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Stupendous Nanomaterials: Carbon Nanotubes Synthesis, Characterization, and Applications

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Abstract

Carbon nanotubes are promising to revolutionize several fields in material science and are suggested to open the way into nanotechnology. These circular rod-shaped carbon nanostructures have novel characteristics that lead them to being potentially beneficial in many applications in nanoscience and nanotechnology. Their precise surface place, stiffness, power, and resilience have brought about lots of exhilaration in various areas. Nanotubes are categorized as single-walled nanotubes, double-walled nanotubes, and multi-walled nanotube. Various techniques have been evolved to produce nanotubes in bulk, including of arc discharge, laser ablation, chemical vapor deposition, electrolysis, and ball milling. Since their first observation nearly 20 years ago by Iijima, carbon nanotubes have been the focus of considerable research. Numerous researchers have reported remarkable physical and chemical properties for this new form of advanced carbon nanomaterials. Carbon nanotubes offer tremendous opportunities for the development of new material systems. This paper provides a concise report on recent advances in carbon nanotubes and their potential applications.

Keywords: carbon nanotubes, SWCNTs, MWCNTs, CVD, spray pyrolysis, SEM, HRTEM, purification

1. Introduction

Up until 1985, it was generally accepted that solid elemental carbon occurs in two different crystalline states: diamond and graphite. In the structure of diamond, every atom is tetrahedrally encircled by four sp^3 covalently neighboring carbon atoms. It brings about a special system of carbon developed on a cube-like face focused lattice. The structure of graphite comprises of graphene layers inside which the sp^2 neighboring carbon atoms form a planar polygon honeycomb arrangement. The bonding of carbon atoms in a graphene plane is through very strong valence bonds though the holding between two graphene layers is feeble Vander Waals bonds. In 1985, vital revolution in carbon research was realized by the work of Kroto et al [1] that resulted in the discovery of an enormous family of all carbon molecules, referred to as fullerenes. The fullerenes are closed cage carbon molecules formed by 12 pentagonal rings and 20 hexagonal rings. The molecular structure of

C60 shows that each of its pentagon is enclosed by 5 hexagons. The crucial particularity is the presence of five-membered rings, which help the arc form a confined cage structure. In 1990, Kratschmer et al. [2] found that the residue made by arcing carbon electrodes contained C60 and different fullerenes. A year after multi-walled carbon nanotubes (MWNT), hollow long thin cylinders of carbon consisting of concentric graphite layers with diameters in the nanometer range and consisting of carbon atoms were primarily observed in 1991 by Sumio Iijima at the NEC research lab, when he studied the carbon residue made up of by-products obtained throughout the synthesis of fullerenes by the electrical arc discharge technique.[3] from that point after 2 years, single-walled carbon nanotubes (SWNTs) were produced. Iijima along with Ichihashi [4] used carbon electrodes with a small amount of iron and filled the chamber around the carbon arc with methane and argon gas, which yielded the single-walled carbon nanotubes. [5]. In 1996, Smalley synthesized bundles of single-walled carbon nanotubes for the first time [6]. These miracle materials have remarkable properties such as excellent tensile strength, thermal conductivity, and electrical conductivity that make them potentially useful in many applications in nanotechnology, electronics, optics, and composites.

2. Allotropes of carbon

Carbon, the sixth element in the periodic table, is the most versatile element in terms of the variety of materials it may form. Each carbon atom has four electrons in its valence shell ($2s^2 2p^2$) that can be used to form covalent bonds with other atoms. With different hybridizations, carbon atoms can be arranged into materials with different structures, such as diamond, graphite, fullerene, and CNTs. Diamond and graphite are two of the most common forms in the carbon family. In diamond, the sp^3 -hybridized carbon atoms are covalently bonded to four neighboring carbon atoms and therefore have tetrahedral structure. Due to the strength of the carbon-carbon bond and its three-dimensional structure, diamond is the hardest known material. Since there are no free electrons in diamond, it is an electric insulator. Graphite, on the other hand, is composed of sp^2 -hybridized carbon atoms. Each of these sp^2 -hybridized carbon molecules is attached to three other carbon atoms, departing one free electron in a $p-\pi$ orbital. This gives graphite a two-dimensional layer-like structure. The π electrons are delocalized inside the layers, which furnish the graphite with superb thermal and electrical conductivity. Notwithstanding, this sort of layered structure makes graphite exceptionally delicate, because the layers can slide in analogous direction with ease. Other important members in the carbon family are the fullerenes that were discovered in 1985. Fullerenes are closed convex cage molecules made of sp^2 -hybridized carbon atoms. Each of the carbon atoms is connected to three neighboring carbon atoms to form only pentagonal and hexagonal faces. C60, which looks like a soccer ball, is the simplest fullerene molecule containing 12 pentagons and 10 hexagons[7] (**Table 1**).

2.1 Structure of carbon nanotubes

CNTs can be regarded as giant fullerenes, with a one-dimensional tubular structure. CNTs have a high aspect ratio and their length can be millions of times greater than their tiny diameter. All carbon atoms in CNTs are sp^2 hybridized and connected with each other to form six-member rings that uniformly cover the surface of the CNT sidewall. Unlike graphite, there are no dangling carbon bonds in a perfect CNT. CNTs are classified as single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) according to the number of graphene layers.

Property	Graphite	Diamond	Fullerenes (bucky ball)	Carbon nanotubes
Color	Steel black to gray	Colorless	Black solid/magenta in solution	Black
Crystal structure	Tabular	Cubic	Truncated icosahedron	Cylindrical
Density (g/cm ³)	1.9–2.3	3.515	1.69	1.33–1.4
Melting point (°C)	3652–3297	3550	>800	Similar to graphite
Boiling point (°C)	4200	4827	NA	NA
Hybridization	Sp ² —trigional planar	Sp ³ —tetrahedral	Sp ² —trigional planar	Sp ² —trigional planar
Bond angle	120°	109°5′	120°	NA
Nature of bonds in structure	One double and two single bonds	All single bonds	One double and two single bonds	NA
Electrical conductivity	Conductor	Insulator	Semiconductor to conductor	Semiconductor and metallic

Table 1.
Properties of different carbon allotropes.

2.2 Single-walled carbon nanotubes

Single-walled nanotubes (SWNTs) have a diameter of close to 1 nm, with a tube length that can be many thousands of times larger than their diameter. Single-walled nanotubes with length up to orders of centimeters have been produced. The structure of a SWNT may be envisaged by wrapping a one-atom-thick layer of carbon known as graphene into a seamless cylinder. The approach of wrapping the graphene sheet is drawn by a combination of indices (n,m) known as the chiral vector. The integers n and m denote the number of unit vectors on two directions within the honeycomb space lattice of graphene. Assuming that m = 0 with $\theta = 0^\circ$, the nanotubes are called “zigzag.” If n is equal to m with $\theta = 30^\circ$, the nanotubes are called “armchair.” Otherwise, they are known as “chiral” (when m and n are not the same) with $0 < \theta < 30^\circ$ [8].

2.3 Multi-walled carbon nanotubes

Multi-walled nanotubes (MWNTs) can be considered as a gathering of concentric SWNTs with various diameters. The length and diameter of these structures contrast a great deal from those of SWNTs and, obviously, their properties are also very different. There are two models that can be utilized to depict the structures of MWNTs. In the event that the sheets of graphite are organized in concentric chambers (single-walled nanotube inside a bigger single-walled nanotube), then it is Russian doll model, whereas in the parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper. The interlayer distance is close to the distance between graphene layers in graphite [9].

3. Different properties of CNTs

3.1 Electrical conductivity

CNTs can be very conducting and henceforth can be said to be metallic. Their conductivity has been demonstrated to be a function of their chirality, the level

of bend just as their width. CNTs can be either metallic or semidirecting in their electrical conduct. Conductivity in MWNTs is quite complex. A few sorts of “arm chair”-structured CNTs seem to lead superior to other metallic CNTs. Moreover, the current between divider responses inside multi-walled nanotubes has been found to redistribute over individual cylinders nonconsistently. Be that as it may, there is no variation in current across various parts of metallic single-walled nanotubes. The conduct of the ropes of semiconducting single-walled nanotubes is unique; in that, the transport current changes unexpectedly at different situations on the CNTs.

3.2 Strength and elasticity

The carbon atoms of a solitary sheet of graphite structure a planar honeycomb cross segment, in which each atom is related by means of a strong bond to three neighboring atoms. With a perspective on these solid bonds, the basal plane flexible modulus of graphite is one of the greatest of any known material. In this way, CNTs are depended upon to be extremely high-quality fibers. Single-walled nanotubes are stiffer than steel and are incredibly impenetrable by damage from physical forces. Pushing on the tip of a nanotube will make it twist, yet without damage to the tip. Exactly when the force is cleared, the nanotube returns to its unique state. This property makes CNTs significant as test tips for high-resolution scanning probe microscopy. Assessing these effects has been to some degree inconvenient, and a cautious numerical worth has not been settled upon. Utilizing atomic force microscopy, the unanchored terminations of an unattached nanotube can be pushed out of its balance position, and the power required to push the nanotube can be assessed. The present Young's modulus estimation of single-walled nanotubes is around 1 Tpa. Others have shown theoretically that the Young's modulus depends upon the size and chirality of the single-walled nanotubes going from 1.22 to 1.26 Tpa.

3.3 Thermal conductivity and expansion

CNTs have been appeared to show superconductivity underneath 20°K (roughly at -253°C). Investigations propose that these intriguing strands, as of now proclaimed for their unparalleled strength and unique capacity to promote the electrical properties of either semiconductors or perfect metals, may sometime in the not-so-distant future too discover applications as smaller than expected warm conduits in gadgets and materials. The solid in-plane graphitic carbon-carbon bonds make them especially solid and solid against pivotal strains. The nearly zero in-plane thermal expansion but huge interplane extension of single-walled nanotubes infer solid in-plane coupling and high plasticity against nonaxial strains. Numerous applications of CNTs, such as in nanoscale molecular electronics, sensing and actuating gadgets, or as strengthening-added substance filaments in utilitarian composite materials, have been proposed. CNTs appear exceptionally as a tall warm conductivity. It is anticipated, hence, that nanotube reinforcement in polymeric materials may also appreciably progress the thermal and thermomechanical properties of the composites.

3.4 Field emission

Field emission comes about from the tunneling of electrons from a metal tip into vacuum, underneath utilization of a strong electric field. The little breadth and high aspect ratio of carbon nanotubes is extraordinarily ideal for field discharge. Undeniably for direct voltages, a strong electric field makes at the free conclusion of backed carbon nanotubes because of their sharpness.

3.5 High aspect ratio

Carbon nanotubes address an extremely minimal high aspect ratio conductive-added substance for plastics of numerous types. Their high aspect ratio suggests that a lower stacking of carbon nanotubes is required contrasted with other conductive-added substances to perceive the equivalent electrical conductivity. This low loading protects more of the polymer resins' robustness, mostly at low temperatures, as well as keeping up other key performance properties of the matrix resin. Carbon nanotubes have shown to be an astounding added substance to give electrical conductivity in plastics. Their high angle proportion, around 1000:1, gives electrical conductivity at lower loadings, contrasted with standard included substance materials, for example, carbon dark, cleaved carbon fiber, or stainless steel fiber.

3.6 Highly absorbent

The huge surface area and high absorbency of CNTs make them perfect contender to utilize in air, various gases, and water purification. A lot of investigation is being done in substituting activated charcoal with CNTs in certain ultra high purification purposes.

4. Synthesis of carbon nanotubes

The development of carbon nanotubes during synthesis accepted to commence from the recombination of carbon molecules came apart by warm from its precursor. In spite of the fact that a number of more up-to-date fabrication procedures are being designed, three fundamental strategies are the laser ablation, electric arc discharge, and the chemical vapor deposition. Chemical vapor deposition is getting to be exceptionally well known because of its potential for scale-up generation (Figure 1).

Figure 1.
Schematic diagram of different synthesis methods of CNTs.

4.1 Arc discharge

The arc discharge strategy produces a number of carbon nanostructures such as fullerenes, whisker, carbon soot, and profoundly graphitized carbon nanotubes from high-temperature plasma that approaches 3700°C. The crucial ever delivered nanotube was fabricated with the DC arc discharge methodology between two carbon anodes, anode and the cathode in a good gas (helium or argon) condition. For the most part, large-scale yield of carbon nanotubes of roughly 75% was made by Ebbesen and Ajayan with measurement between 2 and 30 nm and length 1 μm kept on the cathode at 100–500 torr helium and around 18 V DC. It has supportively been used to deliver both SWNTs and MWNTs as revealed by transmission electron microscope (TEM) assessment. Typical nanotube deposition rate is around 1 mm/min and the combination of transition metals, for example, cobalt, nickel, or iron into the terminals as impetus, favors nanotubes course of action against different nanoparticles, and low working temperature. The arc discharge unit must be given with cooling component whether catalyst is utilized or not, since overheating would not as it were comes about into safety dangers, but also into coalescence of the nanotube structure [10].

4.2 Laser ablation

Laser ablation strategy incorporates the use of laser bar to vaporize an object of a mix of graphite and metal impetus, for example, cobalt or nickel at temperature around 1200°C in a surge of controlled inert gas and weight, where the nanotube deposits are recuperated at a water cooled collector at much lower and steady temperature. This system was used in early days to deliver ropes of SWNTs with strikingly uniform limited width reaching out from 5 to 20 nm, and high return with graphite change more noticeable than 70–90% [11]. In any case, by the ethicalness of relative operational complexity, the laser removal strategy shows up to be financially disadvantageous, which on impact slow down its scale-up possibilities as compared to the CVD strategy.

4.3 Hydrothermal process

In a typical synthesis, ferrocene and sulfur in 1:2 proportion were dissolved in a mixed solution of water, and ethanol and NaOH pellets were added to the above solution under stirring for 30 min in a magnetic stirrer. The resulting homogeneous mixture was transferred to the reactor. The autoclave was heated to 200°C and maintained at this temperature for 20 h and then it was cooled to room temperature naturally and the resulting black precipitate was filtered, washed, and dried at 60°C in air [12].

4.4 Electolysis process

Soluble base and alkaline earth chloride salts are generally hygroscopic. Thermally drying (250°C) the salt in air can typically be acceptable for CNT production. (For CNT production, on account of the utilization of graphite crucible, melting the salt ought to be directed under inert climate). The tests were led at temperatures to some extent over the melting point of LiCl (600°C). To prepare the example approximately, the blend comprises of LiCl-1% SnCl₂ was taken in a graphite crucible. The graphite crucible was put in an electrical warmed heater and the temperature level set at 600°C. The free streaming inert gas was passed onto the furnace all through the experiment to diminish the oxidation of salt and carbon materials. The temperature came to 600°C and to equilibrate the melt for 1 h. This

Production method	Name of the product	Comments on product	Reaction conditions (catalyst)	Year & references	Author
Water assisted	Vertically aligned SWNTs, DWNTs	High yield	With buffer layer	2003 [15]	Liu et al.
O ₂ assisted				2004 [16]	Chaisitsak et al.
Microwave plasma-enhanced				2004 [17]	Hata et al.
Hot filament-enhanced	SWNTs, MWNTs	Perpendicularly or vertically aligned	Fe-Co/SiO ₂ with or without of Si support	2007 [18]	Zhu et al.
Alcohol CVD	CNTs	Multibranched morphology	Cu/MgO	2006 [19]	Terrado et al.
High power laser pulse alcohol CVD	SWNTs		Solid metal target	2005 [20]	Okamoto et al.
Alcohol CVD		High purity	Ferrocene-ethanol	2002 [21]	Maruyama et al.
Thermal CVD	CNTs	Aligned	Co/SiO ₂ , Ar/H ₂ and NH ₃ /N ₂	2009 [22]	Khatri et al.
Microwave plasma-enhanced	CNTs	Well aligned, curved with random orientation	Fe/sapphire, Ni-Fe/glass, Cr-Fe/glass, Fe/Si, stainless steal	2009 [23]	Qi et al.
CVD	CNTs, carbon onions		Ni/Al	2006 [24]	Zhao et al.
		Metal filled, bamboo shaped	Ni/Cu/Al, methane	2008 [25]	Kang et al.
	MWNTs		K-doped Co and Co-Fe/zeolite and CaCO ₃	2008 [26]	Balogh et al.
	SWNTs, DWNTs		Fe-Mo/MgO	2006 [27]	Ago et al.
	CNTs		Different metals and rare-earth promoters	2000 [28]	Willems et al.
CVD	Aligned CNTs		Single-crystal of sapphire or quartz	2004 [29]	Ismach et al.
	CNTs, graphite layers, filaments		Different types of catalysts	1999 [30]	Fan et al.
	Helicoidal CNTs	Regular and irregular shape		1995 [31]	Ihara et al.
Alcohol CCVD	CNTs	Various morphology depending on the metal film thickness	Co/Si, Co-Mo/Si, Co/quartz, Co-Mo/quartz	2004 [32]	Nishide et al.
Thermal CVD	SWNTs & MWNTs	Controlled diameter distribution	Fe-Co/Zeolite	2005 [33]	Mukul Kumar et al.

Production method	Name of the product	Comments on product	Reaction conditions (catalyst)	Year & references	Author
CVD	MWNTs	Pure & high quality	CaCO ₃	2003 [34]	Herandi et al.
CVD	MWNTs	Clear helical structure	Iron nanoparticle catalyst	1993 [35]	Yacaman et al.

Table 2.
Carbon nanotubes synthesized by CVD method using different carbon sources.

Production method	Name of the product	Comments on product	Reaction conditions (catalyst)	Year and references	Author
Spray pyrolysis	MWNTs	Bamboo-shaped structure	<i>Brassica juncea</i>	2014 [37]	Kalaiselvan et al.
		Well-graphitized MWNTs	<i>Madhuca longifolia</i>	2013 [38]	
		Well-graphitized MWNTs	Pine oil	2010 [39]	Karthikeyan et al.
		Well-graphitized MWNTs	Bio-diesel oil	2010 [40]	
			<i>Cymbopogon flexuosus</i> oil	2012 [41]	Mageswari et al.
		Vertically aligned CNTs	<i>Helianthus annuus</i> oil	2013 [42]	Angulakshmi et al.
		Entangled MWCNTs	<i>Madhuca longifolia</i> oil	2014 [43]	Kalaiselvan et al.
			<i>Cymbopogon flexuosus</i> oil	2014 [44]	Mageswari et al.
	MWNTs	Magnetic metal encapsulated	<i>Pongamia pinnata</i> oil	2014 [45]	Mahalingam et al.
	Few-walled CNTs		Aliphatic alcohols	2013 [46]	Ordonez Casanova et al.
	CNTs	Nitrogen doped	Imidazole and Acetonitrile	2011 [47]	Jian Liu et al.
	MWNTs	Well-graphitized MWNTs	<i>Oryza sativa</i> oil	2016 [48]	Kalaiselvan et al.
		Multilayer of walls	<i>Citrus limonum</i> oil	2018 [49]	Angulakshmi et al.
		Multilayer of walls	<i>Zingiber officinale</i> oil	2018 [50]	Kalaiselvan et al.

Table 3.
Carbon nanotubes synthesized by spray pyrolysis method using different carbon sources.

procedure was called pre-electrolysis. After the pre-electrolysis, graphite bar of 1.4 cm² diameter with 5 cm² height was embedded into the melt as cathode. The cathode was embedded into the melt up to 4 cm² deepness in the graphite crucible as anode just as holding vessel for electrolyte. The control of DC power supply additionally needs to give an adequately wide range of currents and voltages. This procedure was completed at the steady present 3 A, and voltage 4.6 V. The current, voltage, and temperature of the bath are recorded all through the procedure [13].

4.5 Chemical vapor deposition

In this system, carbon nanotubes were developed from the breakdown of hydrocarbons at temperature range of 500–1200°C. They can develop on substrates for example, carbon, quartz, and silicon or on floating fine catalyst particle like Fe, Ni, Co, and so forth from various hydrocarbons for example, benzene, xylene, flammable gas, and acetylene. CVD furnished with a level cylindrical heater as the reactor. The cylinder is made of quartz and is 30 mm in width and 1000 mm long. Ferrocene and benzene vapors go about as the catalyst (Fe) and carbon atom precursor separately were moved by argon, hydrogen, or blend of both into the response chamber, and disintegrated into individual particles of Fe and carbon atom, coming about into carbon nanostructures. The development of the nanostructures happened in the heating zone, previously, or after the heating zone, which has, on the whole, functioned somewhere in the range of 500 and 1150°C for around 30 min. About 200 ml/min of hydrogen is utilized to cool the reactor [14] (Tables 2 and 3).

4.6 Spray pyrolysis

Progress metal nanoparticles were directly put in a quartz boat and kept at the center of a quartz tube, which was put inside a tubular heater. The inert gas nitrogen was presented at a rate of 100 mL/min into the quartz tube to expel any oxygen from that point and to make inert environment (Figures 2 and 3). The temperature was raised from room temperature to the preferred growth temperature. In this way, carbon precursor was brought into the quartz tube through a spray nozzle and the stream was kept up at a rate of 0.5 mL/min at temperature of 650°C. This process was carried out for 45 min and thereafter the furnace was cooled to room temperature. Nitrogen atmosphere was maintained throughout the experiment [36].

Figure 2.
SEM images of carbon nanotubes from different carbon sources.

Figure 3.
HRTEM images of carbon nanotubes from different carbon sources.

5. CNT growth mechanism

CNT growth mechanism has been debatable right from its discovery. Quite a lot of groups have proposed a few feasible outcomes that are often intricate. Subsequently, no single CNT growth pattern is well recognized till date. Despite the fact that most broadly acknowledged general system can be laid out as follows, hydrocarbon vapor when interacting with the “hot” metal nanoparticles first decompose into carbon and hydrogen species; hydrogen takes off and carbon gets broken down into the metal. Subsequent to achieving the carbon solvency limit in the metal at that temperature, as-disintegrated carbon accelerates out and takes shape as a tube-shaped system having no dangling bonds and hence actively stable.

Presently, there are two general cases. At the point when the impetus substrate collaboration is powerless, hydrocarbon decays on the top surface of the metal, carbon diffuses down through the metal, and CNT encourages out over the metallic base, pushing the whole metal molecule off the substrate insofar as the metal’s top is open for sparkling hydrocarbon decomposition and CNT continues to grow longer and more when the metal is completely encased with surplus carbon, its reactant movement arrives to an end, and the CNT development is halted up. This sort of growth is identified as tip-growth mechanism. In the other case, when the catalyst substrate interaction is strong, starting hydrocarbon decay and carbon dispersion occur like that in the tip-growth case; however, the CNT precipitation fails to drive the metal particle up so the precipitation is bound to rise out from the metal’s top. To begin with, carbon crystallizes out as a hemispherical ring, which at that point stretches out up as seamless graphitic cylinder. Consequently, hydrocarbon deposition happens on the lower fringe surface of the metal, and as broken down carbon diffuses upward. Accordingly, CNT grows up with the catalyst molecule established on its base; henceforth, this is considered as “base-development model.” The formation of single- or multi-walled CNT is governed by the size of the catalyst nanoparticle. Generally speaking, when the particle size is a few nm, SWCNT forms, whereas if the particles are a few tens of nm wide, it favors MWCNT growth [51] (**Figure 4**).

CNTs growth mechanism:-

1. Tip growth model

2. Base growth model

Figure 4.
 Schematic diagram of growth mechanisms of carbon nanotubes.

6. Purification process

Many purification methods that are highly developed show the most promise for industrial-scale production in which most type of impurities such as graphitic nanoparticles, amorphous carbon, fullerenes particles containing (transition) metal catalyst support removed since as-produced CNT soot contains a lot of impurities. These impurities will interfere with most of the desired properties of the CNTs. The common industrial techniques use strong oxidation and acid refluxing techniques, which have an effect on the structure of the tubes. In this chapter, several purification techniques of the CNT will be discussed such as air oxidation, acid treatment, annealing, ultrasonication, microfiltration, ferromagnetic separation, cutting, functionalization, and chromatography techniques. Most of the techniques used are combined with other techniques.

6.1 Air oxidation

Air oxidation treatment of the CNTs is a useful way to eliminate carbon impurities (defect carbon) and metal catalyst. The main disadvantage of this process is that not only the impurities are oxidized but also the CNTs. The reason why impurity oxidation is preferred is that these impurities are most commonly attached to the metal catalyst, which also acts as oxidizing catalyst. Optimum yield of this process is highly dependent on a lot of factors, such as metal content, oxidation time, oxidizing agent, and temperature. When the temperature is raised above 550°C, CNTs will also be oxidized. Optimum oxidation condition is found to be 400°C for 40 min [52].

6.2 Acid treatment

Commonly, the acid treatment will evacuate the metal catalyst. Most importantly, the outside of the metal must be exposed by oxidation or ultra-sonication. The metal catalyst is then presented to be destructive and solvated. The CNTs stay in suspended structure. When utilizing a treatment in HNO_3 , the corrosive just affects the metal catalyst. It has no impact on the CNTs and other carbon particles. On the other hand, if a treatment in HCl is utilized, the corrosive has additionally a little impact on the CNTs and other carbon particles [53, 54].

6.3 Annealing

On account of high temperatures (500–1500°C), the nanotubes will be redesigned and imperfections will be removed [55]. The high temperature furthermore causes the graphitic carbon and the short fullerenes to pyrolysis. When using high temperature vacuum treatment (1500°C), the metal will be mollified and can moreover be evacuated [54].

6.4 Ultrasonication

This process involves that nanoparticles be isolated utilizing ultrasonic vibrations. Agglomeration of various nanoparticles will be compelled to vibrate and will turn out to be scattered. The detachment of the particles is profoundly relying upon the surfactant, dissolvable, and reagent utilized. The stability of the scattered tubes is impacted by the solvent in the system. In poor solvents, the CNTs are increasingly secure in the event that they are as yet attached to the metal. In any case, in certain solvents like alcohols, even monodispersed particles are generally steady. At the point when acid is utilized, the wholesomeness of the CNTs relies upon the contact time. At the point when the tubes are bare to the acid for a short time frame, just the metal solvates, yet for a more drawn out for exposure time, the cylinders will also be chemically reduced [56, 57].

6.5 Magnetic purification

In this process, ferromagnetic nanoparticles are mechanically separated from their graphitic lattice [58]. The CNTs' suspension is blended with inorganic nanoparticles of ZrO_2 or CaCO_3 in a ultrasonic bath to take away the ferromagnetic particles. At that point, the particles are bound with permanent magnetic poles. After a successive chemical treatment, a highly cleaned CNT material will be obtained. This procedure does not require the involvement of big equipment and facilitates the fabrication of optimal quantities of CNTs free of magnetic impurities.

6.6 Microfiltration

This method is employed to remove carbon nanoparticles by microfiltration, which is completely based on size or particle separation. The other nanoparticles such as catalyst metal and fullerenes are also passing through the filter. One way of separating fullerenes from the CNTs by microfiltration is to immerse the as-synthesized CNTs first in a carbon-di-sulfide solution. The contents that are insoluble in carbon-di-sulfide (as-synthesized CNTs) are then trapped in a filter. The fullerenes that are solvated in the carbon-di-sulfide pass through the filter [57].

6.7 Cutting

Cutting of the CNTs is done either by chemically induced method or by mechanical cutting or as a combination of these two. Mechanical cutting of the nanotubes can be induced by ball-milling. Here, the bonds will break due to the high friction between the nanoparticles and the nanotubes will be disordered. CNTs can be chemically cut by partial function of the tube structures, for instance, with fluorinated carbon. Then, the fluorated carbon will be driven off the sidewall with pyrolyzation as CF_4 or COF_2 . This will discard the chemically hacked nanotubes. A blend of mechanical and chemical cutting of the nanotubes is ultrasonical empowered

cutting in acid solution treatment. Along this way, the ultrasonic vibration will give the nanotubes adequate energy to leave the catalyst surface. At that point, while blending with acid, the nanotubes will break at the deformity locales [59].

6.8 Functionalization of carbon nanotubes

Functionalization depends on making carbon nanotubes hydrophilic in nature than the contaminations by appending different groups to the tubes. Presently, it is anything but difficult to isolate them from insoluble contaminations, for example, metal particles by filtration. An added functionalization procedure also leaves the carbon nanotubes' structure unblemished and makes them solvent for chromatographic size division. For recovery of the purified carbon nanotubes, the helpful functional moieties can be evidently cleared by heat treatment process, such as annealing [60].

6.9 Chromatography

This system is primarily used to isolate little amounts of CNTs into fractions with little length and diameter dispersion. The CNTs overflow into a column comprised of permeable material, through which the CNTs will run. The columns utilized are gel permeation chromatography and high performance liquid chromatography-size exclusion chromatography columns. The number of pores the CNTs will move through relies upon their size. This implies, the littler the particle, the more drawn out the pathway as far as possible of the section will be and that the bigger atoms will succeed first. However, a problem is that the CNTs have to be either dispersed or solvated. This can be done by ultrasonication or functionalization with soluble groups [61].

7. Characterization of CNTs

Thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, Raman spectroscopy, infrared spectroscopy, and nuclear magnetic resonance have been used. While TEM, SEM, and AFM have been used for the majority part to qualitatively ascertain the widespread structural studies of carbon nanotubes, infrared spectroscopy, Raman spectroscopy, and nuclear magnetic resonance spectroscopy have been used to authenticate the presence of useful moiety on carbon nanotubes. All procedures have advantages when used in combination with other techniques [62].

7.1 Transmission electron microscopy

It is acclimated affirm the morphology and to give quantitative insight into the purity of incorporated carbon nanotubes. TEM unambiguously gives subjective information on the size, shape, and structure of carbonous materials, in addition to non-CNT-structured contaminations in the sample. Be that as it may, it cannot spot metallic pollutions and does not separate from CNTs. TEM has furthermore been acquainted image cell take-up of CNT-drug composites and to see the result of the CNT component once cell take-up [63].

7.2 Scanning electron microscopy

This is one of the main surface analysis instruments. It is used in the preliminary evaluation of CNT morphology. It can measure the diameter of CNT not precisely

but roughly. In its conventional situation, the technique is controlled by its incapacity to set apart catalyst and carboniferous impurities from CNTs. However, the metallic content of CNT samples is customarily quantifiable by SEM tied with an energy dispersive X-ray analysis detector (SEM-EDX). Despite the consequences, SEM is perhaps the only technique that will give data on each CNT structural information and also the metal impurity content [64].

7.3 Raman spectroscopy

Raman spectroscopy is one of the useful methods to detect carbon nanotubes, which not only shows the regularity and purity of the sample but also defines the diameter distribution of carbon nanotubes. Raman spectroscopy is used with a laser excitation wavelength of 633 nm. In the Raman spectra, there are three peaks or regions we are concerned about: the radial breathing modes (RBM $\sim 100\text{--}300\text{ cm}^{-1}$), D peak ($\sim 1350\text{ cm}^{-1}$), and G peak ($\sim 1570\text{ cm}^{-1}$). The RBM peaks are the distinctive peaks of carbon nanotubes, analogous with the diameters of carbon nanotubes. From radial breathing mode, we can forecast the distribution of carbon nanotubes' diameters. The D and G peaks are a result of unstructured carbon and graphited carbon, correspondingly. We can approximate the purity of carbon nanotubes by the intensity ratio of G peak and D peak (G/D). The larger the resultant value of G/D, the higher the graphited carbon, and if there are not many impurities or defects, then the purity is higher [65].

7.4 Proton nuclear magnetic resonance

It has been accustomed to monitor the advancement of CNT functionalization. The proximity of useful moiety can be predicted by characteristic peaks emerging from the differentiation within the magnetic environment. H^1 -NMR of functionalized CNTs is portrayed by wide peaks for protons close to the CNT, fitting sharper with separation. H^1 -NMR has been accustomed to analyze the synthesis and attachment of functional moiety to CNTs [66].

7.5 Infrared spectroscopy

It is for the most part a subjective method used to recognize valuable moieties and the idea of their connection to CNT sidewalls. Characteristic useful moieties incorporate characteristic frequencies of IR radiation, giving rise to a fingerprint identification of bonds. It is a contrary system to NMR, to affirm the presence of bonds among CNTs and of joined moieties [66].

7.6 Thermo gravimetric analysis (TGA)

It is fundamentally a subjective instrument acclimated set up useful gatherings and furthermore the idea of their connection to CNT sidewalls. Very surprising functional moieties retain characteristic frequencies of IR radiation, offering prompt fingerprint recognition of bonds. It is a harmonizing technique to magnetic resonance, to substantiate the presence of bonds between CNTs and of coupled moieties. The high sensitivity of the TGA, which is in the order of 0.1 mg/min, acceptable weight loss determinations at a given heating rate, within a short time without overwhelming too much material. The oxidation rates of carbon nanotubes measured in air at atmospheric pressure within the TGA are exceptional for each CNT sample of diverse wall thicknesses [67].

8. Recent applications of CNTs

From the time when the discovery of carbon nanotubes was made in 1991, several research teams reported their potential applications in diverse fields including energy storage, molecular electronics, nanoprobe, nanosensors, nanotube composites, and nanotube templates based on their unique electronic properties, size, mechanical strength, and flexibility (**Table 4**).

Potential applications	Author and year	Ref
Medicine applications		
Solid phase extraction of drugs and biochemicals	Xiao et al. 2013	[68]
Drug delivery for cancer therapy	Zhang et al. 2011	[69]
Antioxidants	Pham-Huy et al. 2008	[70]
Antitumor immunotherapy	Yang et al. 2007	[71]
Local antitumor hyperthermia therapy	Madani et al. 2011	[72]
Infection therapy	Jiang et al. 2012	[73]
Gene therapy by DNA delivery	Liao et al. 2011	[74]
Tissue regeneration	MacDonald et al. 2005	[75]
Artificial implants	Zhang et al. 2010	[76]
Biosensor vehicles for diagnostics and detection	Wang 2005	[77]
Neurodegenerative diseases	Zhang et al. 2010	[76]
Alzheimer syndrome	Yang et al. 2010	[78]
Other potential applications		
Composite materials	Zhou et al. 2014	[79]
Coatings and films	Mirri et al. 2012	[80]
Microelectronics	Duesberg et al. 2003	[81]
Transistors	Aissa et al. 2015	[82]
Solar cells	Wang et al. 2015	[83]
Hydrogen storage	Adeniran et al. 2015	[84]
Interconnects	Li et al. 2013	[85]
Electronic components	Cai et al. 2015	[86]
Loudspeaker	Xiao et al. 2008	[87]
Environment	Ong et al. 2010	[88]
Biosensors	Xia et al. 2015	[89]
Superhydrophobic cotton fabric	Makowski et al. 2014	[90]
Oscillators	Kang et al. 2006	[91]
Light bulb filament	Wei et al. 2004	[92]
Magnets	Kyatskaya et al. 2009	[93]
Electromagnetic antenna	Maksimenko et al. 2008	[94]
Air pollution filter	Yildiz et al. 2013	[95]
Water filter	Das et al. 2014	[96]
Nanowires for light-emitting devices	Yu et al. 2015	[97]

Table 4.
Summary of CNTs-based applications.

9. Conclusion

In this work, we have summarized various synthesis techniques of carbon nanotubes, and this advanced carbon nanomaterial has emerged since their discovery about 25 years ago. The broad scope of these applications suggests that a large number of CNT-based technologies will result from their unique properties of high electrical conductivity, mechanical strength, high aspect ratio, and nanoscale diameter. This report on carbon nanotubes reveals also an overview on structure, morphology, purification, and characterization methods. The distinct structural properties of carbon nanotubes, in particular their high aspect ratio, strength, and high surface area, have the added advantage of being potential nanodevices for various medical and industrial applications. Overall, recent studies regarding CNTs have shown a very promising glimpse of what lies ahead in the future of science. In this work, we also reported a variety of familiar methods to synthesis carbon nanotubes such as arc discharge, laser ablation and spray pyrolysis-assisted chemical vapor deposition, types, properties, purifications, characterization, and some notable applications in diverse field and also covered some recent synthesis of CNTs from a range of hydrocarbons using spray pyrolysis.

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