Nanoscience

Consider a homogeneous solid material of compact shape (let us say spherical) and macroscopic dimensions (let us say millimetric). Most of its properties will be related to its chemical composition and crystal structure. This is what is traditionally studied in the physics and chemistry of solids. When the size of the object is reduced to the nanometric range, the properties of materials may become totally different from what is observed in the bulk solid system.

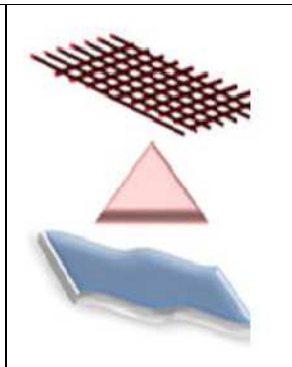
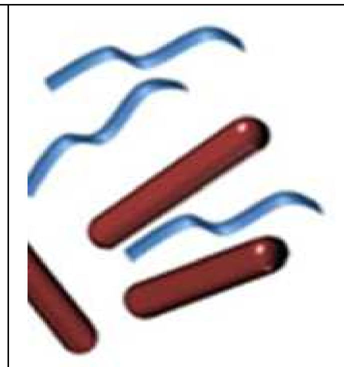
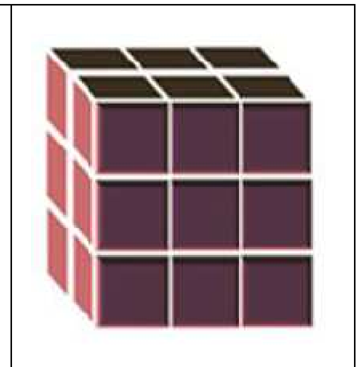
Nanoscience is a new discipline concerned with the unique properties associated with ***nanomaterials***, which are assemblies of atoms or molecules on a ***nano scale***. '**Nano'** refers a scale of size in the metric system. It is used in scientific units to denote one-billionth of the base unit - approximately 100,000 times smaller than the diameter of a human hair. **'Scale'** refers an order of magnitude - of size or length- reference to objects that are sized on a scale that is relevant to nanometer. A nanometer is 10^{-9} meter (1nm = 10^{-9} meter), a dimension in the world of atoms and molecules (the size of H atom is 0.24 nm and for instance, 10 hydrogen atoms lined up measure about 1 nm).

Nanoscience is actually the study of objects/particles and phenomena at very small scale, roughly 1 to 100 nanometers. **Nanoparticles** are those particles which contain from hundred to ten thousand of atoms (100 to 10,000 atoms). So the size of the particle range roughly from 1 to 100 nm.They are the building block of ***Nanomaterials***.

What are nanomaterials? The materials which are created from blocks of nanoparticles or they are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. Nano carbons such as fullerenes and carbon nanotubes are excellent examples of nanomaterials.

Classification of Nanomaterials: Nanomaterials can be nanoscale in one dimension (e.g., surface films), two dimensions (e.g., strands or fibers), or three dimensions (e.g., precipitates, colloids). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes.

Nanostructures (dimensions of the nanomaterials) are the ordered system of one dimension, two dimensions or three dimensions of nanomaterials, assembled with nanometer scale in certain pattern which includes nanosphere, nanotubes, nanorod, noanowire, and nanobelt. Nano-structured materials are classified as zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

			
(a) 0D spheres and clusters	(b) 1D films, plates, and networks	(c) 2D nanofibers, wires, and rods,	(d) 3D nanomaterials or nanocrystallite

The **Clusters** are particles containing a very small number of atoms or simply few hundred atoms or smaller. A **Nanocrystallite** is generally understood to possess crystalline order in addition to nanoscale size. ***Note:*** If one dimension of the three dimensional nanostructure is at nano scale, then it is called a **Quantum Well**. If two dimension of the three dimensional nanostructure is at nano scale, then it is called a **Quantum Wire**. If all the three dimension of the nanostructure is at nano scale, then it is called a **Quantum Dot**. Nanocrystallites are also called quantum dot.

There is considerable variety in the types of nanoparticle systems that have been fabricated and studied. Aside from differences in their size and shape one important variable is their composition. Almost every element in the periodic table, together with various alloys and compounds, can form nanoparticles. They can be metallic, semiconducting, or insulating and typically their properties are very different to those of the corresponding bulk material.

The ***seven main nanomaterial categories*** are (1) Carbon based nanomaterials (2) Nano-composites (3) Nano-metals & Nano-alloys (4) Biological nanomaterials (5) Nano-polymers (6) Nano-glasses (7) Nano-ceramics.

Nanotechnogy is defined as the creation of functional materials, devices, and systems through control of matter on the nanometer length scale and the utilization of new properties and phenomena developed at that scale. It is a field of science whose goal is to control individual atoms and molecules to create devices that are thousands of times smaller than present technologies permit. An important idea that underpins much of nanotechnology is that by controlling composition, size, and structure at the nanoscale one can engineer almost any desired properties.

For an object of the macroscopic size, the ***surface atoms*** comprise a negligible proportion of the total number of atoms and will therefore play a negligible role in the bulk properties of the material. When the size of the object is reduced to the nanometric range the proportion of surface atoms no longer negligible. So a large fraction of the atoms are located at the surface of the object in the nanomaterials, it will modify its properties. The properties of nanomaterials become totally different from what is observed in the bulk solid system.

The properties of nanomaterials are very much different from those at a larger scale. Two principal factors cause the properties of Nano Materials to differ significantly from other materials (1) Increased relative surface area and (2) Quantum confinement effect. These factors can charge or enhance properties such as reactivity, strength and electrical characteristics.

Increase in a Surface Area to Volume ratio: Nanomaterials have a relatively larger surface area when compared to the same volume or mass of the material produced in a larger form. When the given volume is divided into smaller pieces the surface area increases. So the particle size decreases a greater proportion of atoms are found at the surface compared to those inside. Hence Nanoparticles have a much greater surface area per given volume compared with larger particles. It makes materials more chemically reactive.

Quantum Confinement: In nanocrystals, the electronic energy levels are not continuous as in the bulk but are discrete (finite density of states), because of the confinement of the electronic Wave function to the physical dimensions of the particles**.** This phenomenon is called Quantum confinement If one length of three dimensional nanostructures is at nano-dimension, then it is called a ***Quantum Well***. If two sides of three dimensional nanostructures are at nano-dimension, then it is called a ***Quantum Wire***. If all three dimensional nanostructures is at nano-dimension (***Nano Crystals)***, are referred as ***Quantum Dots*** (***QDs***).

Properties of Nanomaterials: Nanomaterials have properties that are different from those of bulk materials**.** Most nanostructure materials are crystalline in nature and they have unique properties. Filling polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties.

Physical Properties: Crystal structure of nanoparticles is same as bulk structure with different lattice parameters**.** The inter-atomic spacing decreases with size and this is due to long range electrostatic forces and the short range core-core repulsion**.** The melting point of nanoparticles decreases with size.

Chemical Properties: A large fraction of the atoms are located at the surface of the nanomaterial which increase its reactivity and catalytic activity. The large surface area to volume ratio, the variations in geometry and the electronic structure of nano particles have a strong effect on catalytic properties.

Electrical properties: The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic properties of the materials. Nanoparticles made of semiconducting materials like Germanium, Silicon and Cadmium are not semiconductor. Nanoclusters of different sizes will have different electronic structures and different energy level separations. So they show diverse electronic properties which depend on its size.

Magnetic Properties: The magnetic moment of nano particles is found to be very less when compared them with its bulk size**.** Actually, it should be possible that non-ferromagnetic bulk exhibit ferromagnetic-like behavior when prepared in nano range. Bulk Gold and Pt are non-magnetic, but at the nano size they are magnetic.

Applications of Nanomaterials: (1) ***Chemical Industry:*** Fillers for point systems. Coating systems based on nano composites, Magnetic fluids (2) ***Automotive Industry:*** Light weight construction, Painting, Catalysts, Sensors (3) ***Medicine***: Drug delivery systems, Active agents, Medical rapid tests, Antimicrobial agents and coatings, Agents in cancer therapy (4) ***Electronic Industry:*** Data memory, Displays, Laser diodes, Glass fibers, Filters, Conductive, antistatic coatings (5) ***Energy Sources:*** Fuel cells, Solar cells, Batteries, Ultracapacitors (6) ***Cosmetics***: Sun protection creams, Tooth paste

Applications of Nanomaterials in Medicine: Medical application of nanomaterials include (a) Fluorescent biological labels (b) Drug and gene delivery (c) Bio-detection of pathogens (d) Detection of proteins (e) Probing of DNA structure (f) Tissue engineering (g) Tumour destruction (h) Separation and purification of biological molecules and cells**.**

Future application of Nanomedicine is as follows: (1) The elimination of bacterial infections in a patient within minutes (2) The ability to perform surgery at the cellular level, removing individual diseased cells and even repairing defective portions of individual cells (3) **Qdots:** that identify the location of cancer cells in the body, here nanomaterials that deliver chemotherapy drugs directly to cancer cells to minimize damage to healthy cells (4) **Nanocells:** that concentrate the heat from infrared light to destroy the cancer cells with minimal damage to surrounding health cells.

Applications of Nanomaterials in Catalysis: The extremely small size of the nanomaterials maximizes the surface area exposed to the reactants, allowing more reactions to occur. The application ranges from fuel cell to catalytic converters (nano-Pt), photocatalytic devices (e.g., nano-TiO_2) and for the production of chemicals (e.g.. nano-ZrO_2 in CO hydrogenation in isobutene synthesis)

There are two ways of approaching the properties of nanoscale objects: the ***Bottom-up*** approach and the ***Top-down*** approach.

In **Bottom-up** approach (or ***Atom-Atom Assembly***), one assembles atoms and molecules into objects whose properties vary discretely with the number of constituent entities, and then increases the size of the object until this discretisation gives way in the limit to continuous variation. The relevant parameter becomes the size rather than the exact number of atoms contained in the object.

In **Top-down** approach (Chisel away atoms), one considers the evolution of the properties of a sample as its size is whittled down from macroscopic toward nanometric lengths.

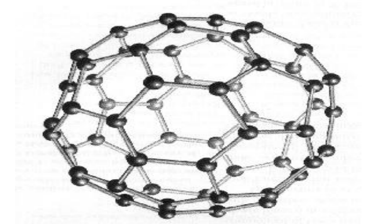
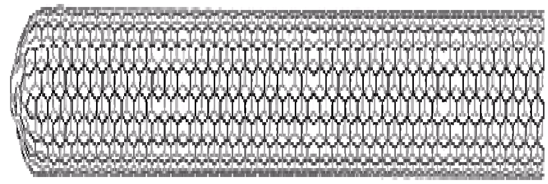
Carbon based Nanomaterials (or Nano carbons): They are defined as materials in which the nanocomponent is pure carbon. Fullerenes and carbon nanotubes are excellent examples of it.

When graphite was vapourized using a laser beam, H. Kroto, R. F. Curl and R. E. Smalley (in 1985) discovered a molecule that contained 60 carbon atoms as the major product called ***Fullerenes***. They realized that the molecule was a closed cage based on rings of 5 and 6 carbon atoms, looking just like a soccer ball**.** ***Carbon nanotubes (CNTs)*** are molecular tubes having diameters of a few nanometers (as low as 1 nm) made up of lattices of carbon atoms. CNTs were discovered in 1991 by the Japanese electron microscopist Sumio Iijima who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes.

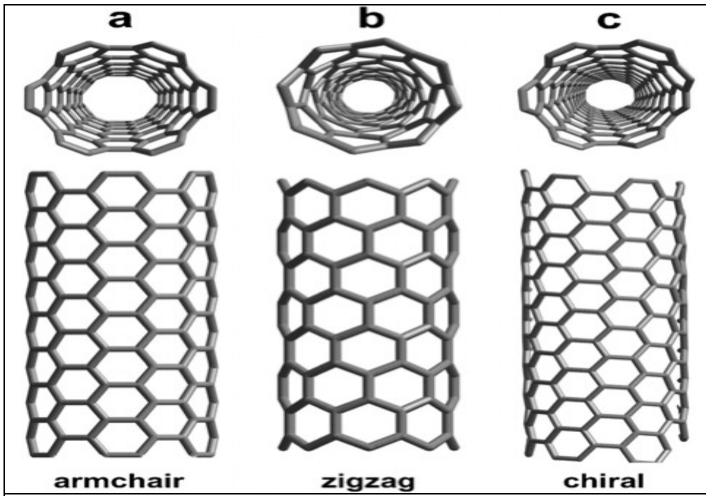
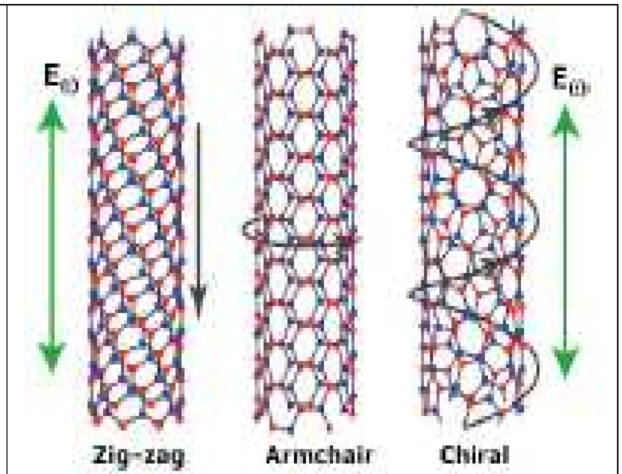
Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourized C_n small molecules consists of mainly C60 with smaller quantity of C70 and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having ‘dangling’ bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called ***Buckminsterfullerene*****.** Spherical fullerenes are also called ***Bucky balls*** in short.

Fullerenes are a class of cage-like carbon compounds that contained 60 carbon atoms, composed of fused pentagonal and hexagonal carbon rings, looking just like a soccer ball. It contains twenty six- membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. C-60 can be used as excellent microscopic ball bearings, lubricant and catalyst. They can cage other molecules, so in the future this may be used to deliver drugs in small amounts for slow release**,** e.g., cancer treatment.

Carbon Nanotubes (CNT) are sheets of graphite rolled to make a tube. They are molecular tubes (cylindrical nanostructure) having diameters of a few nanometers made up of lattices of carbon atoms. CNTs are at least 100 times stronger than steel, but only one-sixth as dense. In addition, they conduct heat and electricity far better than copper. So, CNTs can be used in tiny, physically strong conducting devices. CNTs have been filled with potassium atoms, making them even better electrical conductors.

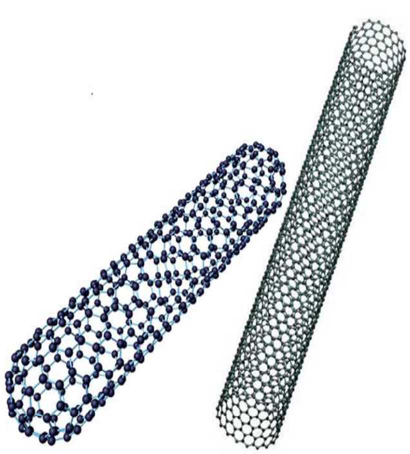
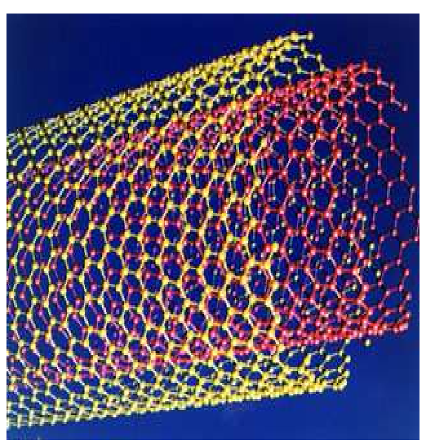
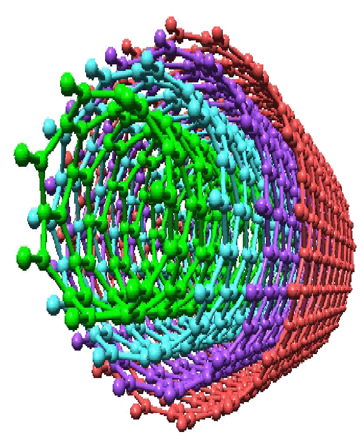
Fullerene (C60)	Carbon nanotube (CNT)
	

There are three kinds of nanotubes: (a) Armchair nanotubes containing a line of hexagons parallel to the axis of the nanotube, (b) Zigzag nanotubes where there is a line of carbon bonds down the centre and (c) Chiral nanotubes which exhibit a twist or spiral around the nanotube.

Armchair $\rightarrow$ metallic, Zigzag $\rightarrow$ semiconducting and Chiral $\rightarrow$ semiconducting

Carbon nanotubes exist as nanotubes within nanotubes, leading to the categorization as ***Single-Walled Carbon Nanotubes*** (**SWCNT**) and ***Multi-Walled Carbon Nanotubes*** (**MWCNT**). An SWNT contains only a single cylinder where as a MWCNT contains multiple concentric nanotube cylinders. They have diameter close to 1 nm. The structure SWNT/MWCNT can be conceptualized by wrapping a one-atom-thick layer/multi-atom-thick layer of graphite (graphine) into a seamless cylinder.

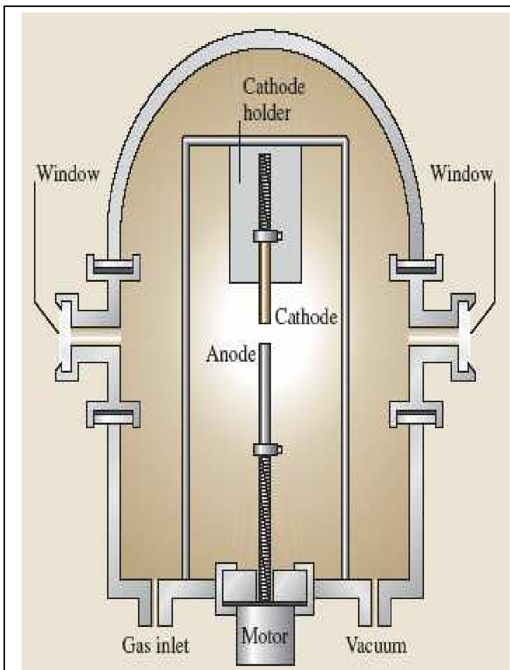
SWCNT	MWCNT	
		

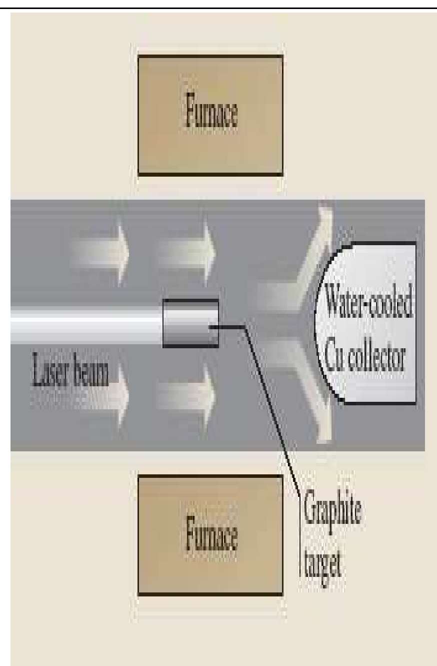
Synthesis of Carbon Nanotubes: Carbon nanotubes are generally produced by three main techniques; (1) ***Arc discharge*** (2) ***Laser ablation*** and (3) ***Chemical vapour deposition***.

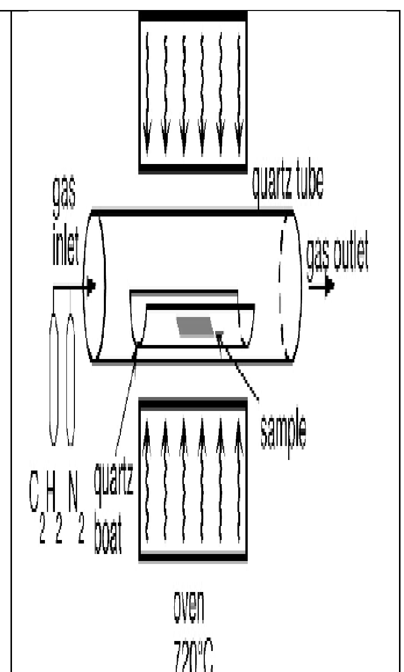
In **Arc Discharge Method,** a vapour of carbon atoms is created by an arc discharge between two graphite electrodes with or without catalyst. This vapour of carbon atoms self-assembles to form the carbon nanotubes. When pure graphite rods are used, the anode evaporates and it is deposited on the cathode, which contains CNTs. These CNTs are MWNTs. When a graphite rod containing metal catalyst (Fe, Co, etc.) is used as the anode with a pure graphite cathode, SWNTs are generated in the form of soot.

In **Laser Ablation Method,** a high power laser beam impinges on a graphite sheet, it vaporizes graphite and the vaporized carbon will then condense on a cooled surface, where carbon nanotubes will collect. High-quality SWNTs are produced from this method.

In **Chemical Vapor Deposition (CVD) Method,** it can be achieved by breaking the carbon-based gaseous molecules (methane, acetylene and carbon monoxide) into reactive atomic carbon in a high temperature furnace and sometime assisted by plasma to increase the generation of atomic carbon. ***To start the process***, a substrate is layered with metal catalyst (Ni or Co). The intended diameter of the carbon nanotubes is related to the size of the metal catalyst deposited or etched on the substrate. The substrate is heated to 700ºC, and carbon-based gases are then slowly delivered into the substrate's chamber. Two gases are used – one is called a "process gas", which would be ammonia, N_2, H_2, while the other is a carbon based gas (methane, acetylene and carbon monoxide). The carbon nanotubes grow on the catalyst because the carbon-based gas breaks apart at the catalyst surface. It is the one of the most common methods of carbon nanotube synthesis.





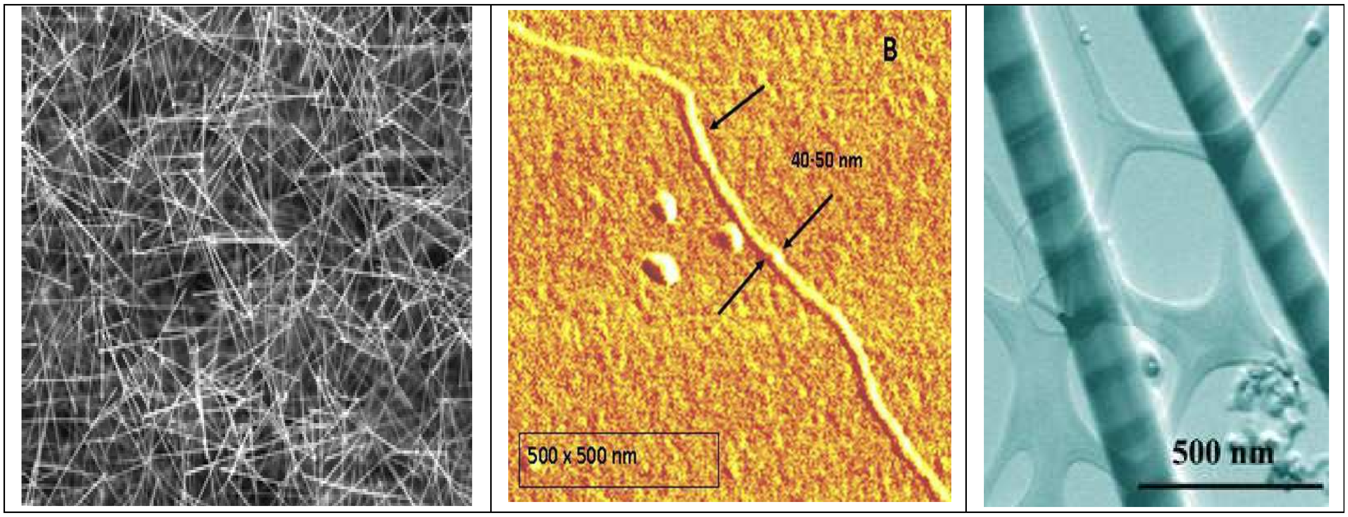


Important Properties of Carbon Nanotubes: It includes [1] **Strength:** They are the strongest and stiffest materials. [2] **Hardness:** SWNTs are used for synthesizing super-hard material, by compressing it at room temperature. [3] **Kinetic:** Multiple concentric nanotubes precisely nested within one another, exhibit telescoping property. [4] **Electrical:** Their electrical conductivity is better than metals. Electron travelling through a CNT behaves like a wave travelling through smooth channel - ***Ballistic Transport***. MWNTs with interconnected inner shells show superconductivity with relatively high temperatures. [5] **Thermal:** Their thermal conductivity also is better than metals. All nanotubes are expected to be very good thermal conductors along the tube but good insulators laterally to the tube axis - ***Blastic Conduction.*** The thermal stability of carbon nanotubes to be upto 2800ºC in vacuum and about 750ºC in air.

Application of Carbon Nanotubes: It includes [1] **Structural:** Its superior mechanical properties, uses ranging from everyday items like clothes and sports gear to combat jackets and space elevators. [2] In **Electrical Circuits:** Nanotube based transistors have been made that operates at room temperature. Carbon nanotubes are used for miniaturizing electronic devices. [3] As **Paper Batteries:** A paper battery is a battery engineered to use a paper thin sheet of cellulose infused with aligned carbon nanotubes. It gives a steady power output. This battery also functions as a super-capacitor which give a quick explode of high energy. [4] **Solar Cells:** It is formed by a mixture of carbon nanotubes and fullerenes. Electrons trapped inside fullerenes, add sunlight lead to the flow of this electrons which produce the current. [5] They are used for making **ultra-capacitors** which provide a large surface to store electrical charge. [6] They act as molecular size test tubes or capsules for drug delivery. [7] They are used as tips for analysis of DNA and proteins by Atomic Fourse Microscopey (AFM).

Nanowire: Nanowires are microscopic wires that have a width measured in nanometers. A nanowire is a connecting structure that has a diameter of 10^{-9} meters, which is extremely small. Typically, the diameter of nanowires range from 40 to 50 nanometers, but their length is not so limited. Since they can be lengthened by simply attaching more wires end to end or just by growing them longer, they can be as long as desired. Nanowires are also known as ***Quantum Wires***, these connectors are used to connect tiny components together into very small circuits.

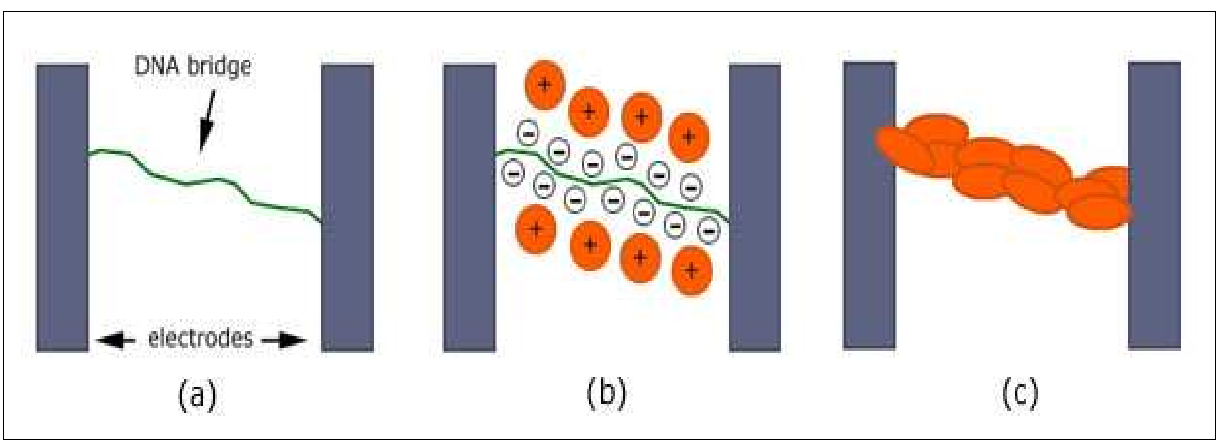
The electrical properties of nanowires are peculiar mainly because of their size and its conductivity is strongly influenced by edge effects. The edge effects arise from atoms that lie at the nanowire surface which are not fully bonded to neighbouring atoms as that in the bulk of the nanowire. These nonbonded atoms often become source of defects within the nanowire causing it to conduct electricity.



Four Different types of Nanowires: They are (a) **Metal nanowires** are made from nickel, platinum or gold (b) **Semi-conducting** wires are comprised of silicon, indium phosphide or gallium nitride, (c) **Insulating** wires are made of silicon dioxide or titanium dioxide (d) To create a **Molecular** nanowire, the process involves repeating organic or inorganic molecular units in a particular format.

Striped nanowires are capable of performing more than one task along the same wire. They are striped with different materials that posses different properties, an attribute which allows different operations to be performed at the same time. This also enables devices to be more compacted because fewer wires are needed; each nanowire is serving multiple functions.

Production of nanowires: A solution containing the desired metal is mixed with DNA and then exposed to UV light. When exposed, the metal in the mixture bonds to the DNA and forms a microscopic wire, a nanowire. Its width is dependent upon how concentrated the solution of the metal is. The more concentrated the metal solution, the wider the nanowire; likewise, the less concentrated, the thinner the wire will be.



Nanowires are not being heavily manufactured because they are still in the development stage and are only produced in the laboratory and have not moved to manufacturing plants. Until production has been streamlined, made easier and faster, they will not be heavily manufactured for commercial purposes.

Some uses of nanowires include: Nanowires are simply very small wires that will be able to greatly reduce the size of electronic devices while allowing us to increase the efficiency of those devices. The most apparent impact this will have on society would be the increase of storage space for MP3 players, computers, and phones without increasing size.

(1) Data storage/transfer - transfer data up to 1,000 times faster, and store data for as long as 100,000 years without degradation (2) Batteries/generators - tiny, efficient solar panels, turning light into energy, able to hold 10 times the charge of existing batteries (3) Transistors, LED's, Optoelectronic devices, Biochemical sensors and Heat-pumping thermoelectric devices.

Nanowires are also being developed for prototype sensors. These sensors will be used on gases and biological molecules. They will be used to detect harmful agents by scanning each gas or chemical on a molecular level. This is possible due to how small these wires can be. They will be made out of materials that react to harmful agents, thus alerting to the presence of harmful agents.

The conductivity and tiny size make them ideal for future computer processors and connectors. The use of nanowire in a transistor is an ideal method of producing smaller and faster microprocessor components for the computer and electronic industry. Although nanowire transistors function better than the current transistors, the high costs required to create them is a barrier to wider manufacturing.

Silicon Nanowires (SiNW): The most promising building blocks for future nanoscale electronic devices. Atomic configurations of silicon nanowires created through assembly of silicon clusters or created through etching of crystalline silicon. The small sizes of SiNWs make their electronic and electrical properties strongly dependent on growth direction, size, morphology and surface reconstruction. A well-known example is the size dependence of the electronic band gap width of SiNWs irrespective of wire direction. As the wire diameter decreases, the band gap of the nanowire widens and deviates from that of bulk silicon gradually

Applications: Silicon nanowire (SiNW) is a very attractive two-dimensional nanomaterial for future nanoelectronic applications.

1) Silicon nanowire solar cells which consists of arrays of radial p-n junction nanowires
2) Silicon nanowires can help to reduce the size of microchips
3) Scientists have fabricated a memory device that combines silicon nanowires with a more traditional type of data-storage. The device is a type of "non-volatile" memory, meaning stored information is not lost when the device is without power

Syllabus:

Introduction to Nanoscience – carbon nanotubes and nanowires – applications