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An Overview Of Current Developments In The Synthesis Of Carbon Nanotubes And Their Use In Medicinal Applications

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Abstract

In order to address problems associated with conventional drug therapy, such as limited drug solubility, poor biodistribution, lack of property, and unfavourable pharmacological medicine, new nanomaterials have been extensively investigated in recent years for drug delivery applications. Among them, carbon nanotubes (CNTs) are well known and rank among the most notable innovations in the field of nanotechnology because to their unique chemical science design, characteristics, and potential for usage in a variety of industries. CNTs are acknowledged as nano-architecture carbon allotropes with length-to-diameter ratios up to 1,000,000. CNTs frequently have single, double, or multiple walls and are square sheets of rolled graphene with SP^2 coupling.The key characteristics of CNTs include their light weight, small size with a high aspect ratio, distinctive surface area, resilience, sensible tensile strength, and sensible conducting properties, which make them useful as fillers in a variety of materials including polymers, metallic surfaces, and ceramics. These cylindrical carbon molecules' potential uses in nanomedicine, nanotechnology, energy, textiles, actuators, sensors, composite materials, membranes, and capacitors have generated a great deal of enthusiasm in the pharmacy community. CNTs are refunctionalized or altered to hold payloads or interact with biological molecules since they are chemically inert and soluble in neither water nor other organic solvents. Due to their widespread use in medical applications such as the delivery of drugs, genes, and DNA as well as for biosensing, CNTs are best functionalized with proteins. They have the ability to cross membranes, transporting medicinal drugs, vaccinations, and nucleic acids deep inside the cell to previously unreachable locations. Numerous processes, such as flame synthesis, sol gel, silane solution, arc discharge, laser ablation, and chemical vapour deposition, have been devised to create nanotubes in significant numbers. The majority of the procedures used to purify CNTs include oxidation, acid treatment, annealing, sonication, chemical filtering, and functionalization techniques. High-purity purification methods must to be developed, though. These structures' striking advantages include their electrical, mechanical, optical, and chemical properties, which pave the way for potential future applications. This in-depth study focused on the synthesis, purification, functionalization, characteristics, advantages, applications, and most recent developments related to the use of CNTs for drug administration. The toxic effect of CNTs was also imparted in an extremely condensed form.

Keywords: Carbon nanotubes, Nanotechnology, Functionalization, Drug delivery, Purification techniques, Toxic effect of CNTs

INTRODUCTION

In order to avoid issues with conventional drug therapies, such as those related to limited drug solubility, poor biodistribution, lack of selectivity, and unfavourable pharmacokinetics, a great deal of attention has been paid to developing novel and more effective drug delivery systems over the past two decades [1, 2]. In example, metabolic or enzymatic conditions present in the gastrointestinal tract might cause bioactive substances such as proteins, nucleic acids, and genes delivered by oral or intravenous routes to breakdown prematurely [3, 4]. Huge obstacles have made it necessary to create new controlled medication delivery systems in order to accomplish a variety of objectives (e.g., delivery of therapeutic agents to the desired site, enhancing bioavailability and drug protection).Due to these difficulties, a brand-new field called nanomedicine-which involves the use of nanotechnology in medicine—is already emerging. It has recently been acknowledged as having the potential to advance therapeutic delivery [5, 6]. As a result, a variety of new nano-scaled materials have been investigated in recent years for drug delivery applications [5, 7–11], including nanoparticles, nanotubes, nanofibers, dendrimers, liposomes, polymer micelles, nanogels, and nanocrystals. For applications in drug delivery, carbon nanotubes (CNTs), which have special chemical and physical properties, have drawn a lot of attention [12–15]. Carbon is a remarkable element, not only because it is essential for all life processes, but also because it can exist in a wide range of allotropic forms [16]. Activated carbon, carbon black, and diamonds are all types of carbon that are typically found in materials as graphite blocks. Nanotextured and nanosized carbons are among the recently created carbon materials. Nanotextured carbons include a wide range of carbon structures, including carbon fibres, pyrolytic carbons, carbons that resemble glass, and carbon compounds that resemble diamonds. The fullerenes, graphene, and CNTs are the nanosized carbons (or nanocarbons) [17]. CNTs are hollow cylinders constructed of graphite carbon atoms that are significantly tiny (109 m) in size than the width of a human hair [18].

These CNTs are fullerene structural family members, and they have a hemisphere-shaped bucky ball cap on each end [19]. Iijima in Japan discovered and identified these nanoscales, nearly flawless whiskers for the first time in 1991 [20]. Because of their nanosize, which can change depending on their length, diameter, and chirality, CNTs have a wide range of distinctive features [21]. Its high thermal conductivity, high aspect ratio, ultra-light weight, young's modulus, large surface area, high current density, ballistic transport on submicron scales, and mass less diracparticle charge carrier abilities [22] are what give them the ability to be used in a variety of applications, including solar cells, photovoltaic devices, molecular separation, drug delivery, sensors, transparent electrodes, super capacitors, and conducting composites [22–24].Their synthesis, purification, and uses have become a challenging and intriguing research field in the nanotechnology meadow due to their unusual features [18]. The use of CNTs in biological systems initially caused a few problems, including their inability to dissolve in organic solvents or aqueous solutions, the production of dense and irregular bundles, the short circulation half-life of 3-3.5 h, and their immunogenicity and biocompatibility [25]. However, numerous recent researches have demonstrated that chemically modified and functionalized CNTs are frequently regarded as a somewhat safer nanobiomaterial. Functional group-containing CNTs will interact with additional biomolecules and organic or inorganic matrices more effectively through vander wall interactions, hydrogen bonding, or covalent bonding, improving the performance of products including the CNTs [26].Proteins are preferred for medicinal purposes because they are more suited to the body and include functional groups that permit chemical alterations, giving them a better opportunity to carry a variety of medications. Some of the proteins that have been converted into films, fibres, nanoparticles, and microparticles for medicinal purposes are collagen, silk, and bovine serum albumin (BSA) [27]. Because the exceptional inherent qualities of individual CNTs do not translate well into their macroscopic forms (e.g., powder, aligned stacks, films/papers, etc.), CNTs cannot be used in bulk (i.e., as powder, aligned stacks, films/papers, etc.). Because of this, the main uses for CNTs entail strategically combining them with other materials to create alloys, mixes, composites, or hybrid materials. In particular, the concept of creating CNTs/polymer nanocomposites [28, 29] by incorporating CNTs as filler within various polymer-based matrices (e.g. conservative polymers like thermoplastics, thermo sets, or elastomer as well as conjugated polymers) has revolutionized materials science and technology. Recent research has focused on the synthesis, purification, functionalization, characteristics, advantages, applications, and most recent developments related to the use of CNTs for drug administration.

History

In the Soviet journal of physical chemistry, Radushkevich and Lukyanovich published in 1952, vivid images of carbon tubes made to a diameter of 50 nanometers [30]. Using a vapor-growth process, hollow carbon fibres with nanometer-scale widths were clearly demonstrated in a 1976 work by Oberlin, Endo, and Koyama [31]. In addition, John Abrahamson presented evidence of carbon nanotubes in 1979 at Penn State University's 14th Biennial Conference on Carbon. The conference article defined carbon nanotubes as carbon fibres produced during arc discharge on carbon anodes [32].The results of the chemical and structural characterization of carbon nanoparticles produced by thermocatalytical disproportionation of CO were published in 1981 by a group of Soviet scientists. The scientists suggested that their carbon multi-layer tubular crystals were formed by rolling graphene layers into cylinders using TEM imaging and XRD patterns [33]. A U.S. patent for the assembly of cylindrical distinct carbon fibrils with a relentless diameter between approximately 3.5 and about 70 nanometers, length 102 times the diameter, an outer region of multiple essentially continuous layers of ordered carbon atoms, and a distinct inner core was granted to Howard G. Tennent of hyperion chemical change in 1987 [34]. A significant percentage of scholarly and popular literature credits Sumio Iijima of the Nippon Electric Company with the invention of hollow, nanometer-sized tubes made of graphitic carbon in 1991. The source of carbon nanotubes was explained in an editorial by Marc Monthioux and Vladimir L. Kuznets published in the journal carbon in 2006 [35].

Structure of CNTs

CNTs are materials composed of thin sheets of benzene ring carbons that have been rolled up into a seamless cylinder. They are frequently capped on at least one end by a spherical fullerene structure. These chemically stable, light-weight, and highly heat-conducting cylinders are among the strongest materials now in use [36]. Researchers from almost every branch of science have been astounded by the amazing physical features of CNTs, which have given them access to a brand-new, very effective instrument. CNTs are hollow carbon structures with one or more walls, a nanometer-sized diameter, and an excessively long length in comparison. As in graphite, every atom in carbon nanotubes is connected to three of its neighbors by a sp2 bond. Therefore, the tubes can be thought of as rolled-up graphene sheets (graphene is an individual graphite layer). The molecules' particular strength comes from a bonding structure that is stronger than the sp3 bonds found in diamond. Under the weight of the air, nanotubes will combine and trade some sp2 bonds for sp3 bonds, opening the possibility of creating robust, limitless-length lines by aggressive nanotube linking [37, 38]. CNTs are being thoroughly researched for their potential use in cutting-edge electrical production as well as in the pharmaceutical industry for the treatment of a wide range of ailments [39].

Types of CNTs

According to the number of tubes present within the CNTs, CNTs are sometimes categorized into three types. Below is a portrayal of these.

Single-walled CNTs

A single graphene sheet with a diameter of 1-2 nm is used to create single-walled CNTs (SWCNTs) (Fig. 1). Depending on your preparation methods, the length will change.

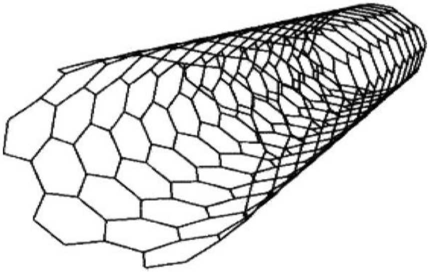

Fig.1 Single-walled carbon nanotubes, surface and internal view, reprinted from ***Saether et al*** [40]

Double-walled CNTs

These nanotubes are produced using two concentric carbon nanotubes, with the outer tube encasing the inner tube as illustrated in Figure 2.

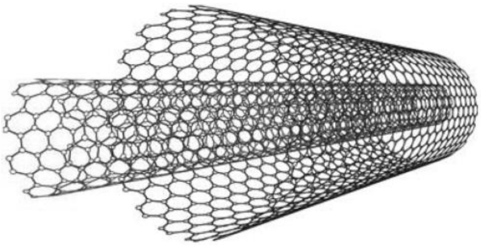

Fig. 2 Double-walled carbon nanotubes, reprinted from ***Pichler*** [41]

Multi-walled CNTs

MWNTs are made of rolled-up layers of graphene with diameters ranging from 2 to 50 nm, depending on the quantity of tubes. The inter-layer spacing in these tubes is roughly 0.34 nm [42].

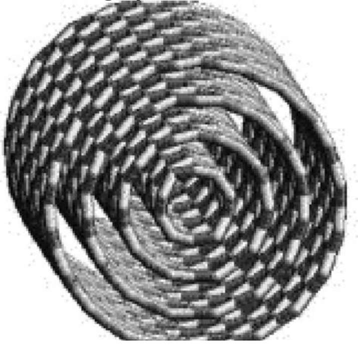

Fig. 3 Multi-walled carbon nanotubes, reprinted from ***Dresselhaus et al*** [43]

Types on the basis of chirality

The chirality of CNTs is a crucial component in determining their electrical characteristics. There are three different forms of CNTs based on chirality: chiral, armchair, and zigzag [44]. Figure 4 depicts these three categories. The main distinctions between SWCNTs and MWCNTs are compared in Table 1. The optical features, thermo physical parameters, and photo-thermal conversion of CNTs are all impacted by their morphologies [45].

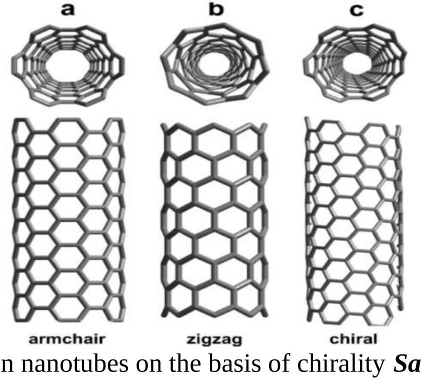

Fig. 4 Different types of carbon nanotubes on the basis of chirality ***Sarangdevot and Sonigara***[46]

Table 1 Comparison between SWCNTs and MWCNTs [47].

SWCNTs	MWCNTs
Single graphene layer	Multiple graphene layers
Synthesis requires catalyst	No catalyst is required
Difficult bulk synthesis due to the requirement ofappropriate growth and atmospheric condition.	Easy bulk synthesis
Poor purity	High purity
Greater chances of defects during functionalization	Lesser defect chances but when this occurs, it is hard to recover
Aggregation in the body is less	Aggregation in the body is greater
Easy assessment and characterization	Structure is complicated
More pliable and easily twisted	Twisting is not easy
Characterization and evaluation is easy	It has very complex structure.

Synthesis of CNTs

There are numerous ways to synthesize CNTs and produce the desired CNTs with the desired qualities for a specific application. Typically, the techniques that produce CNTs with fewer structural and chemical faults are preferred. This section provides a quick summary of several CNT synthesis techniques.

Arc-discharge method

Iijima [48] claimed in 1991 that a brand-new species with a tabular shape existed; this species is now known as CNTs. The tubes were created using an arc-discharge evaporation method that was previously employed to synthesize fullerene. The negative end (cathode) of a carbon electrode was used to grow carbon needles with diameters ranging from 4 to 30 nm and lengths of up to 1 mm using direct current (DC) arc-discharge evaporation of carbon in an argon-filled tank (100 torr). Ebbesen and Ajayan [49] speculated that this method may be used to synthesize MWNTs on a massive scale. Two vertical, thin electrodes installed in the chamber's middle make up the arc-discharge assembly.A little particle of iron is carried by a short dip in the bottom electrode (cathode) during the evaporation phase. Running a DC current between the two electrodes at a voltage of 20 V for 200 A can produce an arc discharge. For the synthesis of SWNTs, the use of three components-argon, iron, and alkane series-is essential. Bethune et al [50] employed thin electrodes with drilled holes filled with a mixture of pure powdered metals (Fe, Ni, or Co) and graphite as anodes in the arc-discharge synthesis of nanotubes. The electrodes were vaporized in a He environment at 100–500 Torr at a relatively modest current of 95–105 A. Journet et al. [51] created enormous amounts of CNTs using this technique.The arc was produced in a reactor with two graphite electrodes and helium gas (660 mbar).

Laser ablation

Thess et al [52] reduced high yields (>70%) of CNTs in 1996 by suggesting that graphite rods with small quantities of Ni and Co be laser-ablated at 1,200°C. The graphite target is blasted with laser light during this process. The tube continues to expand until too many catalyst atoms gather at the nanotubes end. The huge particles either separate or get too heavily covered with carbon, which taints the catalysis. This makes it possible for the tube to end with a catalyst particle or a fullerene-like tip.

Chemical vapor deposition

The conclusion of each large-scale manufacturing and ordered synthesis are the two key concerns that still exist in the aforementioned artificial approaches [53]. However, a CVD for the synthesis of carbon nanotubes was discovered in 1996 [54,55]. This method is capable of producing many nanotubes and dominating the expansion direction on the substrate [54]. In this process, the reaction chamber is filled with a mixture of hydrocarbon gas, acetylene, methane, or ethylene. In the course of the process, the hydrocarbon decomposes at temperatures between 700°C and 900°C under air pressure to form nanotubes on the substrate [55]. This system offers two key benefits. The catalyst is coated across the substrate, which enables CNTs to adopt well-organized patterns, and the nanotubes are produced at a much lower temperature but with inferior quality.

Vapor-phase growth

This is a tailored type of CVD that is relatively recent. The main characteristic is that the CNTs are synthesized in the chamber without a substrate directly from the reaction gas and catalytic metal [56]. The reaction chamber contains two furnaces. Ferrocene is the catalyst in this situation. The first furnace keeps the vaporization of catalytic carbon at a relatively low temperature. Here, tiny catalytic particles are created, which, once they enter the second furnace and are exposed to the rotting carbons there via diffusion, regenerate into CNTs wherever they are.

Flame synthesis technique

The flame synthesis method is another method for producing CNTs. Hydrocarbon flames are used in this approach. These flames aid in the beginning and development of CNTs. In the post-flame region, gases such as CO, CH4, C2H2, C2H4, and C2H6 are abundant sources of carbon. The process is exothermic, and endothermic carbon deposition reactions are supported by chemical energy released as heat in the flame throughout the reaction. In order to create reaction sites for the deposition of solid black carbon, catalysts are also required. CNTs develop in a way similar to CVD. Large volumes of CNTs can be obtained commercially if the right catalyst, flame, and reaction conditions are offered [57].

Saline solution technique

A stainless steel mesh or carbon paper is used as the substrate in the saline technique for the assembly of CNTs. This substrate is then immersed in a different solution containing a metal catalyst, ideally Co:Ni, in a very 1:1 quantitative relationship. The substrate is heated by an electrical current. CNTs supported on the conductive substrate are produced as a result of a reaction between the gas and catalyst [58].

Recent trends within the synthesis of CNTs

MWNTs have recently been created via a combined nebulized spray transmutation method. The main component of this approach, a nebulized spray, is produced by a specialized, silent dispenser. Through the use of this technique, aligned bundles of MWNTs with generally regular diameters are produced. Ferrocene (the catalyst) and ethyl alcohol (the solvent and carbon source) are sprayed into a hollow chamber using an inaudible nebulizer with an argon flow of 1 L/min at a predetermined temperature of 800°C. Ethanol is utilized as a solvent and a carbon source because it is inexpensive, non-polluting, and produces harmless byproducts (like CO) and is easy to handle. MWNTs frequently form large surface growths.Because the reactants are continuously delivered into the chamber, using a nebulized spray has the advantage of being easy to scale up to an industrial-scale technique [59].

Purification of CNTS

In excessive amounts of impurities such metal ions, amorphous carbon, and multishell can occasionally be found in nanotubes. Purification of nanotubes involves a variety of processes [60].

Air oxidation

The purity of carbon nanotubes is lower than average; it typically ranges between 5 and 10%. Purification is therefore necessary before attaching drugs to CNTs. Reducing the amount of amorphous carbon and metal catalyst particles is made easier by air oxidation (Ni, Y). Beat 673 k for 40 minutes is shown to be the best oxidation condition.

Acid refluxing

The amount of metal particles and amorphous carbon can be effectively reduced by refluxing the sample in strong acid. Hydrochloric acid (HCl), nitric acid (HNO3), and sulfuric acid (H2SO4) were all completely different acids that were utilized, but HCl was known to be the best refluxing acid.

Surfactant aided sonication, filtration and annealing

The CNTs were purer after acid refluxing, but the tubes were entangled, holding most of the contaminants, such as carbon particles and catalyst particles, which were difficult to remove using filtration. So, surfactant-assisted sonication was used. Because CNTs took the longest to settle down after using ethanol (or methanol) as the organic solvent, suggesting an even suspension condition was obtained, sodium dodecyl benzene sulphonate (SDBS) power-assisted sonication was the most often used method. The sample was then treated at 1273 k in N2 for 4 hours after being filtered with an ultra filtration machine. The CNT structures can be optimized using annealing. It was found that CNTs can be effectively untangled using surfactant-assisted sonication, which releases the particle contaminants trapped inside the trap. Additionally, a multi-step purification method can be used to clean nanotubes.

Properties of carbon nanotubes

Electrical properties

CNTs can be either metallic or semiconducting in terms of their electrical performance, depending on their chirality and diameter [61–64]. A CNT will be metallic in terms of the chiral index if $|n-m| = 3q$; otherwise, it will be semiconducting [65]. The electrical current density that metallic nanotubes can withstand is 4 ×109 A/cm2, which is more than 1000 times more than that of metals like copper [66]. Only the tube axis experiences electron proliferation because of the tube's nanoscale cross-section. As a result, one-dimensional conductor is a common term used to describe carbon nanotubes. A single-wall carbon nanotubes maximum electrical conductance is 2G0, where $G0 = 2e^2/h$ is the conductance of one ballistic quantum channel [67].

Thermal properties

Ballistic conduction is a feature that all nanotubes are predicted to exhibit, making them very good thermal conductors along the tube axis, but excellent insulators crosswise to the tube axis [68–71]. At room temperature, a SWCNT has been demonstrated to have a thermal conductivity along its axis of roughly 3500 $Wm^{-1} K^{-1}$ [72]. This figure is over ten times greater than copper's thermal conductivity, which is 385 $Wm^{-1} K^{-1}$, a metal widely renowned for its strong thermal conductivity. A SWCNT has a thermal conductivity in the radial direction at room temperature of approximately 1.52 $W/m/K^2$, which is quite similar to soil's thermal conductivity. According to estimates, CNTs can withstand temperatures of up to 2800°C in vacuum and 750°C or so in air [61].

Mechanical properties

In terms of tensile strength and elastic modulus, CNTs are the stiffest and strongest materials that have been found to date [61, 62, 73-75]. The covalent sp2 connections that have formed between the individual carbon atoms are the primary cause of this strength. CNTs have proven to be incredibly robust in the axial direction. Tensile strength of 11–63 GPa and a Young's modulus in the order of 270–950 GPa were attained [76]. As an alternative, it was confirmed that they are highly squashy when viewed from the radial angle. Even the van der Waals forces can deform two nearby nanotubes, according to the first observation of radial elasticity made using a transmission electron microscope [77]. Later, tapping/contact mode atomic force microscopy was also used to SWCNTs [78] and nanoindentations with an atomic force microscope were used by numerous groups to quantitatively evaluate the radial elasticity of MWCNTs [68, 79]. The findings demonstrate that MWCNTs are significantly malleable in the radial direction despite their axial rigidity and strength under tensile pressure.

Magnetic properties

The majority of synthetic CNTs (both SWCNTs and MWCNTs) are known to have magnetic properties, which can be attributed to the presence of entrapped catalyst nanoparticles in their inner cavity, despite the fact that pure CNTs are not magnetic by nature. Such catalytic particles are produced either in situ as CNTs develop. SWCNTs often possess a higher level of catalytic residues and a greater magnetic property than MWCNTs. As the magnetism is caused by the metallic impurities, CNTs have a tendency to lose their magnetic properties when subjected to rigorous processing, such as acidic functionalization [62, 80] or high-temperature annealing [81]. However, the hysteresis loop (i.e., nonzero corecivity and retentively values) seen in the CNTs indicates that they exhibit ferromagnetic behavior [82].The electron paramagnetic resonance (EPR) spectra, which demonstrate the presence of a large density of delocalized electrons and correlate to g values of 2.1365 and 2.2132 for the first and second peaks, respectively, provide additional evidence for the ferromagnetic nature of CNTs. The achieved g values are close to those of ferromagnetic textiles' inherent g values. The inclusion of an iron catalyst inside CNTs has been hypothesized to aid in manipulating their magnetic properties, such as forming magnetic alignment of CNTs in composites [61, 83] or for targeted drug administration [82]. Additionally, the magnetic characteristics aid in the absorption of electromagnetic energy and improve the effectiveness of the overall microwave shielding [84].

Optical activity

Theoretical studies have revealed that when chiral carbon nanotubes grow larger, their optical activity vanishes. It follows that other physical attributes will also be affected by these parameters. Utilizing optical activity may result in optical devices in which CNTs are essential [85].

Surface properties/wettability characteristics

Graphitic cylindrical walls made of carbon atoms gave rise to pure CNTs. As a result of their non-polar nature, CNT surfaces, particularly MWCNT surfaces, exhibit a strong affinity for non-polar substances such as hydrocarbons, paraffin's, oils, and organic solvents. The intrinsic hydrophobicity of CNTs, along with their relatively high specific surface area, makes them useful for water purification applications, such as the separation of non-polar contaminants like oils, solvents, or potentially organic colors. CNTs are difficult to spread in water and in organic media due to their chemical immobility, and they produce a strong resistance to wetting. For a very long period, different fullerenes' chemistry was traditionally measured to be very bad. Compositing such inert nanotube with other materials, which is essential for many device applications, presents further challenges. For artificial chemists and materials scientists, an acceptable functionalization of nanotubes (i.e., the attachment of "chemical functions") is a method for getting through these obstacles.

Characterization techniques for CNTs

In addition to confirming CNT uniformity and thermal stability, thermo gravimetric analysis is used to quantitatively confirm the amount of carbon and non-carbon components in bulk CNT samples. This method of evaluating CNT quality is frequently nonselective since it cannot tell CNTs from metallic contaminants present in the sample. The methods that are utilized the most frequently are nuclear magnetic resonance, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, and Raman spectroscopy (NMR). IR spectroscopy, Raman spectroscopy, and NMR have all been used to confirm the presence of functional groups on CNTs, whilst TEM, SEM, and AFM are mostly employed to qualitatively establish the overall morphology of CNTs. When combined with other approaches, each strategy has advantages [86].

Solubility and functionalization of CNTs

The largest barrier to medicinal uses of CNTs is their poor water solubility, and over the past 20 years, a wide range of studies have concentrated on finding solutions to this problem [87]. The biocompatibility of CNTs and their therapeutic administration may need their solubility in aqueous media and physiological settings. Therefore, having uniform and stable CNTs dispersions in water media is essential [87]. For this purpose, recent advances in CNT functionalization and/or chemical modification have made it possible to solubilized and dissolve CNTs in water. It has been demonstrated that this potential results in CNTs being simple to manipulate and process in physiological contexts. Recent experiments on the conjugation of biological and bioactive species, such as proteins, carbohydrates, and nucleic acids, with carbon nanotubes [88, 89], are also significant. It is crucial for their controlled dispersion that CNTs be functionalized chemically using the right surfactants and dispersants to increase their solubility. In addition, functionalization results in the conjugation of bioactive substances to CNTs, which may serve as a carrier for drugs, antigens, and gene delivery [90–92]. Either the side walls or the oxidatively expanded tips of CNTs can be functionalized [93]. The tips are reactive and sensible, suggesting the structure of a fullerene hemisphere. The degree of curvature of the sidewalls, which are roughly viewed as curved graphite, depends on the tube's diameter. However, the side walls' reaction time is considerably slower than the tips' [94]. Therapeutic drugs can be used to further modify all new functional groups, in addition to amines and carboxylates, to create CNTs conjugates that have some level of pharmacological action [94]. Functionalization alter SWNTs' structure and electrical characteristics, but they also make them more soluble and process able [95, 96].

Noncovalent functionalization of CNTs

The following qualities should be present in a flawless noncovalent functionalization coating on CNTs for biological applications.

- The covering molecules must be harmless and biocompatible.
- The coating's stability needs to be high enough to withstand separation from the CNTs' surface in biological fluids, particularly in serum with high salt and protein concentrations.
- To produce multiple functional CNTs conjugates for various biological applications, functional groups of the coated molecules should be available for bioconjugation with antibodies or other molecules [97].

Noncovalent functionalization takes advantage of advantageous interactions between the CNTs surface and the hydrophobic domain of an ampiphillic molecule since the noncovalent dispersion of CNTs in solution preserves their aromatic structure and corresponding physicochemical properties [97, 98]. Simple dispersion techniques can be carried out using filtering, centrifugation, and ultrasonication. Surfactants are utilized among the molecules for CNT dispersion since they are readily available and affordable. The dispersion technique is effective with polymers and biopolymers (nucleic acids and peptides) [98]. The stability of CNT suspensions was greatly improved by noncovalent alteration of the CNT surface [99]. The type, concentration, length, and presence of inorganic salts in the solution all contributed to the stability of the suspension of non covalently functionalized CNTs [100-102].

Polymers

Even with a modest degree of functionalization, functionalization of SWNTs with polymers employing long polymer chains was used to dissolve the CNTs in the proper solvents [95]. CNTs had been functionalized using a variety of synthetic polymers, including polyvinyl pyrrolidone, poly (ethylene glycol), and natural organic matter [99]. Recently, Chen et al. discovered that SWNTs may be effectively dispersed in aqueous solution using the poly (ethylene glycol) terminated malachite green derivative PEG-MG. The π- π stacking, van der Waals interaction and hydrophobic interactions with PEG-MG were used as the foundation for the dispersion properties [103].

Biopolymers

Biomolecules like DNA, proteins, amino acids, lipids, and carbohydrates (such starch and cyclodextrines) have all been evaluated as CNT dispersants [96, 99]. It is common practice to noncovalently immobilize DNA on SWNT surfaces to avoid DNA denaturation and to enhance DNA release from the gene delivery scaffold inside the cell [104]. According to Pantarotto et al research's [105], an ammonium-functionalized nanotube can connect electro statically with plasmidDNA. Streptavidin, ferritin, and biotinyl-3,6-dioxaoctanediamine have all been immobilized using functionalized SWNTs with 1-pyrene butanoic acid succinimidyl ester. The succinimidyl ester group interacts with amine groups through lysine residues in proteins to produce amide bonds, while the pyrenel group permanently binds to the hydrophobic surfaces of SWNTs by π-π contact [106]. A biosensor for the early detection of breast cancer was developed using functionalized SWNTs with antibodies that are specific to cell surface receptors (such as Her2) of breast cancer cells [106]. Ciofaniet al. had previously described non-covalent dispersion based on the self-assembling of a lipidic layer surrounding CNTs [96]. They demonstrated that lipid functionalized CNTs had good aqueous environment stability due to their amphiphilic properties. They utilized cationic and anionic lipids, both of which shown high CNT concentrations, excellent cytocompatibility, and dispersion stability. Furthermore, it was demonstrated that the lipidic layer surrounding CNTs may be functionalized very effectively, facilitating the attachment of particular functional groups to nanotubes without chemically altering the surfaces of the nanotubes themselves [96].

Surfactant

Richard and his colleagues originally reported noncovalent functionalization of CNTs via chemical adsorption of several anionic surfactants, who claimed that the negative charge created by the surfactant adsorbed on the nanotubes surface prevents their aggregation and induces stable suspensions in water. Amphiphilic Gd3+ chelates later performed the first example of noncovalent functionalization of the outer surface of carbon nanotubes and their impact on water proton relaxation in vitro and in vivo [107, 108]. Due to the system's compatibility with water, toxicity issues are avoided. The Gd3+ ions are complexed to DTPA, a powerful chelator, and are present on the whole surface of the nanotubes (and not only around side-wall defects), making it readily tunable and immediately accessible to water molecules [107]. Other surfactants employed as noncovalent functionalizes include sodium dodecylsulfate (SDS), triton X-100, and triton x-405 [97, 99].

Covalent functionalization of CNTs

Covalent polymer-SWNT conjugates can be made using one of two techniques: either grafting from procedures that use initiator-functionalized SWNTs or grafting from radical coupling methods [104, 109]. The second approach has an advantage since it may be used to covalently attach biocompatible compounds to the surface of SWNTs with high grafting densities, such as carbohydrates and phosphorylcholine. However, since these functionalized CNTs were made via the ATRP process, concerns have been raised about the toxicity of the leftover copper [104]. By altering the carboxylic acid groups on SWNTs or by directly adding chemicals to the side walls of SWNTs, covalent functionalization can be understood. Due to its versatility in reactions and ease of formation on CNTs through oxidizing treatment, the carboxylic acid group is frequently the optimum option [91, 95]. Nitric acid oxidation caused carboxylic acid groups to develop at the SWNT defect sites, and etherification and amidation processes were employed to connect lengthy alkyl chains, polymers, and sugars [95]. Fluorine, aryl radicals, aryl cations, hydrogen, nitrenes, carbenes, radicals, styrene, poly styrene, and 1, 3-dipoles are among the reagents applied to the side walls. SWNT bundle dispersion and dissolution are greatly facilitated by polymer covalent connection [95]. A change from sp2 to sp3 in hybridization and a potential partial loss of conjugation are caused by the covalent or irreversible van der Waals bonds with the CNTs, which have an impact on the electron-acceptor and/or electron transport characteristics [91, 110]. An important method for the covalent attachment of medicines is the covalent functionalization of CNTs. Amphotericin B, which was covalently linked to MWNTs and SWNTs with ammonium functionalization, is the most effective antibiotic for treating long-lasting fungal infections [110].

Functionalization of CNTs using click chemistry

The Huisgenet al. (3+2) dipolar cycloaddition process developed the click chemistry, which has recently gained popularity as the most effective method for surface modification and functionalization of nanomaterials [111]. Recent years have seen the application of a 1,2,3-triazole-forming Huisgen (3+2) dipolar cyclo addition reaction between terminal alkynes and azides, which is catalysed by Cu(I) [112]. Small molecules, dendrimers, dendronized polymers, and biologically generated macromolecular structures can all be synthesized using this procedure [113, 114]. By briefly adding azide and alkyne groups to organic and polymer molecules, click chemistry promotes. Major advantages of click chemistry are its tolerance of the presence of other functional groups, a quick reaction time, high yield, high purity, and region specificity, as well as its adaptability for usage in aqueous settings [115]. According to reports, click chemistry is a modular mechanism for adding different chemicals to the surface of CNTs [116, 117]. This technique makes it possible to add beneficial chemicals to CNTs, thus expanding the range of possibilities for them, from nanoelectronics to nanobiotechnology. Many biomolecules, including -cyclodextrin, amino acids, and a variety of polymers, including 4-(2-trimethylsilyl)ethynylaniline, poly (2-azidoethyl methacrylate), polymer containing abundant azide groups, and polymer containing abundant alkyne groups, have been used to functionalize CNTs through click chemistry [116–118].

CNT Nanocomposites

It has been demonstrated that CNT composites with nanoparticles, polymers, dendrimers, protein enzymes, and DNA can enhance their mechanical, dispersion, and drug-loading capabilities. Numerous researches claim that immobilizing these assemblies on the CNT's surface or creating their composites reduces their toxicity. The characteristics of CNTs can be changed for a variety of applications by linking them with external fields, chemicals, and nanoparticles [25]. Enzyme-protein CNT composites have been demonstrated to be possible electrode systems in biosensors. Strong binding capabilities of MWNTs make them perfect for creating biocompatible composites. Although pure MWNTs are difficult to dissolve in organic solvents, composites made of different polymers have demonstrated good dispersibility. It is thought that these polymeric hybrid materials may prove useful in the pharmaceutical industry as novel biomaterials composites with potential uses in drug delivery, dental, and orthopedics materials. Applications for magnetic CNT nanocomposites in industry (such as data storage and magnetic recording) as well as medicine (such as targeted medication delivery and magnetic resonance imaging) are possible [119,120]. Iron-filled Fe-MWNTs and water-soluble hybrids of MWNTs and gold nanoparticles have both been reported to be created [25].

Toxicity of CNTs and its control

The use of CNTs in industry has been carefully explored because of their exceptional physical and chemical capabilities, but there are some drawbacks, particularly those linked to their toxicity. The human pulmonary system is one of the main exposure routes for CNTs, which can have harmful consequences on human health [121]. There is currently a great deal of anxiety among scholars about this. Therefore, specific actions are necessary to reduce the toxicity of CNTs. Inflammation and oxidative stresses are also brought on by excessive exposure to CNT dust [122]. The length and rigidity of the nanotubes have a significant impact on the pro-inflammatory action of CNTs, according to a recent study [123]. To determine the possible impact of different physiochemical features, however, more research is needed [124].It is reasonable to assume that adding CNTs to polymeric materials will alter the surface properties of CNTs, potentially modifying their toxicity without affecting their precise properties or potential for use in future applications. This is because the pro-inflammatory effects of spherical nanoparticles are influenced by their surface characteristics [125]. Recent research has examined the protective effects of the suitable solute ectoine against CNT-induced respiratory or gen inflammation [125]. A strategy based on the combination of inherently safer nanomaterials, however, appears to have far more potential. Such methods are crucial for the further advancement and secure application of CNTs, both for professional and everyday users. According to a number of research on the toxicity of CNTs, surface modifications are essential to reduce CNT toxicity [126–127]. Because it allows for adjustment of the external surface setting of CNTs without changing their intrinsic structure or fundamental qualities, a coating may be an excellent tool.

Application of CNTs:

The physicochemical characteristics of CNTs are incredibly intriguing, including their ordered structure with high feature ratio, ultra-light weight, great mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior, and high surface area. These traits are combined to create CNTs, which are unique materials with a wide range of possible applications.

CNTs in medical application

According to a relatively recent report, there would be almost 180 billion US dollars in economic prospects for nanostructured materials in science and medicine in 2015.

CNTS as carriers for medicines, genes and proteins

Chemotherapy suffers greatly from the development of multidrug resistance, and novel types of transporters are actively looked for to overcome it [128]. Multi-walled carbon nanotubes (MWCNTs) that have been PEGylated with poly(ethylene glycol) are being investigated as a medication delivery system to combat multidrug resistance. Folic acid (FA) receptors are known to be over expressed in cancer cells, and various research teams have created nanocarriers with modified exteriors to which FA derivatives may be attached. Furthermore, compared to spherical nanocarriers, nonspherical nanocarriers (such as CNTs) are said to be kept in the lymph nodes for longer periods of time (e.g., liposomes). Numerous researchers have demonstrated that CNTs can be utilized to target lymph node tumors. In other investigations, folic acid-functionalized MWCNTs have been incorporated with magnetic nanoparticles containing the anticancer drug cisplatin. The nanotubes were dragged to the lymph nodes using an external magnet where the medicine released over many days and inhibited the growth of the tumour. Because of their hydrophobicity and vast molecular size, macromolecules (such as genes) have a particularly difficult time entering a target cell and expressing themselves. As a result, the employment of viral or nonviral vectors to hold the gene and internalize it into the cell is crucial. Although nonviral vectors are less effective than viral vectors and have a shorter lifespan, they are significantly less dangerous.Confocal microscopy and flow cytometry have demonstrated that protein and DNA coupled to SWCNTs exhibit substantially better fluorescence activity than the naked macromolecules, indicating that CNTs are suitable vectors for gene and protein delivery. Carbon nanotube spearing is a method of gene transfer developed by Cai and colleagues. On nickel-embedded CNTs, plasmid DNA with a fluorescent protein was immobilized. A magnetic field was used to propel the formulation into Bal 17 B lymphoma cells, resulting in high transfection in the target cells. Functionalized SWCNTs are intended to transport siRNA into K562 cells, where it will subsequently impede the assembly of cyclinA (2) and be used to treat chronic myelogenous leukaemia [129]. It has been discovered that utilizing siRNA-CNTs to reduce cyclinA(2) expression will encourage apoptosis in the targeted tumour. A protein called streptavidin possesses anticancer properties, but because of its extraordinarily high molecular weight (60,000 KDa or thereabouts), it cannot enter cells. The protein was taken up by model cancer cells through adsorption-mediated endocytosis after being conjugated with streptavidin and SWNTs-biotin.

Photothermal therapy of cancer using CNTS

CNTs are prepared to heat up as a result of absorbing light in the near infrared (NIR) range [130]. This unique characteristic of CNTs has been used to kill cancer cells through thermal impacts. In the near infrared (NIR) ranges (NIR I: 700-900 nm, NIR II: 1-1.4 µm), CNTs exhibit strong optical absorption. The penetration depth of 1.6 mm of NIR optical radiation into living tissue. By absorbing light, CNTs produce heat and encourage the thermal obliteration of cancer cells that have sufficient CNT concentrations. Targeted CNTs are prepared via the covalent attachment of tumor-specific ligands to the CNTs, preventing damage to normal tissues. Under physiological settings, the conjugated CNTs demonstrated reasonable stability and produced an incredibly accurate photo-thermal death of the targeted cells. According to antenna theory, optical coupling of light with CNTs peaks whenever their length exceeds 50% of the wave length of the incident light beam [131]. The antenna properties of MWNTs may be improved by intentionally creating surface flaws in the nanotubes' structure. Such artificial flaws or dopants can disperse currents as they travel and also increase the nanotube's heating.

Solid phase extraction of the drugs

CNTs have also been used as SPE sorbents to extract medications such as antibiotics, anxiolytics, anti-inflammatories, and antidepressants [132]. According to the literature review, small amounts of CNTs (less than those of conservative SPE cartridges) will be utilized as SPE materials, and as a result, they will contribute significantly to the shortening of the extraction process. These materials can sometimes cost more than traditional SPE cartridges, but several studies have shown that extremely affordable CNTs can achieve appropriate SPE performance, therefore they will also be a better economic choice. Commercial CNTs-SPE cartridges are quite likely to become available in the near future, hence bigger quantities of CNTs should be produced.

Preparation of biocatalysts, biosensors and biofuel cells

The manufacturing of biosensors, biofuel cells, and the creation of biocatalysts using enzyme immobilizations on carbon nanotubes are rapidly emerging as new research fields [133]. Enzymes have typically been investigated while mounted on a solid platform to increase enzyme stability. Because they offer the ideal features for balancing the crucial elements that confirm the effectiveness of biocatalysts, such as surface area, mass transfer resistance, and effective enzyme loading, nanomaterials serve as excellent supporting materials for enzyme immobilization. Enzymes will be less denatured when immobilized using non-covalent methods, and CNTs' intrinsic electronic structure and characteristics will also be conserved.The regulated immobilization of enzymes on CNTs has received more focus recently. To conclude, particular groups, such as chemical, polymeric, and biological compounds, are added to CNTs. Enzymes can be selectively and specifically bound to CNTs through the functional groups. Studying the interactions between connecting molecules and enzymes, as well as how they affect the structure of the enzymes and how they adhere to CNTs, is also crucial.

Detection of toxic organ phosphoric compounds

Organ phosphorus substances harm the central nervous system (CNS) by preventing the enzyme acetylcholinesterase from acting on cholinergic neurotransmitters [134]. When immobilizing enzymes, carbon nanotubes can facilitate the electron transfer reaction by acting as the electrode material. On the surface of nanotubes, acetylcholine esterase is immobilized. Thiocholine ester hydrolysis is catalyzed by acetylcholine to yield thiocholine. Electrochemical methods will be used to find this thiocholine hydrolysis. When acetylcholinesterase interacts with organ phosphoric chemicals, its catalytic activity is reduced, and at the same time, the oxidation of thiocholine is blocked. Amperometric analysis utilizing CNT electrodes can be used to detect these effects.

Detection of chemical substances

Due to their high specific surface area and nanoscale geometries, which provide a significant number of sites for chemical reactions in gaseous form, CNTs demonstrate outstanding surface assimilation capabilities [135–137]. After the CNTs' electrical qualities, molecules adsorb on their surface, enabling the CNTs to function as a gas sensor. Researchers created a gas sensor based on SWCNTs that responds swiftly to gaseous molecules by changing its electrical conductance (e.g. NO2, NH3). They used a composite film of SWCNTs mash doped with alkane thiol monolayer protected gold cluster to accomplish ultrahigh sensitivity detection of NO2 gas (MPC).

Carbon nanotubes as a nanocomposite material

For the development of medical devices, CNTs will produce nanocomposites materials [138,139]. A nanocomposites material made of pure carbon nanotubes and nylon-12 could be used to create micro catheters for arterial cannulation. When compared to nylononyl micro catheters, this CNT-based device had a higher biocompatibility, less cellular infiltration, and no evidence of an inflammatory response.

Carbon nanotubes in tissue engineering

By increasing cellular performance, seeing it, and tracking and identifying cells, carbon nanotubes are frequently used in tissue engineering [140,141]. As tissue engineering develops, new instruments for more in-depth analysis of manufactured tissues as well as novel biomaterials to guide tissue growth are needed. Carbon nanotubes are also a crucial component of tissue engineering materials for better cell tracking, microenvironment sensing, transfection agent delivery, and scaffolding. Incorporating carbon nanotubes into scaffolds could provide structural reinforcement and endow the scaffolds with unique features like electrical conductivity, which could promote directed cell development. By chemically functionalizing the surface, carbon nanotube-related potential cytotoxic effects are further lessened [142-146].

Detection of toxic proteins, micro organisms and alkylating agent containing sulphur and nitrogen

The CNTs are frequently utilized as a measurement platform for various hazardous proteins that can immobilize on the CNTs by altering electrical signals [147]. Checking the interactions of proteins with antibodies on a CNTs substrate is frequently done using a scanning electron microscope (SEM) and electrochemical chemiluminescence (ECL). Finally, the detection is frequently accomplished by fusing these sensor tips to a single conditioning and processing circuit, measuring electrical signals and conductance, and analyzing the results. This is done in the presence of hazardous proteins. The biological recognition component of alkylating agents (nitrogen mustards, ethylenimes, alkylsulphonates, triazenes, piprazenes, and nitrosureas) may be identified by DNA sensing [148-152].

Adsorption and photo-catalytic performance

CNTs can be widely used in the processes of catalysis, adsorption, and photo catalysis [153, 154]. These qualities are put to use in the air and water pollution remediation processes. This sparked the creation of nanosensors, which have a wide range of uses in drug discovery and manufacturing. Nanocomposites give extra adsorption sites and chemically inert surfaces with large specific surface areas for physical adsorption. TiO2's photo catalytic activity will be improved by the presence of a little amount of CNTs. Rhodamine B, methyl orange, and poly vinyl alcohol are all readily degraded by carbon-coated TiO2 in water when exposed to UV light.

CNTs in lithium-ion batteries

Due to its unique features (low electro negativity and easy electron donation from Li+), Li is one of the best elements for the construction of powerful and light batteries. However, due to Li's strong reactivity, the negative Li electrode reacts quickly, making the metal no longer cost-effective. However, it is possible to introduce Li ions into structures that resemble graphite so that Li+ will move from a graphitic anode to the cathode (usually LiCoO2, LiNiO2, and LiMn2O4). Typically, polyolefin is used to divide the electrodes. Since graphite has a 372mAh/g (LiC6) theoretical capacity for Li storage, the charge and discharge phenomena in these batteries are dependent on the Li+ interval and de-intercalation. Like graphite, lithium ions, which are frequently utilized in some batteries, can be stored in nanotubes. However, because to its tubular form, nanotubes, unlike graphite, are also prepared to hold the Li ions both inside and outside. If all the interstitial sites-including the inner cores and inter-tube channelsare open to Li intercalation, it has been hypothesized that a higher Li capability will also be attained in carbon nanotubes [46].

CNTs in biological imaging

The inherent optical qualities of SWNTs make them useful as optical probes in addition to uses in drug administration and treatment. SWNTs have strong resonance Raman scattering, high optical absorption, and photoluminescence in the near-infrared (NIR) range, all of which are exploited for imaging in biological systems in vitro and in vivo due to their quasi 1-D nature [46].

Other application of carbon nanotubes

- In electronic devices as field-emission sources
- CNTs in supercapacitors and actuators
- Electromagnetic interference (EMI) shielding
- Gas and chemical vapour sensors
- Gas and hydrogen storage
- Scanning probe tips
- Electronic devices using CNTs
- Genetic engineering
- Biomedical applications
- Artificial implants
- Preservative
- Diagnostic tool
- As catalyst
- Supercapacitor electrodes
- Photovoltaics
- Thermo electrics
- Water purification
- CNTs as fillers

Conclusion

This research discussed the structure, synthesis, physico-chemical characteristics, as well as several uses, of CNTs. The laser ablation, arc-discharge technique, CVD, and many more important strategies for the synthesis of CNTs (SWNTs and MWNTs) were briefly covered. It was discovered that CNTs had a singular collection of mechanical, electrical, and thermal capabilities after a review and bestowal of several of the material's well-known qualities. It is apparent that new technologies will emerge in the near future due to the maximum amount of CNTs that can be produced, however the challenge associated with these technologies is the quantity and cost of CNTs. If composite materials are to be created, more nanotubes must be used.In the future, CNTs are likely to be used to create low-cost gas sensors, innovative catalytic supports, nanotube textiles, heat exchangers, three-dimensional composite materials, biological micro filters, and virus inhibitors. Uncertainty over CNT's biocompatibility and toxicity is considered one of the biggest barriers to their widespread deployment for medication and gene delivery. The toxicity of CNT materials is one of the issues that need thorough examination despite the fact that CNTs have the potential to be effective medication delivery systems. The most recent research has demonstrated that the primary factor increasing CNTtoxicity is the presence of unreacted catalysts in CNTs. This suggests that finding appropriate and fresh artificial ways to make CNTs might be the solution to the problem of their toxicity.The second option is to functionalize CNTs because recent studies have shown that they offer improved biocompatibility with little cytotoxicity. In fact, the considerable research in this field is to be expected and may provide a solid foundation for the examination of innovative CNT drug delivery applications for attaining successful therapeutic silencing of a variety of illness indications wherever alternative delivery is interesting or conceivable. It is believed that CNTs play a crucial function as example nanomaterials that can be created for use in clinical settings and serve as archetypical cases in the developing field of nanomedicine. So, in the near future, it is anticipated that there will be active research efforts and innovative, exciting applications of CNTs in biology and medicine.

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