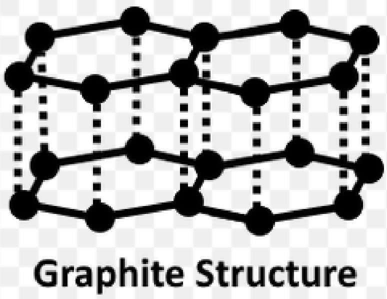
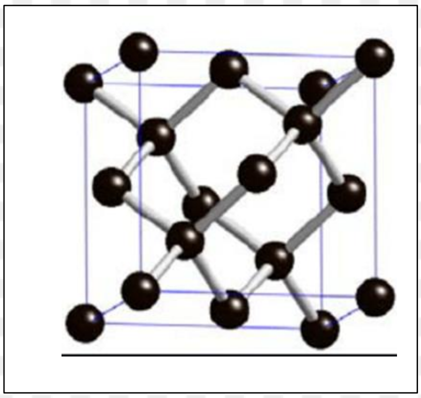
Dental chemistry **First year**

Second Course **Lec.3**

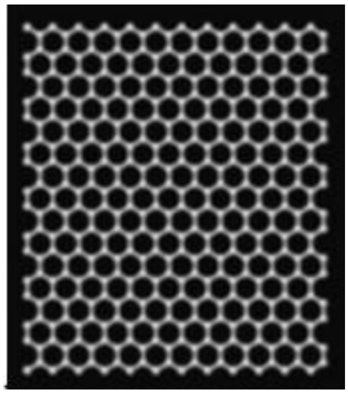
Carbon nanotubes

Many allotropes are formed from carbon due to its valiancy. Diamond and graphite are the well known forms of carbon structures.

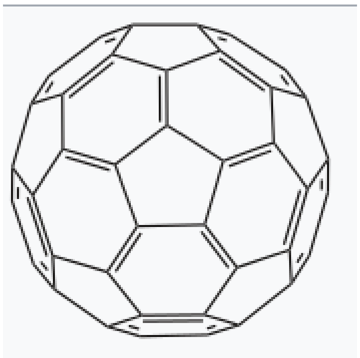




In recent decades, more structures were discovered such as fullerene (ball shapes) and graphene (sheets).



Graphene



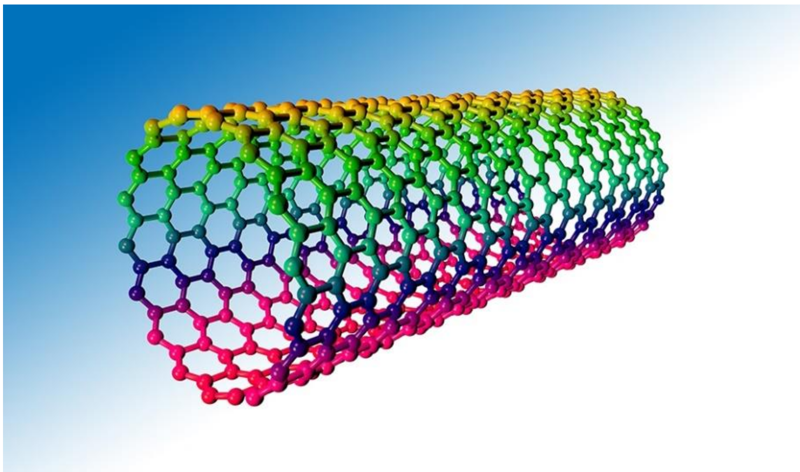
Fullerene

Allotropes : structurally different forms of the same element

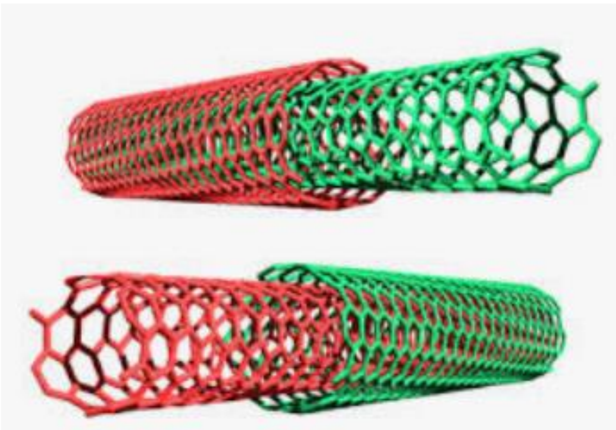
Also, larger nanoscale structures of carbon are discovered. They are made of carbon with tubes forms, abbreviated (CNTs) and measured in nanometers.

CNTs are several types:

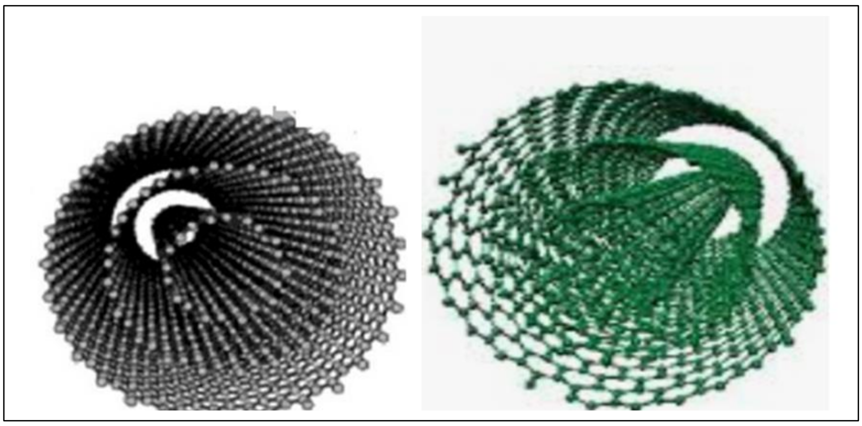
Single-wall carbon nanotubes (SWCNTs):



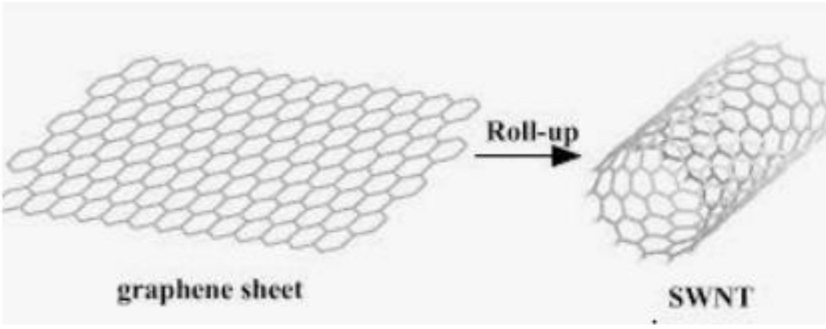
Double- wall carbon nanotubes (DWCNTs):



Multi-wall carbon nanotubes (MWCNTs



SWCNTs are synthesized from grapheme sheet by rolling up:



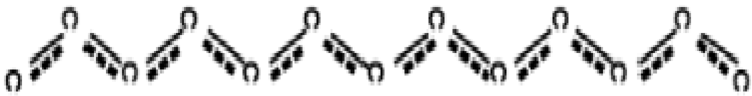
CNTs can exhibit unique properties such as:

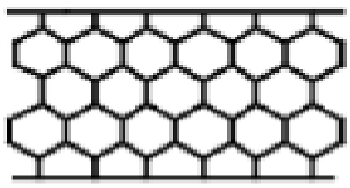
1-Tensile strength

2-Thermal conductivity

3- Electrical conductivity

Because the covalent sp^2 bonds between the carbon atoms in CTNs, it is considered the strongest materials according to both tensile and elastic modulus





A bond between sp^2 is stronger than a bond between sp^3 because sp^2 contains 33.33% s-character while sp^3 contains 25% .

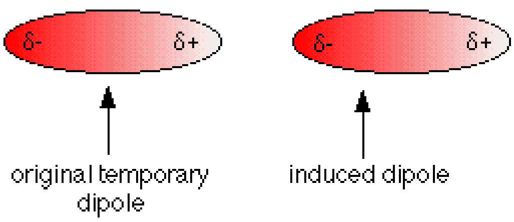
(The more s-character, the stronger a bond)

Multi-walled carbon nanotubes (MWCNTs) consist of two or more SWCNTs with an interlayer of non-covalent *van der Waals* force acting between the carbon atoms of different walls.

Although van der Waals forces are considered to be weak intermolecular forces, they become significant at the nanoscale due to large surface area per unit mass of the material.

Van der Waals forces:

This sets up an ***induced dipole*** in the approaching molecule, which is orientated in such a way that the δ+ end of one is attracted to the δ- end of the other.



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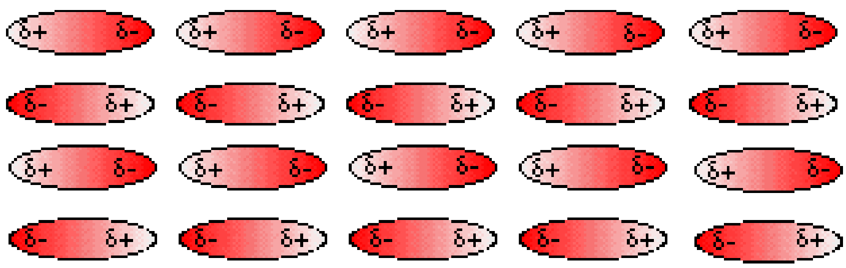
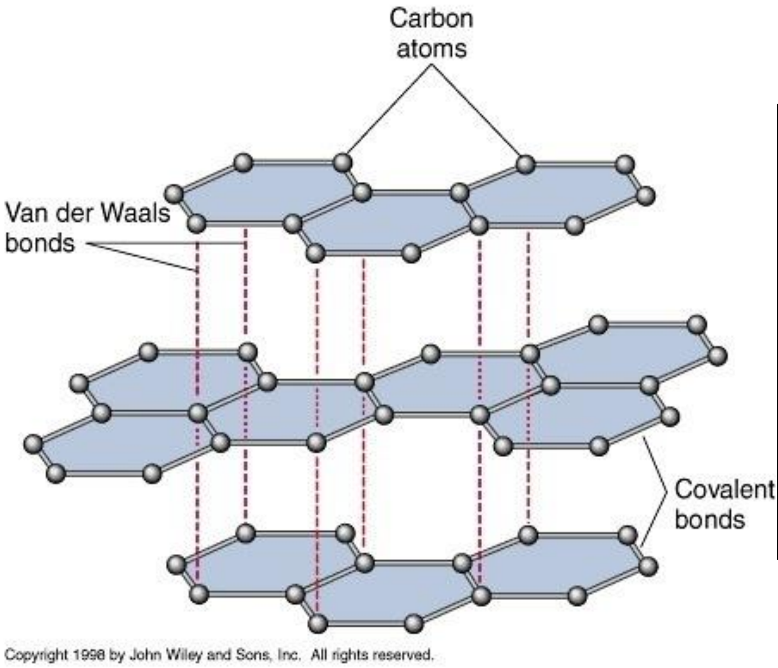




Van der waals in graphite

the bonds in graphite are purely covalent in the rings and Van der Waals from one plane to the next

Carbon has the unique ability to assume a wide variety of different structures and forms. At the nanoatomic atomic scale, carbon nanotubes (CNTs) are hexagonal sheets of graphic wrapped into single or multiple sheets. They have unqiue mechanical, thermal, and electronic properties that drive from the special properties of carbon bond, their cylindrical symmetry, and their unique one dimensional nature.

Nanotubes can also be metallic or semiconducting, depending on their chirality. They are stable up to $2800C^{o}$ in a vacuum, posses a thermal conductivity whose value is twice that of diamond, and have an electric current-carrying capacity that is 1000 times that of copper.

Studies have shown that nanotubes display extraordinary mechanical properties- young modulus of 1TPa, tensile strength in the range of 50-150 GPa. The elastic modulus and strengths are one to two orders of magnitude higher than that of the strongest steel. They also display outstanding ellectrical and thermal properties. These extraordinary properties of nanotubes have sparked an interest in using them as reinforcing materials in composites or as additives to impart novel functionalities. Given their unique properties, CNT-based materials have attracted attention in the field of biometerials with potential applications in radiotracers, MRI contrast agents, drug delivery, and sensors.

Young modulus, is a mechanical property that measures the stiffness of a solid material.

tensile strength (**TS**: is the maximum stress that a material can withstand while being stretched or pulled before breaking.

Strain to **failure** gives the measure of how much the specimen is elongated to **failure**..

In addition, CNT-based scaffolds that are electrically conducting are also an attractive proposition. However, before their widespread usage, the safely of CNT-based materials

Carbon nanotube applications in dentistry

The use of CNTs in the dentistry field has been explored modestly since its introduction in the early 1990s. the applications of CNTs in the dental field can be categorized into the following areas:

(1) Application to dental restoration materials.

(2) Application to bony defect replacement therapy.

Dental restorative materials

Dental composite resin is a tooth-colored restorative material used to replace a decayed portion of the tooth structure. Its aesthetic appearance is the main advantage over conventional dental amalgam. Typical composite resin is composed of a resin-based matrix, such as bisphenol A-glycidyl methacrylate (BIS-GMA) and an inorganic filler like silica. The filler gives the composite improved mechanical properties, wear resistance and translucency. Functionalized SWCNTs have been applied to the dental composite to increase its tensile strength and Young modulus to help improve the longevity of composite restoration in the oral cavity. The addition of Functionalized SWCNTs increased its flexural strength significantly by absorbing more stress.

CNTs have been applied to the interface of dentin and compensate for microleakage development in long term use, which is a major cause of restoration failure.

Microleakage may be defined as the passage of bacteria, fluids, molecules or ions between a cavity wall and the restorative material applied to it.

Once microleakage develops between the tooth and composite resin interface, it works as a nidus for bacterial colonization, thus secondary decay can develop. SWCNTs allow the nucleation and crystallization of hydroxyapatite (HA). CNTs have shown the potential to provide protection against bacteria and initiate the nucleation of (HA) on their surface..

One of the most common complications of denture prostheses is cracking of the denture base from either accidental dropping or long-term fatigue failure. The denture base is usually made of polymethyl methacrylate (PMMA) because of its excellent aesthetics, low density, low cost, and ability to be repaired. However, it has a relatively low fracture strength which makes denture bases vulnerable to cracking from either impact or Flexural fatigue under chewing. Recently. MWCNTs (0.1-1.0 wt.%) have been incorporated into (PMMA) to increase the flexural strength and fracture toughness of denture base materials. A similar application of MWCNTs (0.1-10 wt.%) to PMMA-based bone cement used in orthopedic areas has been shown to improve the fatigue performance of bone cement. It was speculated that well dispersed MWCNTs were able to reinforce the PMMA matrix prior to crack initiation and to retard the early phase of crack propagation.

Bony defect replacement therapy

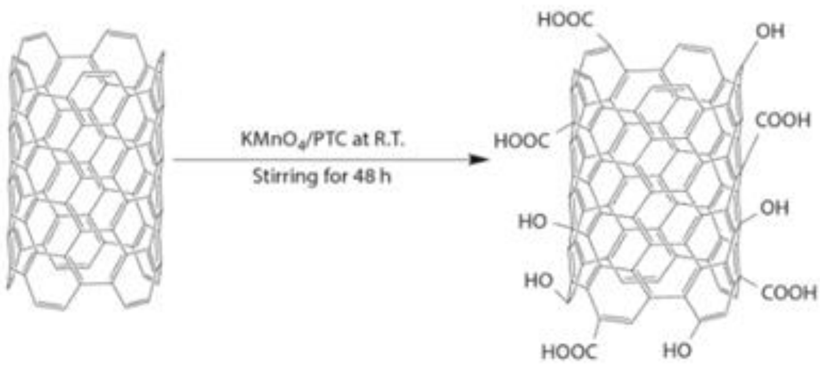
As dental implant treatment of replacing missing teeth becomes highly predictable, supplemental bone augmentation therapy using synthetic and bone biomaterials also attains increased popularity. Insufficient volume or bony defects of a alveolar bone can be caused by the periodontal disease, tooth loss, and or trauma. It was reported that nanoscale HA was formed on the surface of MWCNTs when immersed in calcium phosphate solution at 37 C^{o} for 2 weeks, indicating the CNTs potential use for bone tissue engineering.

MWCNTs have higher ability to absorb proteins when the maturation of osteoblasts by MWCNTs was examined. This finding of CNTs ability to adsorb protein on their surface has indicated their potential role as a carrier for protein or gene delivery. Also the adsorption of the recombinant human bone morphogenic protein-2 (rhBMP-2) on the surface of MWCNT-chitosan scaffolds was shown to be able to induce bone formation by implanting MWCNT-chitosan scaffold adsorbed with rhBMP-2 in mouse muscle.

Chitosan *is a polycationic biopolymer with wide biological applications due to its unique chemical nature, positive charge, presence of reactive hydroxyl, and amino group. Chitosan has excellent physiochemical properties such as bioadhesive, biocompatible, and biodegradable.*

Chemical functionalization of nanotubes was discovered in an attempt to purify single-walled CNTs (SWCNTs) with acids. Depending on the method of nanotube production, CNTs are often mixed with impurities such as metal catalysts, amorphous carbon and soot. Strong acids are utilized to remove the impurities, leaving behind pure CNTs. The acid reacts with the nanotube caps, which are reactive. This method of functionalization creates bonds that are progressively oxidized, depending on the intensity of treatment to hydroxyl (-OH), carbonyl (C=O) and carboxyl (-COOH)groups. The carboxylic acid groups are employed as anchoring cites for functional groups that make the nanotubes soluble in organic solvents. Other oxygenated functionalities include anhydrides, quinines and esters. Such functionalities can also be introduced by treatment with ozone

The following figure show the carboxylic/hydroxyl functionalization of CNTs using mild oxidizing acids at room temperature, An improved process is presented to functionalize carbon nanotubes by potassium permanganate with the help of phase transfer catalyst (PTC). The PTC helps to extract potassium permanganate from the solid phase to an organic solvent phase and improves the efficiency of nanotube oxidation



Carboxylic/hydroxyl functionalization of CNTs using mild oxidizing acids at room temperature.

The surface of the carbon nanotubes can be modified to reduce the hydrophobicity and improve interfacial adhesion to a bulk polymer. Chemical functionalization is necessary to reduce the hydrophobicity and improve the solubility of CNTs.

Reducing the hydrophobicity property is need to increase the interfacial adhesion and dispersion in the polymer matrix.

CNT can be viewed as a hollow cylinder formed by rolling graphene sheets. Bonding in nanotubes is essentially sp^2. The pi orbital is more delocalized outside the tube. This makes nanotubes mechanically stronger, electrically and thermally more conductive and chemically and biologically more active than graphite.

The chemically functionalized CNTs have been shown to be less cytotoxic than pristine ones on different types of cells like epithelial cells, neurons and osteoblasts. MWCNTs that were chemically functionalized with carboxylic acid, ethylene diamine or poly-m-aminobenzene sulfonic acid were also shown to be biocompatible and observed to provide a suitable substrate for neurite extension.

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