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Review On Carbon Nanotubes in Pharmaceutical Analysis

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ABSTRACT

Carbon nanotubes (CNTs) are allotropes of carbon, made of graphite and constructed in cylindrical tubes with diameters in the nanometer range and lengths of several millimeters. Their impressive structural, mechanical, and electronic properties are due to their small size and mass, strong mechanical potency, and high electrical and thermal conductivity. CNTs have been successfully applied in pharmacy and medicine due to their high surface area, which is capable of adsorbing or conjugating with a wide variety of therapeutic and diagnostic agents such as drugs, genes, vaccines, antibodies, and biosensors. They have been proven to be an excellent vehicle for drug delivery directly into cells without metabolism by the body. Furthermore, applications extend to tissue regeneration, biosensor diagnosis, enantiomer separation of chiral drugs, and the extraction and analysis of drugs and pollutants. Recently, CNTs have also been revealed as promising antioxidants. This review focuses on the applications of CNTs in pharmacy and medicine, examines their pharmacokinetics, metabolism, and toxicity, and discusses the future perspectives of this bionanotechnology.

KEY WORDS: Bionanotechnology, CNT, Biosensors, Antioxidants.

INTRODUCTION

Carbon nanotubes (CNTs) are allotropes of carbon usually referred to as graphite sheets, which mainly consist of -sp^2-hybridized carbon atoms. They are wrapped into cylindrical structures and commonly capped by a fullerene-like structure. The structure of the carbon nanotube is hybridized as sp^2 bonding, which is even stronger than the -sp^3 bonding found in diamond. The aspect ratio of CNTs is greater than 10,000,000, which is clearly larger than any other existing material.

Since the beginning of the 21st century, CNTs have been introduced in pharmacy and medicine for drug delivery systems in therapeutics. Thanks to their high surface area, excellent chemical stability, and rich electronic polyaromatic structure, CNTs are able to adsorb or conjugate with a wide variety of therapeutic molecules (drugs, proteins, antibodies, DNA, enzymes, etc.). They penetrate cells directly, keeping the drug intact without metabolism during transport in the body. Studies have demonstrated that when bonded to CNTs, molecules are delivered more effectively and safely into cells than by traditional methods. This discovery has opened a new way for drug preparations, radically changing anterior concepts of pharmacology. Initially applied to bind antineoplastic and antibiotic drugs for cancer and infection treatments, they have since been assayed for gene therapy, immunotherapy, tissue regeneration, and diagnosis.

HISTORY

The Carbon Nanotube (CNT) was first discovered in 1991. In 1993, Iijima and Ichihashi reported the synthesis of single-walled carbon nanotubes with a diameter of 1 nanometer. Also known as the "Bucky tube," this class of nanomaterials is composed of a two-dimensional hexagonal lattice of carbon atoms bent in one direction to form a hollow cylinder. CNTs are described as allotropes existing between Fullerene (0-dimensional) and Graphene (2-dimensional). Most research focuses on tubes ranging in circumference from a few graphene cells to hundreds of cells. CNTs up to half a meter long have been produced, with aspect ratios in excess of 100,000,000:1.

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TYPES OF CARBON NANOTUBES

Based on their structure, CNTs are classified into two kinds:

1. Single Walled Carbon Nanotubes (SWCNTs)

SWCNTs consist of carbon atoms bonded into a tube shape with a single wall. They are considered a single long wrapped graphene sheet.

Dimensions: They possess a length-to-diameter ratio of nearly 1000, making them nearly one-dimensional structures.

Properties: SWCNTs are excellent electric conductors and possess thermal conductivity in the range of 6000 W/m·K. They are suitable candidates for miniaturizing electronics to replace micro-electromechanical systems.

Synthesis: Production remains expensive and requires a catalyst.

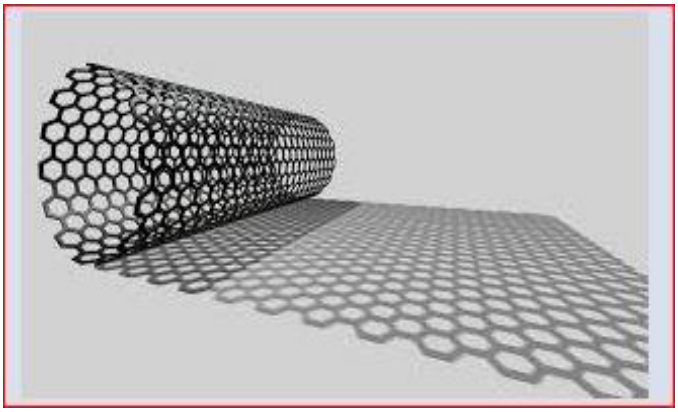

Fig 1: Single walled carbon nanotubes (SWCNTs)

2. Multi-Walled Carbon Nanotubes (MWCNTs)

MWCNTs consist of multiple layers of graphite rolled coaxially to form a tubular shape, as shown in **Fig-2**.

Structure: They consist of carbon atoms bounded into a tube shape with multiple walls. They are structurally sound but frequently contain regions of structural imperfection.

Properties: MWCNTs are stronger than steel yet only one-sixth of the weight. Depending on chirality, they can act as conductors or semiconductors and possess intrinsic superconductivity. Their thermal conductivity is in the range of 3000 W/m·K.

Defects: Structural defects can be minimized by using the arc discharge method.

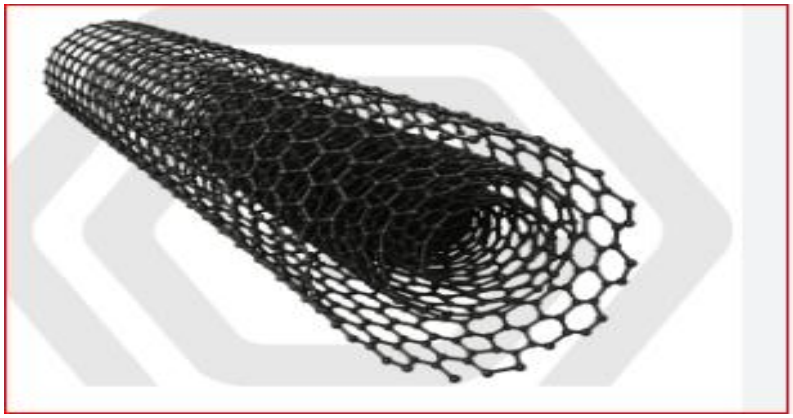

Fig 2: Multiwalled carbon nanotubes (MWCNTs)

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METHODS OF PREPARATION OF CARBON NANOTUBES

The following methods are available for the production of carbon nanotubes:

Arc Discharge Method: This method is employed to produce large quantities of carbon nanotubes and is the simplest approach. It uses a direct current of 50A to 100A, powered by approximately 20V, to generate a high-temperature discharge between two electrodes.

Laser Ablation Method: Graphite is vaporized at high temperatures in an inert atmosphere using a laser. Carbon species are collected on a water-cooled copper collector. Small carbon nanotubes are obtained when metals like Ni, Co, and Fe are added in small quantities. The diameter and size distribution depend on growth temperature, catalyst composition, and gas pressure.

Chemical Vapour Deposition (CVD): This serves as a primary procedure for bulk production. It includes Thermal CVD and Plasma Enhanced CVD.

Process: Carbon sources (methane, carbon monoxide, acetylene) in the gaseous phase are used as energy sources. A catalyst (Fe, Ni) is prepared via physical vapor deposition or dip coating on a substrate. Heating to 500-1000°C in a carbon-rich environment leads to cluster formation and nanotube growth.

Flame Synthesis Method: A scalable, continuous flow method with lower costs. The flame temperature is maintained high for nanotube preparation using transition metals like Fe and Ni. Carbon-rich gases (-CO_2, -CH_4, C-$2H_2$, etc.) are used, where exothermic reactions supply the heat required for the endothermic carbon deposition.

Saline Solution Method: CNTs are created by immersing a substrate (carbon paper or stainless-steel mesh) in a saline solution of a metal catalyst (Co: Ni 1:1). The substrate is heated by electrical current while exposed to a feedstock gas like ethylene.

Nebulized Spray Pyrolysis Method: Uses a specialized ultrasonic atomizer to create a nebulized spray. This method produces MWCNTs with aligned bundles and fairly consistent diameters using ferrocene and a catalyst on high-growth surfaces.

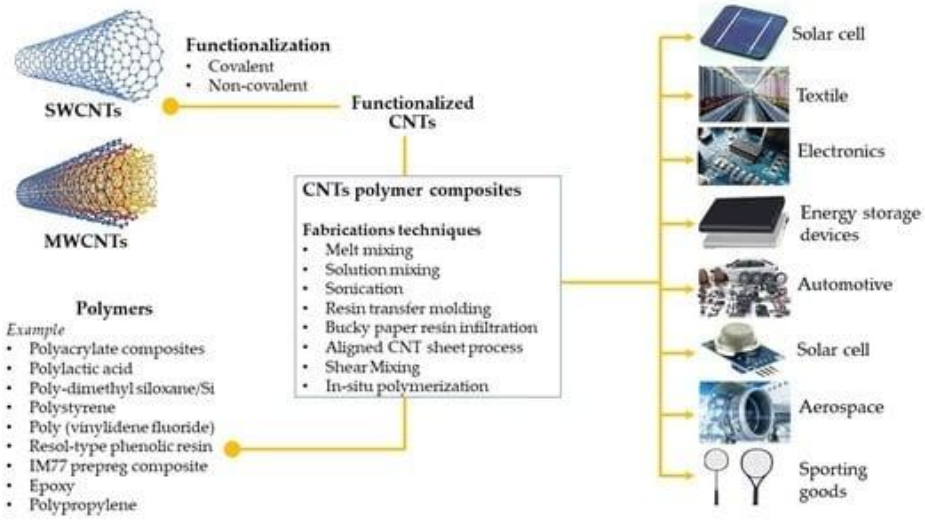

Fig 3: Fabrication and Functionalization Overview

TECHNIQUES FOR INCORPORATING CARBON NANOTUBES (FUNCTIONALIZATION)

A. Covalent Functionalization

Covalent functionalization involves the direct attachment of functional groups to the graphitic surface or the derivatization of existing groups.

Fluorination: Treatment with molecular fluorine at 150–600 °C results in heavily functionalized CNTs with increased solubility in alcohols. Confirmed by C–F valence vibration at 1220–1250 cm^{-1}. Temperatures above 250 °C make CNTs insulators. Fluorine atoms can be displaced by nucleophiles like Grignard reagents to add organic moieties.

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Hydrogenation: Achieved via Birch reduction or gas-phase functionalization with atomic hydrogen. This is a clean method compared to wet chemical methods. Confirmed by C–H vibrations at 1370 and 1457 cm^{-1}.

1, 3-Dipolar Cycloadditions: Reaction of azomethine ylides (from alpha-amino acids and aldehydes) with CNTs. This attaches substituted pyrrolidine rings to the sidewalls, resulting in high solubility in water and organic solvents.

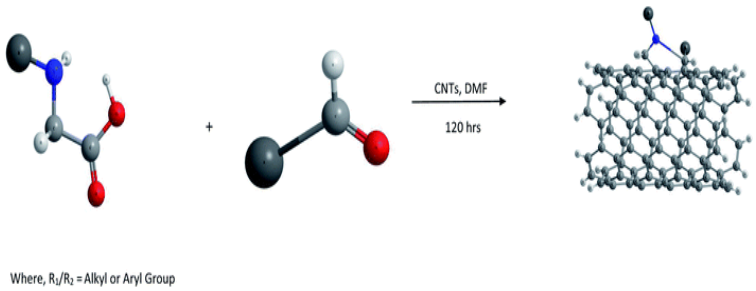

Fig-4: Cycloaddition reactions of CNTs

Arylation (Diazonium Salts):

Reduction of aryl diazonium salts attaches aryl moieties to SWCNTs. This improves solubility in organic solvents. Functional groups can be removed by heating in argon. In-situ generation of diazonium species is often advantageous.

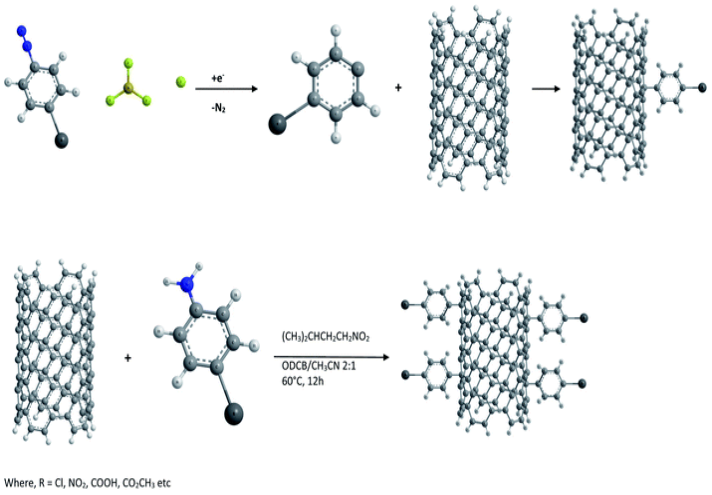

Fig-5: Arylation of CNTs via reduction of diazonium salts

Reactive Species Functionalization: Direct reaction with highly reactive groups like nitrenes, carbenes, and radicals. For example, alkyl azidoformates thermally react to form alkoxycarbonylaziridino derivatized CNTs soluble in DMSO.

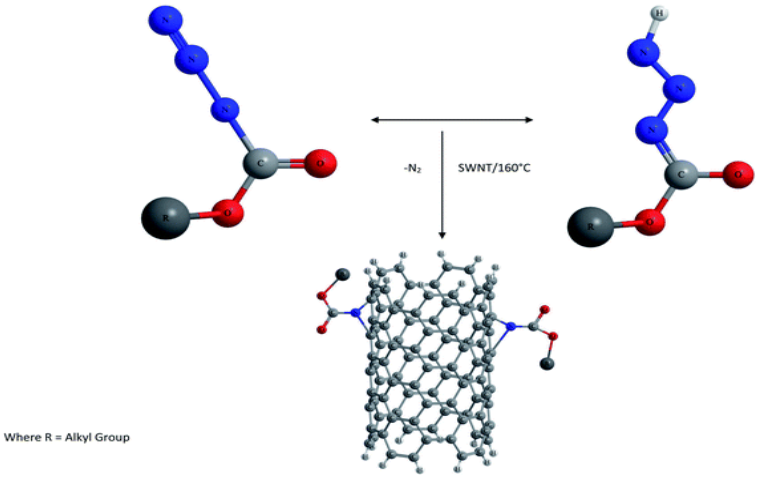

Fig 6: Functionalization of CNTs with nitrenes

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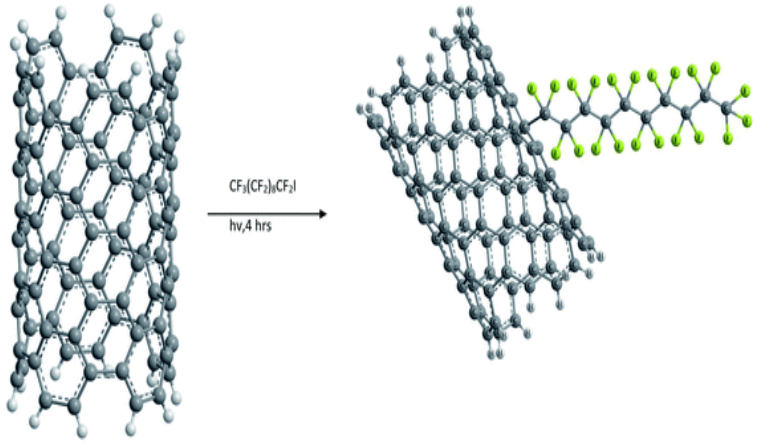

Fig 7: Functionalization of CNTs with radicals

Electrophilic Addition: Mechanochemical reaction with chloroform in the presence of $AlCl_3$ adds dichlorocarbene to the sidewalls. Chlorine atoms can be exchanged with hydroxyl groups for further esterification.

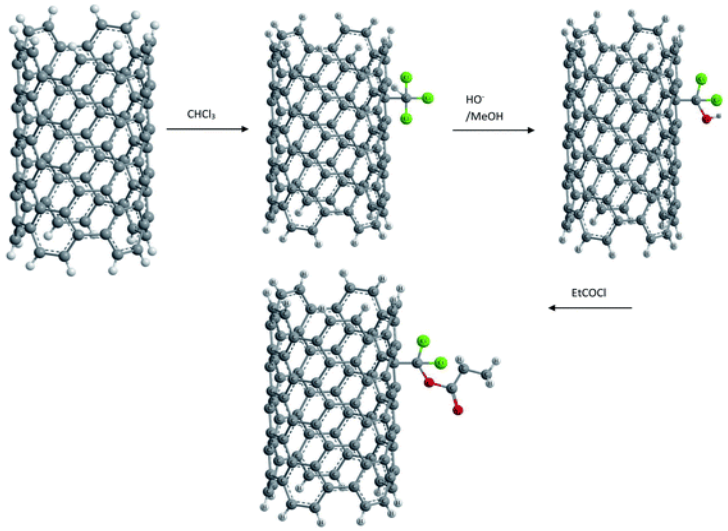

Fig 8: Electrophilic addition reaction of CNTs

Functionalization with Metal-Containing Complexes: CNTs can be functionalized with Vaska's compound (trans-IrCl (CO)(PPh3)2) or Wilkinson's complex (-RhCl (PPh3)3). The nanotube acts as a primary ligand to the central metal atom.

Carboxylation and Further Derivatization: Oxidative purification (using HNO_3, H_2SO_4, $KMnO_4$) opens nanotube tips and creates acidic (–COOH) and hydroxyl (–OH) groups. These can be used to link nanotubes or attach sensors.

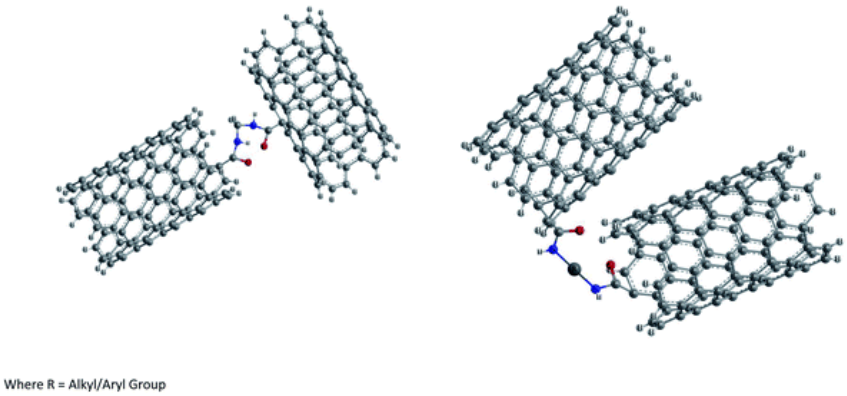

Fig-9: Linking of CNTs via surface and tip functionalized groups

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Amidation/Esterification: Activation of carboxyl groups with thionyl chloride ($SOCl_2$) followed by reaction with amines or alkyl chains forms soluble functionalized CNTs.

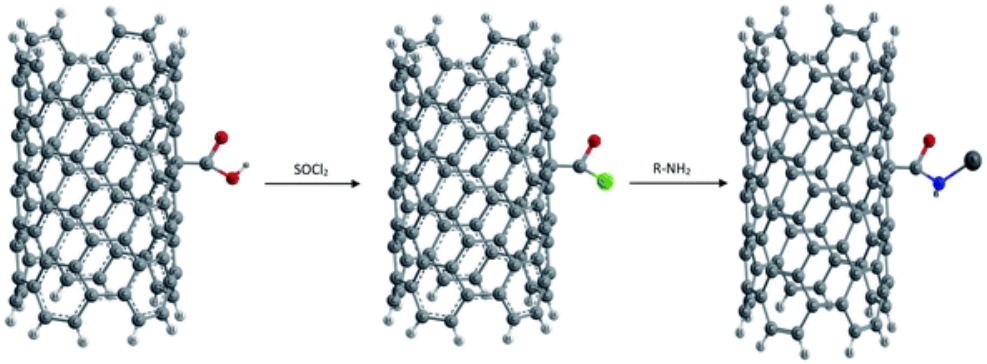

Fig-10: Amidation of COOH functionalized CNTs

Ionic Functionalization: Reaction of –COOH groups with octadecyl amine forms soluble SWCNT-carboxylate zwitterions. This allows for high yields of soluble nanotubes.

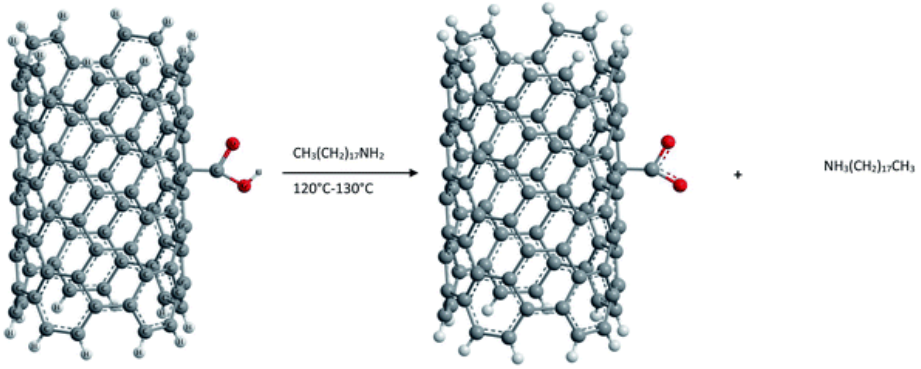

Fig-11: Ionic functionalization of COOH functionalized CNTs

Attachment of Metallic Nanoparticles: Carboxylic and sulfonic acid functional groups serve as molecular sites for adsorbing metal ions like Pt, Ru, and Au, which are then reduced to nanoparticles. Applications include Au nanoparticles on mercaptobenzene-functionalized MWCNTs and Pd-coated MWCNTs using polymerized citric acid.

B. Non-Covalent Functionalization

Non-covalent treatment allows for the adsorption of groups without disturbing the pi system of the graphene sheets.

Polymer Wrapping: Amphiphilic polymers like polyvinyl pyrrolidone (PVP) coil around the nanotube. The hydrophobic backbone contacts the nanotube while hydrophilic groups are exposed to the solvent.

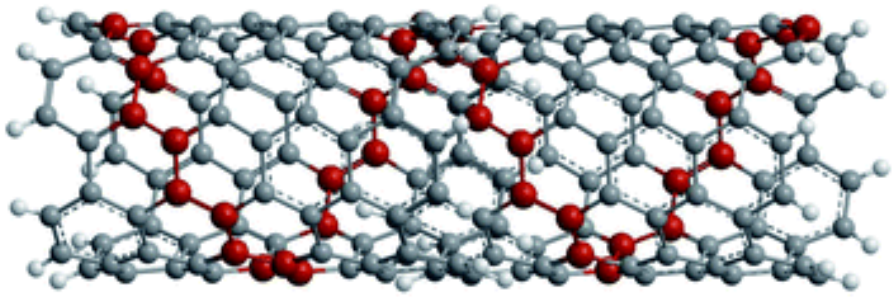

Fig-12: Functionalization of CNTs via polymer wrapping

Surfactant Functionalization: Surfactants (SDS, SDBS, CTAB) disperse CNTs via physical adsorption. Nanotubes reside in the hydrophobic interior of surfactant micelles.

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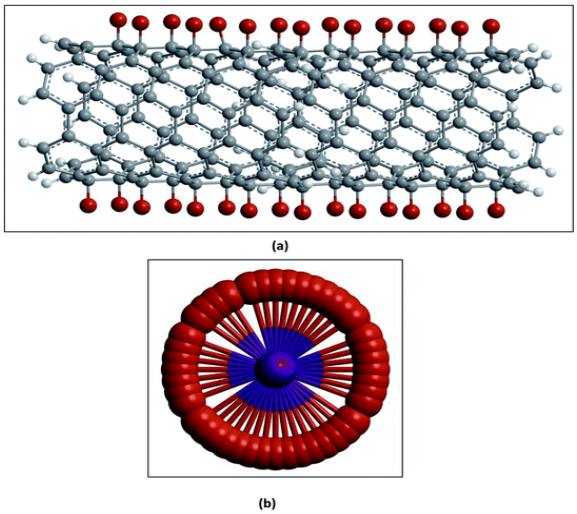

Fig-13: Surfactant functionalization of CNTs

Polymer Absorption (pi-pi Stacking): Polyaromatic molecules like pyrenes and anthracenes stack on the nanotube surface via pi-pi interactions. Pyrenes are effective for anchoring proteins and small biomolecules.

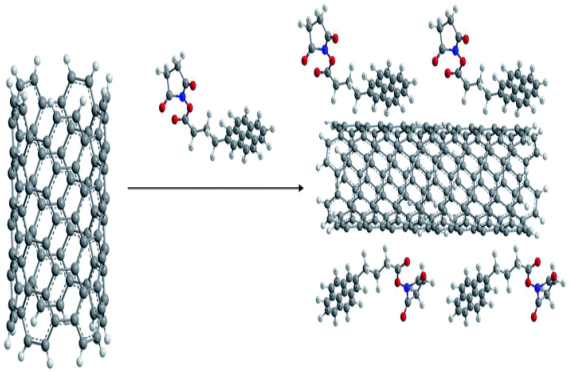

Fig-14: Functionalization of CNTs by substituted pyrenes

Polymer Encapsulation: CNTs can be encapsulated within crosslinked copolymer micelles or peptide amphiphiles. This improves dispersion in both polar and non-polar solvents.

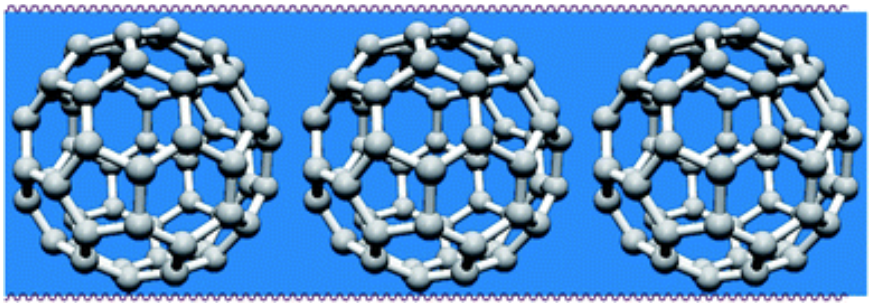

Fig-15: Fullerene encapsulation inside CNTs

Metal Deposition (Electroless): Spontaneous nucleation of bare Pt, Au, and Pd particles on SWCNT sidewalls can occur via electroless deposition without reducing agents, or via electrodeposition where the nanotube acts as a template.

CARBON NANOTUBES APPLICATIONS

CNTs possess extraordinary material properties such as very high thermal and electrical conductivity, stiffness, strength, and toughness.

Field Emission: CNTs are the best-known field emitters due to their sharp tips and high electrical conductivity. They are used in flat-panel displays and electron microscope sources.

Conductive Plastics: CNTs are used as fillers in plastics for electrostatic dissipation (ESD) and electromagnetic shielding. Due to their high aspect ratio, they require low loading to achieve conductivity.

Energy Storage: CNTs are preferred for electrodes in supercapacitors and lithium-ion batteries due to their high reversible capacity and surface area (~1000 m^2/g). They also serve as catalyst supports in fuel cells.

Molecular Electronics: Their precise geometry and conductivity make them suitable candidates for connections and switches in molecular electronic circuits.

Pharmaceutical Applications: Their high aspect ratio and ability to be functionalized make them useful as carrier vectors for pharmaceutical nano delivery. They can serve as targets in controlled drug delivery systems.

CONCLUSION

This review reveals the structure, morphology, synthesis, and purification methods of carbon nanotubes alongside their properties and applications. The distinct structural properties of CNTs, particularly their high aspect ratio and propensity for functional modification, make them useful for pharmaceutical nano delivery. They act as potential nanodevices for controlled drug delivery, allowing for easy functionalization on their sidewalls and core. With the prospect of gene therapy, cancer treatments, and innovative answers for life-threatening diseases, the science of nanomedicine is an ever-growing field. Single and multi-walled carbon nanotubes have already proven to be safer and more effective alternatives to previous drug delivery methods, capable of passing through membranes to carry therapeutic drugs deep into the cell.

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