotubes, *Science* 273 (1996) 483–487.
- [88] W.K. Maser, E. Muñoz, A.M. Benito, M.T. Martínez, G.F. De La Fuente, Y. Maniette, E. Anglaret, J.L. Sauvajol, Production of High-Density Single-Walled Nanotube Material by a Simple Laser-Ablation Method, *Chem. Phys. Lett.* 292 (1998) 587–593.
- [89] C.D. Scott, S. Areppalli, P. Nikolayev, R.E. Smalley, Growth Mechanisms for Singlewall Carbon Nanotubes in a Laser-Ablation Process, *Appl. Phys. A Mater. Sci. Process.* 72 (2001) 573–580.
- [90] Guo, T., Nikolaev,P., Rinzler, A.G., Tomanek, D., Colbert, D.T., Smalley, R.E. Self-Assembly of Tubular Fullerenes, *J. Phys. Chem.* 99 (1995) 10694–10697.
- [91] A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodriguez-Macías, P. J. Boul, A.H. Lu, D. Heymann, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P. C. Eklund, R.E. Smalley, Large-Scale Purification of Single-Wall Carbon Nanotubes: Process, Product, and Characterization, *Appl. Phys. A Mater. Sci. Process.* 67 (1998) 29–37.
- [92] F. Kokai, K. Takahashi, M. Yudasaka, R. Yamada, T. Ichihashi, S. Iijima, Growth Dynamics of Single-Wall Carbon Nanotubes Synthesized by CO₂ Laser Vaporization, *J. Phys. Chem. B* 103 (1999) 4346–4351.
- [93] N. Braidy, M.A. El Khakani, G.A. Botton, Effect of Laser Intensity on Yield and Physical Characteristics of Single Wall Carbon Nanotubes Produced by The Nd: YAG Laser Vaporization Method, *Carbon* 40 (2002) 2835–2842.
- [94] H.Y. Zhang, K.X. Chen, Y.J. Zhu, Y.M. Chen, Y.Y. He, C.Y. Wu, J.H. Wang, S. H. Liu, Formation and Raman spectroscopy of Singlewall Carbon Nanotubes Synthesized by CO₂ Continuous Laser Vaporization, *J. Phys. Chem. Solids* 62 (2001) 2007–2010.
- [95] F. Kokai, K. Takahashi, D. Kasuya, M. Yudasaka, S. Iijima, Growth Dynamics of Single-Wall Carbon Nanotubes and Nanohorn Aggregates by CO₂ Laser Vaporization at Room Temperature, *Appl. Surf. Sci.* 650–655 (2002).
- [96] H. Zhang, Y. Ding, C. Wu, Y. Chen, Y. Zhu, Y. He, S. Zhong, The Effect of Laser Power on the Formation of Carbon Nanotubes Prepared in CO₂ Continuous Wave Laser Ablation at Room Temperature, *Phys. B Condens Matter.* 325 (2003) 224–229.
- [97] W. Jiang, P. Molian, H. Ferkel, Rapid Production of Carbon Nanotubes by High-Power Laser Ablation, *J. Manuf. Sci. Eng.* 127 (2016) 703–707.
- [98] J. Chrzanowska, J. Hoffman, A. Malolepszy, M. Mazurkiewicz, T.A. Kowalewski, Synthesis of Carbon Nanotubes by the Laser Ablation Method: Effect of Laser Wavelength, *Phys Status Solidi B* 252 (2015) 1860–1867.
- [99] Y. Zhang, H. Gu, S. Iijima, Single-Wall Carbon Nanotubes Synthesized by Laser Ablation in a Nitrogen Atmosphere, *Appl. Phys. Lett.* 73 (1998) 3827–3829.
- [100] A.P. Bolshakov, S.A. Uglov, A.V. Saveliev, V.I. Konov, A.A. Gorbunov, W. Pompe, A. Graff, A Novel CW Laser-Powder Method of Carbon Single-Wall Nanotubes Production, *Diam. Relat. Mater.* 11 (2002) 927–930.
- [101] E. Munoz, W.K. Maser, A.M. Benito, M.T. Martínez, G.F. De La Fuente, Y. Maniette, A. Righi, E. Anglaret, J.L. Sauvajol, Gas and Pressure Effects on the Production of Single-Walled Carbon Nanotubes by Laser Ablation, *Carbon* 38 (2000) 1445–1451.
- [102] G. Radhakrishnan, P.M. Adams, L.S. Bernstein, Room-Temperature Deposition of Carbon Nanomaterials by Excimer Laser Ablation, *Thin Solid Films* 515 (2006) 1142–1146.
- [103] R. Yuge, S. Bandow, M. Yudasaka, K. Toyama, S. Iijima, Boron and Nitrogen Doped Single-Walled Carbon Nanohorns with Graphite-Like Thin Sheets Prepared by CO₂ Laser Ablation Method, *Carbon* 111 (2017) 675–680.
- [104] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Large Scale Synthesis of Aligned Carbon Nanotubes, *Science* 274 (1996) 1701–1703.
- [105] S. Xie, W. Li, Z. Pan, B. Chang, L. Sun, Carbon Nanotube Arrays, *Mater. Sci. Eng. A* 286 (2000) 11–15.
- [106] Nitin Choudhary, Sookhyun Hwang, A Review, *Handbook of Nanomaterials Properties*, Wonbong Choi/ Carbon Nanomaterials, 2014.
- [107] C.J. Lee, S.C. Lyu, H.-W. Kim, C.-Y. Park, C.-W. Yang, Large Scale Production of Aligned Carbon Nanotubes by the Vapor Phase Growth Method, *Chem. Phys. Lett.* 359 (2002) 109–114.
- [108] Gore and Sane, A. Flame Synthesis of Carbon Nanotubes, Purdue University, USA, (2011).
- [109] T. Nozaki, K. Ohnishi, K. Okazaki, U. Kortshagen, Fabrication of Vertically Aligned Single Walled Carbon Nanotubes in Atmospheric Pressure Non-Thermal Plasma CVD, *Carbon* 45 (2006) 364–374.
- [110] N.M.A. Rafique, J. Iqbal, Production of Carbon Nanotubes by different Routes- A Review, *J. of Encapsulation and Adsorption Sciences* 1 (2011) 29–34.
- [111] S. Shukrullah, N.M. Mohamed, M.S. Shaharun, M.Y. Naz, Effect of Ethylene Flow Rate and CVD Process Time on Diameter Distribution of MWCNTs, *Mater. and Manuf. Processes.* 31 (2016) 1537–1542.
- [112] Y. Brhane, T. Gabriel, Production, Purification and Functionalization of Carbon Nanotubes for Medical Applications, *International Research Journal of Pharmacy* 7 (2016) 19–27.
- [113] C.N.R. Rao, R. Sen, B.C. Satishkumar, Govindaraj, *Chem. Commun.*, A. Large Aligned-Nanotube Bundles from Ferrocene Pyrolysis, 1998, pp. 1525–1526.
- [114] A.M. Cassell, J.A. Raymakers, J. Kong, H. Dai, Large Scale CVD Synthesis of Single-Walled Carbon Nanotubes, *J. Phys. Chem. B* 103 (1999) 6484–6492.

- [115] B.C. Satishkumar, A. Govindaraj, C.N.R. Rao, Bundles of Aligned Carbon Nanotubes obtained by the Pyrolysis of Ferrocene-Hydrocarbon Mixtures: Role of the Metal Nanoparticles Produced In Situ, *Chem. Phys. Lett.* 307 (1999) 158–162.
- [116] Cummings, J., Mickelson, and W., Zettl, A. Simplified Synthesis of Double-Wall Carbon Nanotubes, *Solid State Commun.* 126 (2003) 359–362.
- [117] G.S.B. McKee, C.P. Deck, K.S. Vecchio, Dimensional Control of Multi-Walled Carbon Nanotubes in Floating-Catalyst CVD Synthesis, *Carbon* 47 (2009) 2085–2094.
- [118] N.M. Mubarak, F. Yusof, M.F. Alkhatib, The Production of Carbon Nanotubes using Two-Stage Chemical Vapor Deposition and Their Potential Use In Protein Purification, *Chem. Eng. J.* 168 (2011) 461–469.
- [119] Y. Li, X.B. Zhang, X.Y. Tao, J.M. Xu, F. Chen, L.H. Shen, X.F. Yang, F. Liu, G. Van Tendeloo, H.J. Geise, Single Phase MgMoO₄ as Catalyst for the Synthesis of Bundled Multi-Wall Carbon Nanotubes by CVD, *Carbon* 43 (2005) 1325–1328.
- [120] M.H. Rummeli, F. Schafel, A. Bachmatiuk, D. Adebimpe, G. Trotter, F. Bornert, A. Scott, E. Coric, M. Sparing, B. Rellinghaus, P.G. McCormick, G. Cuniberti, M. Knupfer, L. Schultz, B. Buchner, Investigating the Outskirts of Fe and Co Catalyst Particles in Alumina-Supported Catalytic CVD Carbon Nanotube Growth, *ACS Nano* 4 (2010) 1146–1152.
- [121] J. Colomer, C. Stephan, S. Lefrant, G. Van Tendeloo, I. Willems, Z. Konyaa, A. Fonseca, C. Laurent, J. Nagy, Large-Scale Synthesis of Single-Wall Carbon Nanotubes by Catalytic Chemical Vapor Deposition (CCVD) Method, *Chem. Phys. Lett.* 317 (2000) 83–89.
- [122] H.M. Cheng, F. Li, G. Su, H.Y. Pan, L.L. He, X. Sun, M.S. Dresselhaus, Large-Scale and Low-Cost Synthesis of Single-Walled Carbon Nanotubes by the Catalytic Pyrolysis of Hydrocarbons, *Appl. Phys. Lett.* 72 (1998) 3282–3284.
- [123] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass, *Science* 282 (80) (1998) 1105–1107.
- [124] J. Liu, Z. Jiang, H. Yu, T. Tang, Catalytic Pyrolysis of Polypropylene to Synthesize Carbon Nanotubes and Hydrogen through a Two-Stage Process, *Polym. Degrad. Stab.* 96 (2011) 1711–1719.
- [125] E. Terrado, M. Redrado, E. Mun, W.K. Maser, A.M. Benito, M.T. Mart, Carbon Nanotube Growth on Cobalt-Sprayed Substrates by Thermal CVD, *Mater. Sci. Eng., C* 26 (2006) 1185–1188.
- [126] Y. Shirazi, M.A. Tofghy, T. Mohammadi, A. Pak, Effects of Different Carbon Precursors on Synthesis of Multiwall Carbon Nanotubes: Purification and Functionalization, *Appl. Surf. Sci.* 257 (2011) 7359–7367.
- [127] K. Hata, D.N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes, *Science* 306 (80) (2004) 1362–1364.
- [128] H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Single-Wall Nanotubes Produced by Metal-Catalyzed Disproportionation of Carbon Monoxide, *Chem. Phys. Lett.* 260 (1996) 471–475.
- [129] B. Kitiyaran, W.E. Alvarez, J.H. Harwell, D.E. Resasco, Controlled Production of Single-Wall Carbon Nanotubes by Catalytic Decomposition of CO on Bimetallic Co-Mo Catalysts, *Chem. Phys. Lett.* 317 (2000) 497–503.
- [130] Chris Bower, Otto Zhou, Wei. Zhu, D.J. Werder, Sungho. Jin. Nucleation and Growth of Carbon Nanotubes by Microwave Plasma Chemical Vapor Deposition, *Appl Phys Lett.* 77 (2000) 2767–2769.
- [131] J. Qiu, Y. An, Z. Zhao, Y. Li, Y. Zhou, Catalytic Synthesis of Single-Walled Carbon Nanotubes from Coal Gas by Chemical Vapor Deposition Method, *Fuel Process. Technol.* 85 (2004) 913–920.
- [132] A. Eftekhar, S. Manafi, F. Moztarzadeh, Catalytic Chemical Vapor Deposition Preparation of Multi-wall Carbon Nanotubes with Cone-like Heads, *Chem. Lett.* 35 (2006) 138–139.
- [133] S.P. Patole, P.S. Alegaonkar, H.-C. Lee, J.-B. Yoo, Optimization of Water Assisted Chemical Vapor Deposition Parameters for Super Growth of Carbon Nanotubes, *Carbon* 46 (2008) 1988–1993.
- [134] Maio, A., Botta, L., Tito, A.C., Pellegrino, L., daghetta, M., and Scaffaro, R. Statistical Study of the Influence of CNTs Purification and Plasma Functionalization on the Properties of Polycarbonate-CNTs Nanocomposites Plasma Process. Polym., (2014) 664-667.
- [135] D. Chattopadhyay, I. Galeska, F. Papadimitrakopoulos, Complete Elimination of Metal Catalysts from Single Wall Carbon Nanotubes, *Carbon* 40 (2002) 985–988.
- [136] A.L. Mohana Reddy, S. Ramaprabhu, Hydrogen Storage Properties of Nanocrystalline Pt Dispersed Multi-Walled Carbon Nanotubes, *International J of Hydrogen Energy* 32 (2007) 3998–4004.
- [137] H. Hu, B. Zhao, M.E. Itkis, R.C. Haddon, Nitric Acid Purification of Single-Walled Carbon Nanotubes, *J. Phys. Chem. B* 107 (2003) 13838–13842.
- [138] S. Mohanapriya, V. Lakshminarayanan, Simultaneous Purification and Spectrophotometric Determination of Nickel present in as-prepared Single-Walled Carbon Nanotubes (SWCNT), *Talanta* 71 (2007) 493–497.
- [139] S. Delpeux, K. Szostak, E. Frackowiak, F. Beguin, An Efficient Two-Step Process for Producing Opened Multi-Walled Carbon Nanotubes of High Purity, *Chem Phys Letters* 404 (2005) 374–378.
- [140] A. Rasheed, J.Y. Howe, M.D. Dadmun, P.F. Britt, The efficiency of the oxidation of carbon nanofibers with various oxidizing agents, *Carbon* 45 (2007) 1072–1080.
- [141] J.-F. Colomer, P. Piedigrossi, A. Fonseca, J.B. Nagy, Different Purification Methods of Carbon Nanotubes Produced by Catalytic Synthesis, *Synth Metals* 103 (1999) 2482–2483.
- [142] A. Fonseca, K. Hernadi, J.B. Nagy, D. Bernaerts, A.A. Lucas, Optimization of Catalytic Production and Purification of Buckytubes, *J. of Molecular Catalysis A: Chemical* 107 (1996) 159–168.
- [143] K. Hernadi, A. Siska, L. Thien-Nga, L. Forro, I. Kiricsi, Reactivity of Different Kinds of Carbon During Oxidative Purification of Catalytically Prepared Carbon Nanotubes, *Solid State Ionics* 141–142 (2001) 203–209.
- [144] T. Suzuki, K. Suhama, X. Zhao, S. Inoue, N. Nishikawa, Y. Ando, Purification of Single-Wall Carbon Nanotubes Produced by Arc Plasma Jet Method, *Diam. Relat. Mater.* 16 (2007) 1116–1120.
- [145] E. Raymundo-Pinero, T. Cacciaguerra, P. Simon, F. Beguin, A Single Step Process for the Simultaneous Purification and Opening of Multiwalled Carbon Nanotubes, *Chem. Phys. Letters* 412 (2005) 184–189.
- [146] L. Joncourt, M. Mermoux, P.H. Touzain, L. Bonnetaud, D. Dumas, B. Allard, Sodium Reactivity with Carbons, *J. of Phys and Chem of Soilds* 57 (1996) 877–882.
- [147] E. Raymundo-Pinero, P. Azais, T. Cacciaguerra, D. Cazorla-Amoros, A. Linares-Solano, F. Beguin, KOH and NaOH Activation Mechanisms of Multiwalled Carbon Nanotubes with Different Structural Organization, *Carbon* 43 (2005) 786–795.
- [148] Salernitano, E., Giorgi, L., Dikominos Makris, Th., Giorgi, R., Lisi, N., Contini, V., and Falconieri, Purification of MWNTs Grown on a Nanosized Unsupported Fe-based Powder Catalyst, *Diamond & Related Materials* 16 (2007) 1560–1570.
- [149] K.J. Ziegler, Z. Gu, H. Peng, E.L. Flor, R.H. Hauge, R.E. Smalley, Controlled Oxidative Cutting of Single-Walled Carbon Nanotubes, *J. Am. Chem. Soc.* 127 (2005) 1541–1547.
- [150] Y. Zhang, Z. Shi, Z. Gu, S. Iijima, Structure Modification of Single Wall Carbon Nanotubes, *Carbon* 38 (2000) 2055–2059.
- [151] C.-M. Chen, Mi Chen, Y.-W. Peng, H.-W. Yu, C.-F. Chen, High Efficiency Microwave Digestion Purification of Multi-Walled Carbon Nanotubes Synthesized by Thermal Chemical Vapor Deposition, *Thin Solid Films* 498 (2006) 202–205.
- [152] C.-M. Chen, Mi Chen, Y.-W. Peng, C.-H. Lin, L.-W. Chang, C.-F. Chen, Microwave Digestion and Acidic Treatment Procedures for the Purification of Multi-Walled Carbon Nanotubes, *Diam. Relat. Mater.* 14 (2005) 798–803.
- [153] C.-J. Ko, C.-Y. Lee, F.-H. Ko, H.-L. Chen, T.-C. Chu, Highly Efficient Microwave-Assisted Purification of Multiwalled Carbon Nanotubes, *Microelectron. Eng.* 73–74 (2004) 570–577.
- [154] T. Saito, K. Matsushige, K. Tanaka, Chemical Treatment and Modification of Multi-Walled Carbon Nanotubes, *Phys. B* 323 (2002) 280–283.
- [155] M.T. Martinez, M.A. Callejas, A.M. Benito, M. Cochet, T. Seeger, A. Andon, J. Schreiber, C. Gordon, C. Marhic, O. Chauvet, J.L.G. Pierro, W.K. Master, Sensitivity of Single Wall Carbon Nanotubes to Oxidative Processing: Structural Modification, Intercalation and Functionalization, *Carbon* 41 (2003) 2247–2256.
- [156] I.D. Rosca, F. Watari, M. Uo, T. Akasaka, Oxidation of multiwalled carbon nanotubes by nitric acid, *Carbon* 43 (2005) 3124–3131.
- [157] M.S.P. Shaffer, X. Fan, A.H. Windle, Dispersion and Packing of Carbon Nanotubes, *Carbon* 36 (1998) 1603–1612.
- [158] Y. Ando, X. Zhao, H. Shimoyama, Structure Analyse of Purified MultiWalled Nanotubes, *Carbon* 39 (2001) 569–574.
- [159] C. Li, D. Wang, T. Liang, X. Wang, J. Wu, X. Hu, J. Liang, Oxidation of Multiwalled Carbon Nanotubes by Air: Benefits for Electric Double Layer Capacitors, *Powder Technol.* 142 (2004) 175–179.
- [160] G.S. Duesberg, R. Graupner, P. Downes, A. Minett, L. Ley, S. Roth, N. Nicoloso, Hydrothermal Functionalisation of Single-Walled Carbon Nanotubes, *Synth. Met.* 142 (2004) 263–266.
- [161] M.R. Smith Jr, S.W. Hedges, R. Lacount, D. Kern, N. Shah, G.P. Huffman, B. Bockrath, Elective Oxidation of Single-Walled Carbon Nanotubes using Carbon dioxide, *Carbon* 41 (2003) 1221–1230.
- [162] Y. Wang, L. Gao, J. Sun, Y. Liu, S. Zheng, H. Kajiura, Y. Li, K. Noda, An Integrated Route for Purification, Cutting and Dispersion of Single-Walled Carbon Nanotubes, *Chem. Phys. Letters* 432 (2006) 205–208.
- [163] Y. Liu, L. Gao, J. Sun, S. Zheng, L. Jiang, Y. Wang, H. Kajiura, Y. Li, K. Noda, A Multi-Step Strategy for Cutting and Purification of Single-Walled Carbon Nanotubes, *Carbon* 45 (2007) 1972–1978.
- [164] S. Gajewski, H.-E. Maneck, U. Knoll, D. Neubert, I. Dorfel, R. Mach, B. Straub, J. F. Fried, Purification of Single Walled Carbon Nanotubes by Thermal Gas Phase Oxidation, *Diam. Relat. Mater.* 12 (2003) 816–820.
- [165] J.G. Wiltshire, A.N. Khlobystov, L.J. Li, S.G. Lyapin, G.A.D. Briggs, R.J. Nicholas, Comparative Studies on Acid and Thermal based Selective Purification of HiPCO Produced Single-Walled Carbon Nanotubes, *Chem. Phys. Lett.* 386 (2004) 239–243.
- [166] A. Hamui, H. Alvergnat, S. Bonnamy, F. Beguin, Fluorination of Carbon Nanotubes, *Carbon* 35 (1997) 723–728.
- [167] P.X. Hou, S. Bai, Q.H. Yang, C. Liu, H.M. Cheng, Multi-Step Purification of Carbon Nanotubes, *Carbon* 40 (2002) 81–85.
- [168] Z.-X. Jin, G.-U. Xu, S.H. Goh, A Preferentially Ordered Accumulation of Bromine on Multi-Walled Carbon Nanotubes, *Carbon* 38 (2000) 1135–1139.
- [169] D.A. Heller, P.W. Barone, M.S. Strano, Sonication-Induced Changes in Chiral distribution: A Complication in the Use of Single-Walled Carbon Fluorescence for Determining Species Distribution, *Carbon* 43 (2005) 651–653.
- [170] Lu, K.L., Lago, R.M., and chen, Y.K., Green, M. L. H., Harris, P. J. F., and Tsang, S. C. Mechanical Damage of Carbon Nanotubes by Ultrasound, *Carbon* 34 (1996) 814-816.
- [171] C. Yang, X. Hu, D. Wang, C. Dai, L. Zhang, H. Jin, S. Agathopoulos, Ultrasonically Treated Multi-Walled Carbon Nanotubes (MWNTs) as PtRu Catalyst Supports for Methanol Electro Oxidation, *J. Power Sources* 160 (2016) 187–193.
- [172] Abatemarco, T., Stickel, J., Belfort, Frank, B.P., Ajayan, P.M., and Belfort G. Fractionation of Multi-Walled Carbon Nanotubes by Cascade Membrane Microfiltration, *J. Phys. Chem. B*, 103 (1999) 3534–3538.

- [173] K.B. Shelimov, R.O. Esenaliev, A.G. Rinzler, C.B. Huffman, R.E. Smalley, Purification of Single-Wall Carbon Nanotubes by Ultrasonically Assisted Filtration, *Chem. Phys. Letter.* 282 (1998) 429–434.
- [174] E. Frakas, M.E. Anderson, Z. Chen, A.G. Rinzler, Length Sorting Cut Single Wall Carbon Nanotubes by High Performance Liquid Chromatography, *Chem. Phys. Lett.* 363 (2002) 111–116.
- [175] Y. Yang, L. Xie, Z. Chen, M. Liu, T. Zhu, Z. Liu, Purification and Length Separation of Single-Walled Carbon Nanotubes using Chromatographic Method, *Synth. Met.* 155 (2005) 455–460.
- [176] J. Loos, N. Grossiord, C.E. Koning, O. Regev, On the Fate of Carbon Nanotubes: Morphological Characterizations, *Composites Sci. and Technol.* 67 (2007) 783–788.
- [177] L. Jiang, L. Gao, J. Sun, Production of Aqueous Colloidal Dispersions of Carbon Nanotubes, *J. Colloid Interface Sci.* 260 (2003) 89–94.
- [178] O. Matarredona, H. Rhoads, Z. Li, J.H. Harwell, L. Balzano, D.E. Resasco, Dispersion of Single-Walled Carbon Nanotubes in Aqueous Solutions of the Anionic Surfactant NADDBS, *Journal of Phys Chem B.* 107 (2003) 13357–13367.
- [179] Shvartzman-Cohen, R., Levi-Kalisman, Y., Nativ-Roth, E., and Yerushalmi-Rosen, R., Generic Approach for Dispensing Single-Walled Carbon Nanotubes: The Strength of a Weak Interaction, *Langmuir*, 20 (2004) 6085–6088.
- [180] L.A. Montoro, J.M. Rosolen, A Multi-Step Treatment to Effective Purification of Single-Walled Carbon Nanotubes, *Carbon* 44 (2006) 3293–3301.
- [181] H. Huang, H. Kajiura, H. Yamada, M. Ata, Purification and Alignment of Arc-Synthesis Single-Walled Carbon Nanotube Bundles, *Chem Phys Letters.* 356 (2002) 567–572.
- [182] S.J. Strickler, *Encyclopedia of Chemical Physics and Physical Chemistry*, Inst of Physics Pub Inc Bristol UK, 2002.
- [183] B.J. Clark, T. Frost, M.A. Russel, *UV Spectroscopy: techniques, instrumentation, data handling*, Chapman & Hall, London, UK, 1993.
- [184] P.W. Atkins, R.S. Friedman, *Molecular Quantum Mechanics*, 3rd ed, Oxford University Press, New York USA, 1997.
- [185] D.A. Skoog, J.J. Leary, *Principles of Instrumental Analysis*, 4th ed., Saunders College Publishing Orland USA, 1992.
- [186] L. Qu, X. Peng, Control of Photoluminescence Properties of CdSe Nanocrystals in Growth, *Journal of the American Chem. Soc.* 124 (2002) 2049–2055.
- [187] M. Bruchez, M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, Semiconductor Nanocrystals as Fluorescent Biological Labels, *Science* 281 (1998) 2013–2016.
- [188] D.N. Kendall, *Applied Infrared Spectroscopy*, Reinhold Pub. Corp, New York, USA, 1996.
- [189] R.A. Shaw, H.H. Mantsch, *Encyclopedia of Analytical Chemistry*, John Wiley & Sons Ltd, Chichester UK, 2000.
- [190] R.W. Darnabeau, Nuclear Magnetic Resonance (NMR) Spectroscopy: A Review and a Look at Its Use as a Probatative Tool in Deamination Chemistry, *Appl. Spectrosc. Rev.* 41 (2006) 401–425.
- [191] B.E. Warren, *X-Ray Diffraction*, Addison-Wesley Pub Co, Reading USA, 1969.
- [192] J. Drenth, *Principle of Protein X-Ray Crystallography*, 3rd ed, Springer Verlag, New York, USA, 1999.
- [193] L.C. Feldman, J.W. Mayer, *Fundamentals of Surface and Thin Film Analysis*, North-Holland Publishing, New York, USA, 1986.
- [194] G. Bryant, C. Abeynayake, J.C. Thomas, Improved Particle Size Distribution Measurements using Multiangle Dynamic Light Scattering. 2. Refinements and Applications, *Langmuir* 12 (1996) 6224–6228.
- [195] H. Colfen, L. Qi, A Systemic Examination of the Morphogenesis of Calcium Carbonate in the Presence of a Double- Hydrophilic Block Copolymer, *Chemistry-A European Journal* 7 (2001) 106–116.
- [196] Ross and K. T. Carron. In *Encyclopedia of Analytical Science*, edited by C.F. Poole, A. Townsend, and P.J. Worsfold, Academic Press, New York, USA 2004.
- [197] M.V. Ardenne, *Advances in Electronics and Electron Physics. Supplement 16: The beginnings of Electron Microscopy*, Academic Press, Orlando, USA, 1984.
- [198] H.J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, Weinheim, Germany, 2003.
- [199] S. Amelinckx, D.V. Dyck, J.V. Landuyt, G.V. Tandeloo, *Electron Microscopy: Principles and Fundamentals*, Wiley-VCH, Weinheim, Germany, 2003.
- [200] Z.L. Wang, Transmission Electron Microscopy of Shaped – Controlled Nanocrystal and their Assemblies”, *J. Phys. Chem. B* 104 (2000) 1153–1175.
- [201] G. Binnig, C.F. Quate, Ch. Gerber, Atomic Force Microscope, *Phys Rev Letters.* 56 (1986) 930–933.
- [202] T. Nakagawa, K. Ogawa, T. Kurumizawa, Atomic Force Microscope for Chemical Sensing, *J. of Vacuum Sci and Tech. B.* 12 (1994) 2215–2218.
- [203] J. Milling, *Surface Characterization Methods: Principle, Techniques and applications*, Marcel Dekker, New York, USA, 1999.
- [204] P. Harris, E. Hernandez, B.I. Yakobson, Carbon Nanotubes and Related Structures: New Materials for the 21st Century, *American J of Phys* 42 (2004) 414–416.
- [205] M. Meo, M. Rossi, Prediction of Young's Modulus of Single-wall Carbon Nanotubes by Molecular-Mechanics based Finite Element Modeling, *Composites Sci and Tech.* 66 (2006) 1597–1605.
- [206] M. Buongiorno Nardelli, J.-L. Fattebert, D. Orlikowski, C. Roland, Q. Zhao, J. Bernholc, Mechanical properties, defects, and electronic behavior of carbon nanotubes, *Carbon* 38 (2000) 1703–1711.
- [207] B. Chandra, J. Bhattacharjee, M. Purewal, Y.-W. Son, Y. Wu, M. Huang, H. Yan, T. F. Heinz, P. Kim, J.B. Neaton, J. Hone, Molecular-Scale Quantum Dots from Carbon Nanotube Heterojunctions, *Nano Lett.* 9 (2009) 1544–1548.
- [208] H. Dai, A. Javey, E. Pop, D. Mann, W. Kim, Lu, Y., Electrical Transport Properties and Field-Effect Transistors of Carbon Nanotubes, *NANO: Brief Reports and Reviews* 1 (2006) 1–13.
- [209] H. Peng, L.B. Alemany, J.B. Margrave, V.N. Khabashesku, Sidewall Carboxylic Acid Functionalization of Single-Walled Carbon Nanotubes, *J. of American Chem Soc.* 125 (2003) 15174–15182.
- [210] E. Pop, D. Mann, Q. Wang, K. Goodson, H. Dai, Thermal Conductance of an Individual Single-wall Carbon Nanotube above Room Temperature, *Nano Lett.* 6 (2006) 96–100.
- [211] R.S. Ruoff, D.S. Lorents, Mechanical and Thermal Properties of Carbon Nanotubes, *Carbon* 33 (1995) 925–930.
- [212] H. Stahl, J. Appenzeller, R. Martel, Ph. Avouris, B. Lengeler, Intertube Coupling in Ropes of Single-Wall Carbon Nanotubes, *Phys. Rev. Lett.* 85 (2000) 5186–5189.
- [213] K. Matsuda, *Fundamental Optical Properties of Carbon Nanotubes and Graphene*, Kyoto University, Japan, 2013.
- [214] S. Yamashita, Y. Inoue, S. Maruyama, Y. Murakami, H. Yaguchi, M. Jablonski, S. Y. Set, Saturable Absorbers Incorporating Carbon Nanotubes Directly Synthesized onto Substrates and Fibers and their Application to Mode-Locked Fiber Lasers, *Opt. Lett.* 29 (2004) 1581–1583.
- [215] H. Katura, Y. Kumazawa, Y. Maniwa, I. Umezawa, S. Suzuki, Y. Ohtsuka, Y. Achiba, Optical Properties of Single-Wall Carbon Nanotubes, *Synth. Met.* 103 (1999) 2555–2558.
- [216] V. Lordi, N. Yao, Molecular Mechanics of Binding in Carbon-Nanotube-Polymer Composites, *J. of Materials Research* 15 (2000) 2770–2779.
- [217] W. Yang, P. Thordarson, J.J. Gooding, S.P. Ringer, F. Braet, Carbon nanotubes for biological and biomedical applications, *Nanotechnology* 18 (2007) 1–12.
- [218] L. Lacerda, A. Bianco, M. Prato, K. Kostarelos, Carbon nanotubes as Nano medicines: From toxicology to pharmacology, *Adv. Drug Deliv. Rev.* 58 (2006) 1460–1470.
- [219] C.H. Sayes, F. Liang, J.L. Hudson, J. Mendez, W. Guo, J.M. Beach, V.C. Moore, C. D. Doyle, J.L. West, W.D. Billups, K.D. Ausman, V.L. Colvin, Functionalization Density Dependence Of Single-Walled Carbon Nanotubes Cytotoxicity In Vitro, *Toxicol. Lett.* 161 (2006) 135–142.
- [220] K.M. El-Say, Nano diamond as a Drug Delivery System: Applications and Prospective, *Journal of Applied Pharmaceutical Science.* 06 (2011) 29–39.
- [221] Z. Jin, X. Sun, G. Xu, S.H. Goh, W. Ji, Nonlinear Optical Properties Of Some Polymer multi-Walled Carbon Nanotube Composites, *Chem. Phys. Lett.* 318 (2000) 505–510.
- [222] S. Jain, V.S. Thakare, M. Das, C. Godugu, A.K. Jain, R. Mathur, K. Chuttani, A. K. Mishra, Toxicity of Multiwalled Carbon Nanotubes with End Defects Critically Depends on their Functionalization Density, *Chem. Res. Toxicol.* 24 (2011) 2028–2039.
- [223] F. Raymond, Jr Hamilton, C. Xiang, M. Li, I. Ka, F. Yan, Dongling Ma, D.W. Porter, N. Wu, A. Holian, Purification and Sidewall Functionalization of Multiwalled Carbon Nanotubes and Resulting Bioactivity in Two Macrophage Models, *Inhal. Toxicol.* 25 (2013) 199–210.
- [224] K.A. Worsley, I. Kalinina, E. Bekyarova, R.C. Haddon, Functionalization and Dissolution of Nitric Acid Treated Single-Walled Carbon Nanotubes, *J. Am. Chem. Soc.* 131 (2009) 18153–18158.
- [225] J.R. Pietruska, X. Liu, A. Smith, K.M. Neil, P. Weston, A. Zhitkovich, R. Hurt, A. B. Kane, Bioavailability, Intracellular Mobilization of Nickel, and HIF-1 α Activation in Human Lung Epithelial Cells Exposed to Metallic Nickel and Nickel Oxide Nanoparticles, *Toxicol. Sci.* 124 (2011) 138–148.
- [226] M. Foldvari, M. Bagonluri, Carbon Nanotubes as Functional Excipients for Nanomedicines: II. Drug Delivery and Biocompatibility Issues, *Nanomedicine* (2008).
- [227] W. Zhang, Z. Zhang, Y. Zhang, The Application of Carbon Nanotubes in Target Drug Delivery Systems for Cancer Therapies, *Nanoscale Research Lett.* 6 (2011) 555–560.
- [228] S. Sarojini, S. Rajasekar, K. Koumaravelou, Carbon Nanotubes: A New Weapon in Health Care Treatment, *International J of Pharma and Bio Sciences* 1 (2010) 644–649.
- [229] A.L.M. Reddy, N. Rajalakshmi, S. Ramaprabhu, Cobalt-Polypyrrole Multi-walled Carbon Nanotube Catalysts for Hydrogen and Alcohol Fuel Cells, *Carbon* 46 (2008) 2–11.
- [230] C. Park, S. Lee, J.H. Lee, J. Lim, S.C. Lee, M. Park, S.S. Lee, J. Kim, C.R. Park, C. Kim, Controlled Assembly of Carbon Nanotubes Encapsulated with Amphiphilic Block Copolymer, *Carbon* 45 (2007) 2072–2078.
- [231] J. Zou, L. Liu, H. Chen, S.I. Khondaker, R.D. McCullough, Q. Huo, L. Zha, Dispersion of Pristine Carbon Nanotubes Using Conjugated Block Copolymers, *Adv. Mater.* 20 (2008) 2055–2060.
- [232] Z. Zhang, J. Zhang, P. Chen, B. Zhang, J. He, G.-H. Hu, Enhanced Interactions between Multi-Walled Carbon Nanotubes and Polystyrene Induced by Melt Mixing, *Carbon* 44 (2006) 692–698.
- [233] F. Tournus, S. Latil, M.I. Heggie, J.C. Charlier, π -Stacking Interaction between Carbon Nanotubes and Organic Molecules, *Phys rev B* 72 (2006) 75–83.
- [234] G. Wei, C. Pan, J. Reichert, K.D. Jandt, Controlled Assembly of Protein-Protected Gold Nanoparticles on Non Covalent Functionalized Carbon Nanotubes, *Carbon* 48 (2010) 645–653.
- [235] M. Foldvari, M. Bagonluri, Carbon Nanotubes as Functional Excipients for Nanomedicines: I, Pharmaceutical Properties, *Nanomedicine: Nanotechnology, Biology, and Medicine* 4 (2008) 173–182.
- [236] K. Kostarelos, Rational Design and Engineering of Delivery Systems for Therapeutics: Biomedical Exercises in Colloid and Surface Science, *Adv. Colloid Interface Sci.* 106 (2003) 147–168.
- [237] H. Wang, J. Wang, X. Deng, H. Sun, Z. Shi, Z. Gu, Y. Liu, Y. Zhao, Biodistribution of Carbon Single-Wall Carbon Nanotubes in Mice, *J. Nanosci. Nanotechnol.* 4 (2004) 1019–1024.

- [238] A. Nel, T. Xia, L. Madler, N. Li, Toxic Potential of Materials at the Nanolevel, *Science* 311 (2006) 622–627.
- [239] Singh, R., Pantarotto, D., Lacerda, L., Pastorin, G., Klumpp, C., Prato, M., Bianco, A., and Kostarelos, K. Tissue Biodistribution and Blood Clearance Rates of Intravenously Administered Carbon Nanotube Radiotracers, *Proceedings of the National Academy of Sciences of the United States, States of America* 103 (2006) 3357–3362.
- [240] Y.M. Choi, D.S. Lee, R. Czerw, P.W. Chiu, N. Grobert, M. Terrones, M. Reyes-Reyes, H. Terrones, J.C. Charlier, P.M. Ajayan, S. Roth, D.L. Carroll, Y.W. Park, Nonlinear Behavior in the Thermopower of Doped Carbon Nanotubes Due to Strong, Localized States, *Nano Lett.* 3 (2003) 839–842.
- [241] S.T. Stern, S.E. McNeil, Nanotechnology Safety Concerns Revisited, *Toxicological Science* 101 (2008) 4–21.
- [242] H.J. Johnston, G.R. Hutchison, F.M. Christensen, S. Peters, S. Hankin, K. Aschberger, V. Stone, A Critical Review of the Biological Mechanisms Underlying the in Vivo And in Vitro Toxicity of Carbon Nanotubes: The Contribution of Physico-Chemical Characteristics, *Nanotoxicology* 4 (2010) 207–246.
- [243] C.-W. Lam, J.T. James, SivaramArepalli, Robert L. Hunter, A Review of Carbon Nanotube Toxicity and Assessment of Potential Occupational and Environmental Health Risks, *Review of Carbon Nanotube Toxicity* 36 (2006) 189–217.
- [244] K. Donaldson, V. Stone, C.L. Tran, W. Kreyling, P.J.A. Borm, *Nanotoxicology, Toxicology, Occup. Environ. Med.* 61 (2004) 727–728.
- [245] K. Donaldson, R. Aitken, L. Tran, V. Stone, R. Duffin, G. Forrest, A. Alexander, Carbon Nanotubes: A Review of Their Properties in Relation to Pulmonary Toxicology and Workplace Safety, *Toxicol. Sci.* 92 (2006) 5–22.
- [246] L. Lacerda, A. Bianco, M. Prato, K. Kostarelos, Carbon Nanotubes as Nanomedicines: From Toxicology to Pharmacology, *Adv. Drug Deliv. Rev.* 58 (2006) 1460–1470.
- [247] A.D. Maynard, P.A. Baron, M. Foley, A.A. Shvedova, E.R. Kisin, V. Castranova, Exposure to Carbon Nanotube Material: Aerosol Release During the Handling Of Unrefined Single-walled Carbon Nanotube Material, *Journal of Toxicology and Environmental Health Part A* 67 (2004) 87–107.
- [248] A. Helland, P. Wick, A. Koehler, K. Schmid, C. Som, Reviewing the Environmental and Human Health Knowledge Base of Carbon Nanotubes, *Environ. Health Perspect.* 115 (2007) 1125–1131.
- [249] Baughman, R.H., and Zakhidov, A.A., Walt A.de Heer, Carbon Nanotube-the Route toward Application, *Science* 297 (2002) 787–792.
- [250] M.C. Garcia- Gutierrez, A. Nogales, D.R. Rueda, C. Domingo, J.V. Garcia-Romas, G. Broza, Z. Roslaniec, K. Schulte, R.J. Davies, T.A. Ezquerro, Templating of Crystallization and Shear-Induced Self-Assembly of Single-Wall Carbon Nanotubes in a Polymer-NanoComposite, *Polymer* 47 (2006) 341–345.
- [251] E.J. Siochi, D.C. Working, C. Park, P.T. Lillehei, J.H. Rouse, C.C. Topping, A. R. Bhattacharya, and Kumar, S, Melt Processing of SWCNT-Polyimide nanocomposite fibers, Composites: Part B 35 (2004) 439–446.
- [252] A.R. Bhattacharya, P. Potschke, M. Abdel-Goad, D. Fischer, Effect of Encapsulated SWNT on the Mechanical Properties of Melt Mixed PA12/SWNT Composites, *Chem. Phys. Lett.* 392 (2004) 28–33.
- [253] K. Saeed, S.-Y. Park, Preparation of Multiwalled Carbon Nanotube/Nylon-6 Nanocomposites by In Situ Polymerization, *J of Applied Polymer Science* 106 (2007) 3729–3735.
- [254] K. Prashantha, J. Soulestin, M.F. Lacrampe, M. Claes, G. Dupin, Krawczak, P, Multi-walled Carbon Nanotube Filled Polypropylene Nanocomposites Based on Masterbatch Route: Improvement of Dispersion and Mechanical Properties through PP-g-MA Addition, *eXPRESS Polymer Letters* 2 (2008) 735–745.
- [255] Zhang, X-X., Meng, Q-J., Wang, X-C., Bai, and S-H. Poly (adipic acid-hexamethylenediamine)-Functionalized Multi-Walled Carbon Nanotube Nanocomposites, *J. Mater Sci.* 46 (2011) 923–930.
- [256] S.S. Wong, E. Joselevich, A.T. Woolley, C.L. Cheung, C.M. Lieber, Covalently Functionalized Nanotubes as Nanometre-sized Probes in Chemistry And Biology, *Nature* 394 (1998) 52–55.
- [257] A. Modi, N. Koratkar, E. Lass, B. Wei, P.M. Ajayan, Miniaturized Gas Ionization Sensors using Carbon Nanotubes, *Nature* 424 (2003) 171–174.
- [258] K. Besteman, J.-O. Lee, F.G.M. Wiertz, H.A. Heering, C. Dekke, Enzyme-Coated Carbon Nanotubes as Single-Molecule Biosensors, *Nano Lett.* 3 (2003) 727–730.
- [259] A. Bianco, K. Kostarelos, M. Prato, Applications of Carbon Nanotubes in Drug Delivery, *Science Direct* 9 (2005) 674–679.
- [260] T.S. Cho, K.-J. Lee, J. Kong, A.P. Chandrasekaran, A Low Power Carbon Nanotube Chemical Sensor System, *IEEE Custom Integrated Circuits Conference* 11 (2007) 1–4.
- [261] G. Binning, H. Rohrer, C. Gerber, E. Weibel, Surface Studies by Scanning Tunneling Microscopy, *Phys. Rev. Lett.* 49 (1982) 57–61.
- [262] H. Dai, J.H. Hafner, A.G. Rinzler, D.T. Colbert, R.E. Smalley, Nanotubes as Nanoprobes in Scanning Probe Microscopy, *Nature* 384 (1996) 147–150.
- [263] N.R. Wilson, J.V. Macpherson, Carbon Nanotube Tips for Atomic Force Microscopy, *Nat. Nanotechnol.* 4 (2009) 1–9.
- [264] C. Niu, E.K. Sichel, R. Hoch, D. Moy, H. Tennent, High Power Electrochemical Capacitors Based on Carbon Nanotube Electrodes, *App Phys Lett.* 70 (1997) 1480–1482.
- [265] E. Frackowiak, F. Beguin, Electrochemical Storage of Energy in Carbon Nanotubes and Nanostructured Carbons, *Carbon* 40 (2002) 1775–1787.
- [266] Meunier, V., Kephart, J., Roland, C., and Bernholc, J. Ab Initio Investigations of Lithium Diffusion in Carbon Nanotube Systems, *Phys Rev Lett.* 88 (2002) 075506-1–075506-4.
- [267] Stampfer, C., Helbling, T., Obergfell, D., Schoberle, B., Tripp, M.K., Jungen, A., Roth, S., Bright, V.M., and Hierold, C. Fabrication of Single-Walled Carbon-Nanotube-Based Pressure Sensors, *Nano Letters*, 6 (2006) 233–237.
- [268] K. Jensen, J. Weldon, H. Garcia, A. Zett, Nanotube Radio, *Nano Lett.* 7 (2007) 3508–3511.
- [269] T. Rueckes, K. Kim, E. Joselevich, G.Y. Tseng, C.-L. Cheung, C.M. Lieber, Carbon Nanotube-Based Nonvolatile Random Access Memory for Molecular Computing, *Science* 289 (2000) 94–97.
- [270] M. Fennimore, T.D. Yuzvinsky, W.-Q. Han, M.S. Fuhrer, J. Cumings, A. Zettl, Rotational Actuators Based on Carbon Nanotubes, *Nature* 424 (2003) 108–110.
- [271] Yue, G. Z., Qiu, Q., and Gao, B., Cheng, Y., Zhang, J., and Shimoda, H., Chang, S., Lu, J. P., and Zhou, O. Generation of Continuous and Pulsed Diagnostic Imaging X-Ray Radiation using a Carbon-Nanotube-Based Field-Emission Cathode, *Appl Phys Lett* 81 (2002) 355–357.
- [272] Fowler, R.H., and Nordheim, L. Electron Emission in Intense Electric Fields, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* 119(1928) 173–181.
- [273] W.A. De Heer, A. Chatelain, D. Ugarte, A Carbon Nanotube Field-Emission Electron Source, *Science New Series* 270 (1995) 1179–1180.
- [274] R.H. Reuss, B.R. Chalamala, A. Moussessian, M.G. Kane, A. Kumar, D.C. Zhang, J. A. Rogers, M. Hatalis, D. Temple, G. Moddel, B.J. Eliasson, M.J. Estes, J. Kunze, E. S. Handy, E.S. Harmon, D.B. Salzman, J.M. Woodall, M.A. Alam, J.Y. Murthy, S. C. Jacobsen, M. Olivier, D. Markus, P.M. Campbell, E. Snow, Macroelectronics: Perspectives on Technology and Applications, *Proc. IEEE* 93 (2005) (2005) 1239–1256.
- [275] A. Dodabalapur, Organic and Polymer Transistors for Electronics, *Material Today* 9 (2006) 24–30.
- [276] Chason, M., Brazis, P.W., Zhang, J., Kalyanasundaram, K., and Gamota, D.R. Printed Organic Semiconducting Devices, *Proceedings of the IEEE* 93(2005) 1348–1356.
- [277] Cao, Q., Kim, H.-S., Pimparkar, N., Kulkarni, J.P., Wang, C., Shim, M., Roy, K., Alam, M.A., and Rogers, J.A. Medium-Scale Carbon Nanotube Thin-Film Integrated Circuits on Flexible Plastic Substrates, *Nature* 454 (2008) 495–502.
- [278] L. Schlappbach, A. Züttel, Hydrogen-Storage Materials for Mobile Applications, *Nature* 414 (2001) 353–358.
- [279] R. Strobel, J. Garthe, P.T. Moseley, L. Jorissen, G. Wolf, Hydrogen Storage by Carbon Materials, *J. Power Sources* 159 (2006) 781–801.
- [280] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Storage of Hydrogen in Single-Walled Carbon Nanotubes, *Nature* 386 (1997) 377–379.
- [281] L. Wang, X. Zhang, H. Gao, J. Hu, J. Mao, C. Liang, P. Zhang, G. Shao, 3D CuO Network Supported TiO₂ Nanosheets with Applications for Energy Storage and Water Splitting, *Sci of Advanced Materials* 8 (2016) 1256–1262.
- [282] Q. Wang, X. Li, X. He, L. Cao, G. Cao, H. Xu, J. Hu, G. Shao, Two-pronged approach to regulate Li etching for a stable anode, *J. Power Sources* 455 (2020), 227988.
- [283] E.T. Thostenson, Z. Ren, T.W. Chou, Advances in the Science and Technology of Carbon Nanotubes and their Composites: a Review, *Composites Sci and Tech.* 61 (2001) 1899–1912.
- [284] A.B. Dalton, S. Collins, E. Muñoz, J.M. Razal, V.H. Ebron, J.P. Ferraris, J. N. Coleman, B.G. Kim, R.H. Baughman, Super-Tough Carbon-Nanotube Fibres, *Nature* 423 (2003) 703.
- [285] E. Frackowiak, Carbon Materials for Supercapacitor Application, *Phys. Chem.* 9 (2007) 1774–1785.
- [286] R.A. MacDonald, B.F. Laurenzi, G. Viswanathan, P.M. Ajayan, J.P. Stegemann, Collagen- Carbon Nanotube Composite Materials as Scaffolds in Tissue Engineering, *J of Biomedical Matters: Res. Part A* 74 A (2005) 489–496.
- [287] R. Hirlekar, M. Yamagar, H. Garse, M. Vij, V. Kadam, Carbon Nanotubes and its Applications: a Review, *Asian J. Pharm. Clin. Res.* 2 (2009) 17–27.
- [288] P. Pai, K. Nair, S. Jamade, R. Shah, V. Ekshinge, N. Jadhav, Pharmaceutical Application of Carbon Tubes and Nanohorns, *Current Pharma Research Journal* 1 (2006) 11–15.
- [289] A. Bianco, K. Kostarelos, M. Prato, Applications of carbon nanotubes in drug delivery, *Curr. Opin. Chem. Biol.* 9 (2005) 674–679.
- [290] N.W. Shi Kam, M. O'Connell, J.A. Wisdom, H. Dai, Carbon Nanotubes as Multifunctional Biological Transporters and Near-Infrared Agents for Selective Cancer Cell Destruction, *PNAS* 102 (2005) 11600–11605.
- [291] P.R. Bandaru, Electrical Properties and Applications of Carbon Nanotube Structures, *J of Nanosci and Nanotech.* 7 (2007) 1239–1267.