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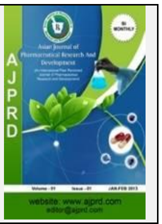

Open Access **Review Article**

Review on Carbon Nanotubes in Drug Therapy

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ABSTRACT

Carbon nanotubes have gained considerable attention as advanced Nano carriers in drug therapy owing to their distinctive structural, physiochemical and biological characteristics. Their exceptionally large surface area, nanoscale size and efficient cellular internationalization facilitate high drug-loading capacity and targeted delivery of diverse therapeutic agent, including small molecules, proteins and nucleic acid. Surface modification of CNTs through covalent or non-covalent functionalization significantly improves their aqueous dispensability, biocompatibility and targeting efficiency, while simultaneously minimizing intrinsic toxicity. CNT-based drug delivery platforms enable controlled and sustained drug release, enhance bioavailability and reduce off-target effects with particular relevance in cancer treatment.

KEY WORDS: Carbon nanotubes, Cancer therapy, Bioavailability, Functionalization, Biocompatibility, Drug loading.

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INTRODUCTION

The primary objective of designing Nanocarrier based drug delivery systems is to improve therapeutic efficacy and minimize the toxicity of active pharmaceutical agent. Traditionally, this goal has been achieved using spherical vesicular Nanocarriers, such as liposomes. In contrast carbon nanotubes (CNTs) are cylindrical nanostructures composed entirely of carbon atoms. Structurally, carbon nanotubes are formed by rolling graphene sheets into seamless tubes, which may be either open ended or capped. They possess a very high aspect ratio, with diameters as small as approximately 1nm and length extending to several micrometers[1,2].

Carbon nanotubes, commonly referred to as bulky tubes are tubular carbon based nanomaterials characterized by an extremely high length- to- diameter ratio which can reach values as high as 132,000,000:1[3].

Carbon nanotubes are key nanotechnology building blocks explored for a drug delivery due to their high cargo-loading capacity and efficient cellular penetration in particularly cancer therapy[4].

Since their discovery in 1991 by Sumio Iijima, carbon nanotubes have attracted extensive interest across numerous fields of science and engineering owing to their exceptional physical and chemical properties. No other materials have demonstrated such extraordinary combination of superior mechanical, thermal, and electronic characteristics. These unique attributes make carbon nanotubes highly suitable not only for a broad range of practical applications[5].But also as an excellent platform for fundamental scientific research[6]. Research has proposed exploiting a high electrical conductivity and large aspect ratio of carbon nanotubes to develop conductive polymer composites with extremely low percolation thresholds[7].

Carbon nanotubes exhibit outstanding mechanical performance, with young`s modulus values ranging from 100 to 1000GPA and tensile strength between 2.5 and 3.5GPa[8]. They typically possess diameters in the range of 1-100nm and length extending up to a several millimeters[9].Carbon nanotubes also have low densities, approximately 1.3g/cm$^3$, and young`s modulus values exceeding those of all conventional carbon fibers, often surpassing 1TPa[10]. Notably, the highest measured tensile strength of an individual carbon nanotube has reached 63GPa [11], highlighting their exceptional mechanical robustness[12].

Two principal approaches are currently employed for the surface modification of carbon nanotubes to improve their dispersion and achieve complete exfoliation of pristine carbon nanotubes. These include covalent functionalization, which involves chemical attachments of functional groups to the CNT side walls or defect sides, and non-covalent functionalization in which functional molecules are associated with CNT surface through non-bonding interactions. Compare to covalent modification, non-covalent functionalization preserves the intrinsic structure and graphene- like structures of CNTs while enabling the incorporation of a wide range of functional moieties. Consequently, CNT functional enhance their processability and significantly influences their physicochemical properties[13, 14, 15].

Early observation of carbon nanotube- like structures date back survival decades. In 1952 Radushkevich and Lukyanovich published transmission electron microscopy images of carbon nanotubes with diameters of approximately 50nm in the Soviet Journal of physical chemistry. Subsequently, in 1976 Oberlin, Endo and Koyama demonstrated the presence of hallow carbon fibers with nanometer scale diameter using a vapor growth method. Further evidence for carbon nanotubes was presented by John Abrahamson at the 14th Biennial conference of carbon held at Penn state university in 1979. In this study, carbon nanotubes were described as carbon fibers formed on carbon anodes during arc discharge experiment[16].

Furthermore, carbon nanotubes exhibit superior electrical and thermal characteristics. It has an electrical conductivity of roughly 103 S/m, a thermal conductivity of almost 1900 W/m (m-K), which is nearly twice that of a diamond, and thermal stability up to 2800^0C in vacuum. These exceptional qualities make carbon nanotubes extremely promising for a wide range of scientific and technological uses[17].

STRUCTURE OF CARBON NANOTUBES (CNTs)

Carbon nanotubes (CNTs) are nanomaterials formed from extremely thin sheets of carbon atoms arranged in hexagonal benzene ring structures. One or both ends of these cylinders are often closed by a hemispherical fullerene cap. CNTs are chemically stable, light weight, and exhibit exceptional thermal conductivity, making them among the strongest materials currently known[18].

The extraordinary physical properties of CNTs have attracted researches across numerous scientific disciplines, as these materials offer highly efficient and novel technological possibilities. Structurally, CNTs are hollow carbon cylinders consisting of one or multiple concentric walls, with diameters in the nanometer range and lengths that are significantly larger in comparison[19].

Similar to graphite, each carbon atom in a CNT is bonded to three neighboring atoms through sp^2hybridized bonds. As a result, CNTs can be considered as graphene sheets that have been rolled into tubular forms, where graphene represents a single layer of graphite. The remarkable mechanical strength of CNTs arises from this bonding arrangement, which is stronger than the sp^3bonds present in diamond[20].

Under external pressure, such as atmospheric compression, carbon nanotubes can merge and partially convert sp^2 bonds into sp^3 bonds. This property provides opportunities for the formation of highly durable, extended-length fibers through controlled nanotube interlinking. Due to these unique characteristics, CNTs are extensively investigated for advanced electronic applications and are gaining significant attention in pharmaceutical research for the treatment of various disease[21].

RATIONALS FOR CARBON NANOTUBES CARRIER SYSTEM

1. High surface area: Carbon nanotubes possess a very large surface area, enabling efficient loading and transport of various therapeutic agents such as drugs, genes and imaging molecules.
2. Controlled drug release: CNTs can be modified to provide controlled and sustained release of loaded drugs, which improves therapeutic outcomes and minimize adverse effects.
3. Targeted drug delivery: Functionalized CNTs can be tailored to selectively target specific cells, tissues, or organs thereby enhancing treatment accuracy and reducing off-target effects.
4. Enhanced solubility: CNT-based carrier systems improve the solubility of poorly water-soluble drugs, facilitating better formulation and bioavailability.
5. Biocompatibility: Proper surface functionalization of CNTs enhances their biocompatibility and lowers the risk of toxic are immune reactions in biological systems.
6. Improved therapeutic efficiency: CNTs protect drugs from degradation, increase their stability, and promote cellular uptake, leading to enhanced therapeutic effectiveness.
7. Versatile drug carrier: CNTs are capable of delivering a wide variety of payloads, including small drug molecules, proteins, nucleic acids, and diagnostic agents.
8. Reduced systemic toxicity: Targeted delivery and controlled release mechanisms limit drug exposure to healthy tissues, thereby reducing overall toxicity[22].

MECHANISM OF CARBON NANOTUBES CARRIER SYSTEM

There are several mechanisms for carbon nanotubes are occur through:

1. Direct penetration through cell membrane

2. Passive uptake

3. Endocytosis: includes
   - Phagocytosis
   - Pinocytosis

Receptors mediate endocytosis these include subtypes; they are

- Caveolin mediated endocytosis
- Clathrin mediated endocytosis
- Clathrin independent endocytosis

PASSIVE UPTAKE MECHANISM: The cellular internationalization of CNTs can occur via a passive pathway or a needle diffusion mechanism across the lipid bilayer of the cell membrane. The high adherence rate and needle-like structure help CNTs overcome these obstacles like structural defect, manufacturing cost, and high toxicity strength and particle dispersion rate.

ENDOCYTOSIS: Endocytosis represents another major pathway for CNT internalization and can be classified into several types, including phagocytosis, pinocytosis (mainly micropinocytosis), clathrin mediated endocytosis, Caveolin-mediated endocytosis, and clathrin/caveolae-independent endocytosis.

Phagocytosis is an intracellular uptake process in which large particles, typically around 1um in size, are engulfed by cells. This mechanism is predominantly observed in specialized immune cells such as macrophages, neutrophils, and monocytes.

Pinocytosis is an ATP-dependent, non-specific endocytic pathway that contributes significantly to the cellular uptake of functionalized carbon nanotubes, particularly particles in the 100-200nm size range. During this process, membrane invagination forms vesicles that internalize CNT-containing extracellular fluid, while large nanotube aggregates are often taken up through micropinocytosis. After entry, vesicles typically traffic through the endo-lysosome-pathway, where acidic conditions may alter the carrier system. Although many CNTs remain lysosome-confined, certain functionalized nanotubes can escape into the cytoplasm and potentially reach other subcellular compartments.

Caveolin mediated endocytosis is a cholesterol-dependent, clathrin-independent uptake pathway in which caveolin-rich membrane invaginations selectively internalize extracellular cargo, supporting signaling and transcytosis in specialized cells. Internalized vesicles traffic to endosomal or caveosome-like compartments, and the pathway can be inhibited by cholesterol depletion while also serving as an entry route for certain viruses.

Endocytosis studies have demonstrated that CNTs with sizes up to approximately 100nm can be internalized through clathrin and caveolin-mediated endocytosis. In contrast, larger CNTs, typically exceeding 300nm, are predominantly taken up via micropinocytosis. While CNTs offer significant advantages as cell-penetrating drug carriers, the limitations and potential disadvantages associated with each uptake mechanism must be carefully evaluated[23].

TYPES OF CARBON NANOTUBES

Carbon nanotubes, which has received enormous global attention from research of various fields over the last few years. CNTs are classified into SWCNTs and MWCNTs, with DWCNTs also recognized; further structural types include arm chair, zigzag and chiral determined by graphene sheet rolled, affecting their unique metallic or semiconducting electrical properties, and can also be categorized based on functionalization like hydroxylate or carboxylate forms[24].

SINGLE WALLED CARBON NANOTUBES (SWCNTs)

Single walled carbon nanotubes represent a significant class of nanotubes materials composed of a single graphene Sheet rolled into a seamless cylindrical hexagonal framework. The individual graphene layer is held together by Vander walls interactions, which impart high flexibility and allow the nanotubes to twist easily[25,26].

SWCNTs have emerged as promising drug delivery vehicle due to their ability to transport a variety of therapeutic agents, including small molecule drug, proteins and nucleic acids. The development of multifunctional SWCNTs based system have been shown to enhance therapeutic efficacy while simultaneously reducing drug-associated toxicity[27].

The solubility characteristics of SWCNTs can be evaluated by dispensing them in surfactant such as polysorbate80, which also aid in assessing their toxicity profile[28], cellular membrane exhibit increased drug-loading capacity, and provide prolonged circulation half-life, making them highly suitable for biomedical applications[29].

PROPERTIES OF SWCNTs:

- A single-walled carbon nanotubes diameter is around 2nm.
- They are also known as a nanowire as they exit in just one dimension.
- A single-walled carbon nanotubes can be used to miniaturized electronics.
- They have a band gap that varies from 0 to 2 electron volts(ev)
- They have conductive properties like that of a semiconductor. Therefore, they show both semi conductive and metallic behavior[30].

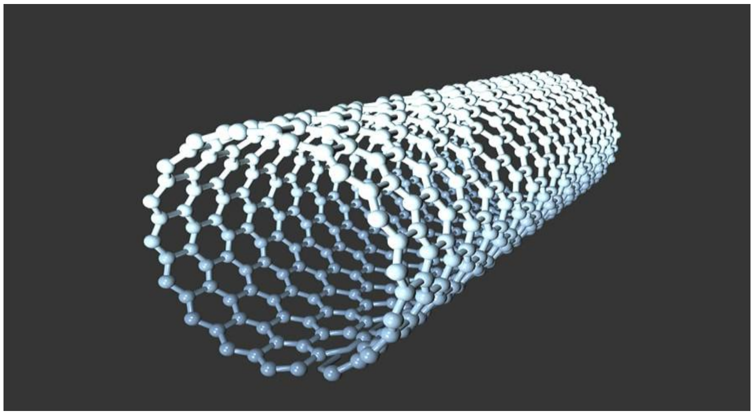


Figure 1: Single walled carbon nanotubes (SWCNTs)

MULTI-WALLED CARBON NANOTUBES (MWCNTs)

Multi-walled carbon nanotubes are made from SWCNTs that generally appear similarly to Russian doll structure. They consist of several rolled graphite layer forming coaxial cylindrical tubes, which results in a large surface area and enhanced drug-loading capacity[31].

MWCNTs can be synthesis in large quantity at relatively low cost. Commonly employed methods for their production include the electric arc discharge technique and chemical vapor deposition (CVD). The sp^2 hybridization present in MWCNTs leads to the formation of delocalized electrons along the nanotubes walls, promoting π-π interactions between adjacent concentric layers. These interactions contribute to structural defects and reduced flexibility of MWCNTs[32,33,34].

PROPERTIES OF MWCNTs:

- The outer diameter of MWCNTs is around 2 to 20 nanometer.
- The inner diameter of MWCNTs is around 1 to 3 nm.
- The length of MWCNTs is around 5 to 6 micrometers[35].

Figure 2: Multi-walled carbon nanotubes (MWCNTs)

PROPERTIES OF CARBON NANOTUBES

Carbon nanotubes CNTs possess a combination of unique chemical, dimensional, optical, electrical, and structural properties that make them highly attractive for applications in drug delivery and bio sensing[36].These characteristics enable CNTs to serve as efficient Nano carriers for therapeutic agents and as sensitive platforms for the non-invasive monitoring of biological parameters, including blood analytes and other physiologically relevant chemical signals[37].

ELECTRICAL AND STRUCTURAL PROPERTIES

The electric behavior of carbon nanotubes strongly depends on their atomic structure and chirality. Based on their (n, m) indices, CNTs may exhibit either metallic or semiconducting properties, a consequence of the symmetry and electronic configuration of graphene. Nanotubes with n=m (armchair configuration) display metallic conductivity, whereas nanotubes in which (n-m) is a multiple of three behave as semiconductors with a very small band gap. In contrast, other configurations exhibit moderate semi conducting behavior. As a result, certain CNTs demonstrate electrical conductivities exceeding that of copper, while others show properties comparable to conventional semiconductors such as silicon.

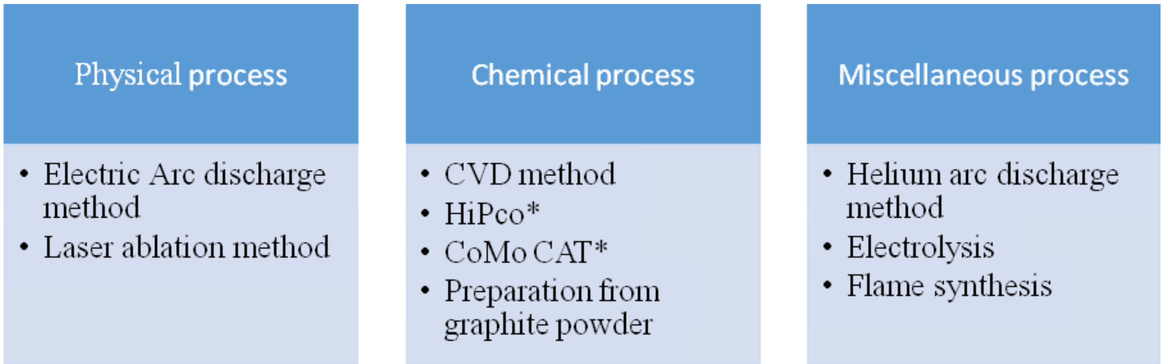
DIMENSIONAL PROPERTIES

Owing to their nanoscale dimensions, charge transport in carbon nanotubes is governed by quantum mechanical effects and predominantly occurs along the longitudinal axis of the tube. These unique dimensional characteristics make CNTs particularly suitable for bio sensing applications, as minor interactions with specific biomolecules can induce measurable changes in electrical conductivity. Furthermore, the nanometric size of CNTs enables precise delivery of low drug doses directly to diseased cells, thereby enhancing targeting efficiency while minimizing systemic toxicity and adverse effects on healthy tissues compared with conventional drug delivery systems[38].

CHEMICAL PROPERTIES

Pristine CNTs exhibit limited solubility; however, surface functionalization significantly improves their dispersibility and biocompatibility. Functionalization with lipids, polymers, or other biomolecules enhances their solubility in biological fluids, facilitates systemic circulation, and reduces the risk of aggregation or obstruction in vital organs. In addition, CNTs display strong optical absorbance in specific spectral regions, particularly in the near- infrared (NIR) range. When functionalized with tumor – specific targeting moieties, CNTs can selectively accumulate in cancer cells and generate localized heat upon NIR irradiation, enabling effective photo thermal destruction of malignant tissues. These favorable chemical and optical properties further support the potential of CNTs as multifunctional platform in advanced drug delivery and therapeutic application[39].

SYNTHESIS OF CARBON NANOTUBES (CNTs) or PRODUCTION OF CNTs



Physical process
- Electric Arc discharge method
- Laser ablation method

Chemical process
- CVD method
- HiPco*
- CoMo CAT*
- Preparation from graphite powder

Miscellaneous process
- Helium arc discharge method
- Electrolysis
- Flame synthesis

ELECTRIC ARC DISCHARGE METHOD: The electric arc discharge method produce carbon nanotubes (CNTs) by vaporizing carbon using a high – temperature electric arc in an inert gas atmosphere. Metal catalysts such as Fe, Co or Ni enhances CNT formation under reduced pressure[40].

The step up consists of two graphite electrodes (anode: 20mm, cathode:7mm), between which a current of 100-200A generate plasma and evaporates carbon[41].

MWCNTs are typically formed without catalysts, whereas SWCNTs require transition metal catalysts. The process operates at temperature above 1700°C and produces mixed products that require purification to remove Morpheus carbon and residual metals[42]. Needle- like CNTs with lengths up to 1mm and diameter of 4-30nm can be obtained on the cathode. CNT yield and quality depend on catalysts type, gas composition, pressure, arc current and electrodes spacing[43,44].

LASER ABLATION METHODS:

The laser ablation technique for carbon nanotubes synthesis was first developed by smalleyet .al[45]. In this method, a high energy pulsed laser is used to vaporize a solid graphite target within a high-temperature reactor under a controlled noble gas atmosphere. The introduction of an inert gas, typically helium or argon, facilitates the transport of vaporized carbon species toward cooler regions of the reactor. As the carbon vapor cools, it condenses and assembles into carbon nanotubes on the inner surfaces of the reactor. The synthesized CNTs are subsequently collected on a water-cooled surface positioned within the reactor. Product analysis indicates that this technique yields approximately 70% carbon nanotubes, predominantly in the form of single-walled carbon nanotubes (SWCNTs). Despite its ability to produce high-purity and well-structured CNTs, the laser ablation method in considered less economical viable, due to higher operational and equipment costs when compared with the arc-discharge technique[46].

The major advantage of this technique include a relatively high CNT yield and reduced metallic impurities. The laser ablation process generally yields approximately 70-90wt% CNTs in the final product. In contrast to arc discharge, the diameter of CNTs synthesized by laser ablation can be more precisely controlled by adjusting the reaction temperature. Moreover, this method minimizes contamination by amorphous and graphitic carbon, resulting in cleaner SWNT samples[47,48].

Despite these advantages, laser ablation is not economically favorable for large-scale production, as it requires high-purity graphite targets and high-power laser system, making it more expensive then arc discharge and chemical vapor deposition methods. In addition, CNTs produced by laser ablation are often not uniformly straight and may exhibit branching, and overall yield is lower than obtained using the arc discharge technique[49].

CVD METHOD (CHEMICAL VAPOUR DEPOSITION METHOD):

Chemical vapor deposition it is an important artificial method for carbon nanotubes synthesis, developed in 1996 to overcome limitations in large-scale and ordered production. It allows better control over nanotubes growth direction on a substrate[50].

In this process, hydrocarbon gases such as acetylene, methane or ethylene are introduced into a reaction chamber. At temperature of about 700-900°C and low atmospheric pressure, there gases decompose and form CNTs on the substrate[51].

CVD of gas advantages, leading to well-aligned CNTs growth, and operation at relatively lower temperature. However, the nanotubes produced may have comparatively lower structure quality[52].

However, the CVD reactor exhibits certain limitation. One of the primary drawbacks of the CVD method is that large-area growth regions, several millimeters, are prone to cracking and shrinking. In addition, this technique may lead to the formation of carbon nanotubes with comparatively lower structural quality[53].

HIGH-PRESSURE CO DISPROPORTIONATION PROCESS (HiPco)

The HiPCO method produces single walled-carbon nanotubes through catalytic disproportionation of carbon monoxide under high-pressure, high-temperature conditions. In this process, iron catalyst particles are generated in situ via thermal decomposition of iron pentacarbonyl [$Fe(CO)_5$], which introduced in a cooled CO stream and rapidly heated in the reaction zone. Decomposition yields iron atoms that aggregate into nanoclusters, serving as active sites for SWCNT nucleation and gas-phase growth. The efficiency of nanotubes formation depends strongly on CO pressure, as the disproportionation rate increases with the square of CO concentration.

HELIUM ARC DISCHARGE METHOD

The synthesis of carbon nanotubes via the arc-discharge method in a helium atmosphere is a widely used technique to produce high-quality single-walled and multi-walled carbon nanotubes. An electric arc is struck between two graphite electrodess in a reactor filled with a low-pressure buffer gas, typically helium. These helium provides a stable plasma environment and aids in cooling and condensation of carbon species, which is crucial for forming cylindrical graphene sheets rather than other carbon forms.

FLAME SYNTHESIS

Flame synthesis represents a fast, economic, and scalable approach for fabricating carbon nanotubes, exploiting the high-temperature, carbon-rich conditions generated in hydrocarbon flames. In this method, transition metal catalysts such as Fe,Ni,or Co are introduced into a fuel-rich flame (e.g., ethylene, acetylene or methane), where rapid thermal reactions promote nanotube growth. The process support continuous, high-throughput production of single or multi-walled CNTs on substrates including metal meshes and fibers, with formation occurring on millisecond timescales.

MISCELLANEOUS PROCESS

These methods are less used, these includes the helium arc discharge method, electrolysis[54] and flame synthesis[55]. In these methods metal ions condense into metal form and attach to the cathode, creating a core point for CNT growth. They are similar to chemical vapor deposition (CVD)[56].

PURIFICATION OF CARBON NANOTUBES

As-synthesized carbon nanotubes typically contain a significant amount of impurities, including residual metal catalyst particle, amorphous carbon, and multi-shelled structures. Therefore, purification is an essential step prior to their use, particularly for biomedical applications such as drug attachment. Various methods are employed for the purification of CNTs, among which air oxidation and acid refluxing are commonly used.

a. Air Oxidation

Raw carbon nanotubes generally exhibit low purity, with an average purity of only about 5-10%. Hence, purification is necessary before functionalization or drug loading. Air oxidation is an effective technique for removing amorphous carbon and residual metal catalyst particle such as nickel (Ni) and yttrium (Y). Optimal oxidation conditions have been reported at temperature of 673K for duration of 40 min.

b. Acid Refluxing

Acid refluxing involves treating the CNT samples with strong acid and is highly effective in eliminating remaining high metal particles and amorphous carbon. A variety of acids have been employed for this purpose, depending on the type of impurities present and the desired level of purification. Hydrochloric acid, nitric acid, sulphuric acid have commonly been employed for acid refluxing; however, hydrochloric acid has been identified as the most suitable refluxing agent due to its effectiveness in removing metal impurities without causing excessive damage to the nanotube structure.

c. Surfactant-Aided Sonication, Filtration and Annealing

Following acid refluxing, carbon nanotubes exhibit improved purity; however, significantly entanglement of the nanotube bundles often remains. Such as carbonaceous debris and catalyst particles, making their removal by simple filtration difficult. To overcome this limitation, surfactant-assisted sonication is employed.

Sonication in the presence of sodium dodecyl benzene sulphonate(SDBS), using ethanol or methanol as the organic solvent, has been shown to be particularly effective. These conditions result in prolonged settling times for CNTs, indicating the formation of a stable and homogenous suspension. Subsequently, the dispersion is subjected to ultrafiltration, followed by annealing at 1273K under a nitrogen atmosphere for 4 hours. The annealing process plays a crucial role improving and stabilizing the structural quality of the CNTs.

Overall, surfactant-aided sonication effectively disentangles CNT bundle, thereby releasing embedded particulate impurities and enhancing purification efficiency. In addition to these approach carbon nanotubes can also be purified using multi-step purification strategies for improved results[57].

FUNCTIONLIZATION OF CARBON NANOTUBES

Despite the considerable potential of carbon nanotubes(CNTs) in targeting a wide range of cancer cells, their biomedical and pharmaceutical applications are significantly limited by poor solubility in aqueous media and concerns related to toxicity arising from their inherently hydrophobic surface. These limitations can be effectively addressed through a process known as functionalization, which modifies the surface characteristics of CNTs and enhances their biocompatibility.

Unmodified CNTs exhibit pronounced cytotoxic effects toward certain classes of cells. For instance, pristine multi-walled carbon nanotubes (MWCNTs) have been reported to cause damage to cell membranes of human macrophages. Consequently, surface modification strategies have been extensively explored to reduce cytotoxicity and improve biological compatibility. Both covalent and noncovalent functionalization techniques are commonly employed on synthesized CNTs to achieve these objectives.

In additions to mitigating toxicity, functionalization plays a crucial role in the conjugation of therapeutic agents or targeting ligands onto CNTs. These bioactive molecules can be attached either to the sidewalls or terminal ends of CNTs, thereby enabling targeted interaction with cancer cells and enhancing therapeutic efficacy[58].

THE MAJOR TECHNIQUES OF CNT FUNCTIONALIZATION INCLUDE:

1. Covalent functionalization
2. Noncovalent functionalization

1. COVALENT FUNCTIONALIZATION

Covalent functionalization provides a more stable and secures attachment of functional molecules. Among the available approaches, cycloaddition and oxidation are the most widely employed. Covalent functionalization of carbon nanotubes can be achieved through several chemical approaches, including nucleophilic substitution, electrophilic addition, and addition-condensation reactions. The underlying mechanism involves the formation of covalent bonds between the unsaturated π-electron system of the CNT sidewalls and various functional groups. One of the most common strategies for covalent modification is the oxidative treatment of CNTs using strong oxidizing agents such as nitric acid (HNO_3), a mixture of sulfuric and nitric acids (H_2SO_4/HNO_3), or potassium permanganate in sulfuric acid ($KMNO_4/H_2SO_4$). Oxidation introduces carboxylic acid (-COOH) groups onto the surface of CNTs, which serve as reactive sites for subsequent conjugation with other molecules[59].

The presence of –COOH groups enables further functionalization through amidation or esterification reactions, facilitating the attachment of various molecules without significantly altering the intrinsic electronic properties of CNTs. However, oxidative functionalization is often accompanied by certain drawbacks, such as shortening of CNTs and the generation of structural defects, particularly at the open ends. To mitigate these limitation, the functional groups introduced during oxidation can be further activated using reagents such as thionyl chloride ($SOCL_2$) and carbodiimidies, resulting in highly reactive intermediates that readily participate in subsequent coupling reactions[60].

Cycloaddition reactions have emerged as an effective alternative to oxidative methods, offering reduced structural damage to CNTs. Among these 1,3-dipolar cycloaddition is the most widely employed technique. In this process, amino acid and aldehydes condense to form azomethine yields, which subsequently react with the CNT sidewalls to generate pyrrolidine ring structures. This modification provides stable anchoring sites that facilitate the conjugation of drug molecules and other functional entities[61].

2. NON COVALENT FUNCTIONALIZATION

Non covalent functionalization represents an alternative approach that preserves the intrinsic chemical and electronic properties of CNTs. This method relies primarily on π-π interactions, Van der Waals forces, and hydrogen bonding between CNTs and functional molecules. Compared to covalent techniques, non-covalent functionalization is generally simpler and less disruptive to the CNT structure. Various biomolecules, including proteins, single- stranded DNA, and fluorescence- labeled polyethylene glycol (PEG), have been successfully immobilized onto CNT surfaces through, π-π stacking interaction demonstrating the versatility of this approach[62].

The mode of functionalization is commonly achieved through the adsorption of deliquescent polymers, biopolymers, and surfactants onto the CNT sidewalls via weak intermolecular interactions. Various classes of surfactants, including anionic, cationic, and non-ionic types, have been extensively employed to enhance the dispersion of CNTs in liquids media. Among these, sodium dodecyl sulfate (SDS) and benzylalkonium chloride are frequently reported as effective surfactants that non-covalently associate with the fullerene – like sidewalls of CNTs, thereby improving their dispersion stability.

The dispersion of CNTs in water is governed by strong adhesion between wetting agents and the walls of carbon nanotubes or fullerenes. This adhesion arises primarily from π-π stacking interactions, which occur due to the attachment of aromatic groups of amphiphilic surfactants to the aromatic network of the nanotube sidewalls. As a result, highly stable interactions are formed between the surfactants molecules and the carbon framework. This phenomenon has been clearly demonstrated in case of the adsorption of N-succinimidyl -1-pyrenebutanoate onto CNT surfaces[63].

APPLICATIONS OF CARBON NANOTUBES

1. Carbon nanotubes in cancer targeted drug delivery

Modern anticancer therapies, such as radiation therapy, surgery or chemotherapy, which uses anticancer medications to kill malignant cells, also harm healthy cells[64]. CNTs are employed as a carrier to transport medications into tumor cells because of their special qualities, which include cellular uptake, high drug loading, and thermal ablation. Because CNTs are hydrophobic, they are insoluble in water, which limits their applications in biomedical and medicinal chemistry. CNTs are therefore functionalized to serve as a drug delivery or carrier system. Different functionalization methods are available such as adsorption, covalent bonding and electrostatic interaction for lowering the hydrophobic nature of CNTs and to aid doping the aggregation of CNTs, hence simplifying their use in various applications[65]. Due to their rapid growth, unchecked proliferation, and high metabolic rates, tumor cells require more oxygen and nutrients, which causes new blood vessels to develop. The glycolysis process provide energy to tumor cells, which also release growth factors and enzymes. This leads to an imbalance in angiogenic regulators, which cause cancer cells blood vessels to widen. Consequently, this leads in large gap junctions between endothelial cells[66].

Carbon Nano horns are the sphere-shaped masses of CNTs bearing an irregular shape that act as a suitable carrier for the drug delivery system. Drug compounds and biomolecules are frequently delivered into tumor cells using SWCNT and MWCNT forms[67].The random bioavailability of relatively low, molecular weight medications is prevented and site-specific drug molecule targeting is improved by conjugating the drug molecules with appropriate conjugating agents and coating them with polymers. Numerous investigations have demonstrated that cancer cells overexpress folic acid receptors[68].

a) Attachment of CNTs to cancer cell receptors

$$\text{CNTs + Cancerous cell} \xrightarrow{\text{Attachment of CNTs}} \text{to cancer cell receptors}$$

CNTs cancerous cell

Attachment of CNTs
to cancer cell receptors

b) Release of drug form CNTs into cancerous cells

$$\text{CNTs +Cancerous cell} \xrightarrow[\text{CNTs into cancerous cells}]{\text{Cell penetration of}}$$

Cancerous cell

Release of drug from
CNTs into the
Cancerous cells

Bio functionalized CNT-based Nano carriers have demonstrated high drug-loading efficiency and enhanced PH-responsive release of model anticancer drugs, including doxorubicin, as well as other chemotherapeutic agents. Owing to their exceptional photo thermal conversion efficiency and precise drug-targeting capability, these Nano carriers have been proposed as promising chemo-photo thermal combinational platforms for improved cancer therapy[69].

Gemcitabine, an anticancer medication, was put onto magnetic MWCNTs and administered subcutaneously to a mouse model in a recent study, it showed strong anti-lymph node metastatic action[70].Various techniques were performed in order to load the drug molecules into the sidewalls of functionalized CNTs and graphene-based nanomaterials by covalent or non-covalent attachment[71, 72].

2. CNTs in Gene delivery system

Gene delivery system represents an advanced therapeutic strategy in modern medical treatment, where in genetic material such as DNA or RNA is administered as a pharmaceutical agent to target cells. This approach enables the replacement or correction of missing or defective genes, allowing cells to produce therapeutic proteins with minimal toxicity for the treatment of various diseases[73].

Due to their ability to pass through cell membranes through endocytosis and their functionalization, which allows DNA to be transferred without degradation, carbon nanotubes appear to be an excellent nonverbal vector for gene therapy[74].One pertinent study examined the use liposomes and functionalized MWCNTs to transport siRNA for the therapy of tumor cells. The results demonstrated that the siRNA administered by MWCNTs significantly inhibited the growth of tumors[75].

3. CNTs in cancer treatment

Blood cancer

Taghdisiet al. achieved enhanced targeted delivery of daunorubicin to acute lymphoblastic leukemia by developing a ternary complex composed of the sgc8c aptamer, daunorubicin, and single-walled carbon nanotubes referred to as Dau-aptamer-SWCNTs[76].

Kidney cancer

Single-walled carbon nanotubes have been shown induce intracellular changes that influence cell cycle progression. These attributed observed effects on cell cycle are attributed to a reduction in the proportion of cell in the S phase, resulting from the upregulated expression of the cyclin-dependent kinase inhibitor P16. Increased P16 expression inhibits the activity of cyclin-dependent kinase Cdk2, Cdk4, Cdk6, thereby preventing entry into the S phase and causing cell cycle arrest at the G1 phase[77].

4. CNTs in Brain targeted drug delivery

A deficiency of acetylcholine is strongly associated with the progression of Alzheimer’s disease and is manifested by impairments in memory and cognitive function. Due to its hydrophilic nature, acetylcholine exhibits limited ability to cross the hydrophobic blood-brain barrier. To overcome this limitation, a novel strategy involving the non-covalent loading of acetylcholine onto single-walled carbon nanotubes has been employed to enhance BBB penetration and drug delivery to the brain[78]. Both in vitro and in vivo studies have demonstrated that single-walled carbon nanotubes are safe and effective.

Nano carriers for drug delivery in the treatment of Alzheimer’s disease and other disorder of the central nervous system[79].

5. Photo thermal therapy

Although the concept of utilizing heat for cancer treatment dates back to the late 19 centuries;however, photo thermal therapy has only recently gained prominence as an innovative and rapidly advancing modality in oncology. Currently, photo thermal therapy is widely regarded as a non-invasive, safe, and cost-effective therapeutic strategy. This approach employs skin-penetrating near-infrared(NIR) irradiation to include localized hyperthermia at tumor sites, resulting in selective destruction of cancer cells while minimizing collateral damage and adverse effects to surrounding healthy tissues[80].

Carbon nanotubes can be engineered to generate heat upon absorption of near-infrared (NIR) light, a property that has been effectively exploited in cancer photo thermal therapy[81]. CNTs exhibit strong optical absorption within the NIR region, including NIR-I (700-900nm) and NIR-II (1.0-1.4µm) where biological tissues display relatively high transparency. NIR radiation can penetrate living tissue to a depth of approximately 1-6mm, enabling localized activation of CNTs. Upon NI irradiation, CNTs convert absorbed light into leading to selective thermal ablation of cancer cells that have accumulated sufficient CNT concentrations.

To enhance treatment specificity and minimize damage to healthy tissues, CNTs are functionalized through the covalent attachment of tumor-specific ligands, allowing targeted accumulation within malignant cells. These conjugated CNTs exhibit adequate stability under physiological conditions and enable highly precise photo thermal destruction of targeted cancer cells. Furthermost, based on antenna theory, the optical coupling efficiency of CNTs reaches a maximum when their length exceeds approximately 50% of the wavelength of the incident light[82].

6. Transdermal drug delivery

These demonstrated that drug delivery to the skin can be precisely regulated reported that functionalized carbon nanotube membranes enable controlled transdermal drug delivery through the application of a low electrical bias, allowing the development of a programmable drug delivery system[83]. Extending this concept Wu et al. successfully fabricated a CNT-based transdermal film for nicotine delivery, demonstrating the potential of CNTs for controlled and responsive transdermal therapeutic applications[84]. Transdermal drug delivery systems represent an attractive approach for medication administration, particularly in the treatment of drug dependence, including nicotine delivery for smoking cessation. Carbon nanotubes exhibit an exceptionally high surface area, which facilitates the efficient adsorption and transport of diverse therapeutic compounds[85].

TOXICITY IN CNTs

These studies on the toxicity of pure nanotubes in cell culture have shown that SWCNT-induced oxidative stress makes CNTs harmful to cells,both in vitro and in vivo tests were carried out to ascertain the harmful effects of CNTs[86].

Mice given CNTs via different ways had a number of negative effects, including the buildup of CNTs in important organs such the liver, spleen and lungs. There have been very few harmful effects observed when CNTs are administered intravenously at increasing concentrations. The body gradually eliminated SWCNTs coated with polyethylene glycol following intravenous delivery and no toxicity was seen during the excretory process[87].

CONCLUSION

Carbon Nanotubes (CNTs) have emerged as highly promising Nano carriers in the field of advanced drug delivery systems due to their unique physicochemical properties, including high surface area, exceptional mechanical strength, electrical conductivity and the ability to undergo diverse functional modifications. These characteristics enable efficient drug loading, targeted delivery, and controlled release of therapeutic agents, thereby enhancing bioavailability and therapeutic efficacy while minimizing systemic toxicity.

Significant advancements have been achieved in the synthesis, purification and functionalization of CNTs, allowing improved dispersibility, biocompatibility, and specificity toward diseased tissues. Both single-walled and multi-walled carbon nanotubes have demonstrated potential in delivering small molecules, proteins, genes and imaging agents, particularly in cancer therapy, gene delivery and diagnostic applications. Functionalization strategies, such as covalent and non-covalent modifications, have been instrumental in overcoming the inherent hydrophobicity and toxicity concerns associated with pristine CNTs.

Despite these promising outcomes, several challenges continue to limit the clinical translation of CNT- based delivery systems. Issues related to large-scale production, reproducibility, long-term toxicity, biodistribution, and regulatory approval remain critical concerns. Therefore, future research should focus on standardized manufacturing processes, comprehensive in vivo safety evaluations, and the development of environmentally and biologically safe CNT formulations. With sustained interdisciplinary research and technological refinement, carbon nanotubes hold substantial potential to revolutionize targeted and personalized drug delivery in the near future.

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