

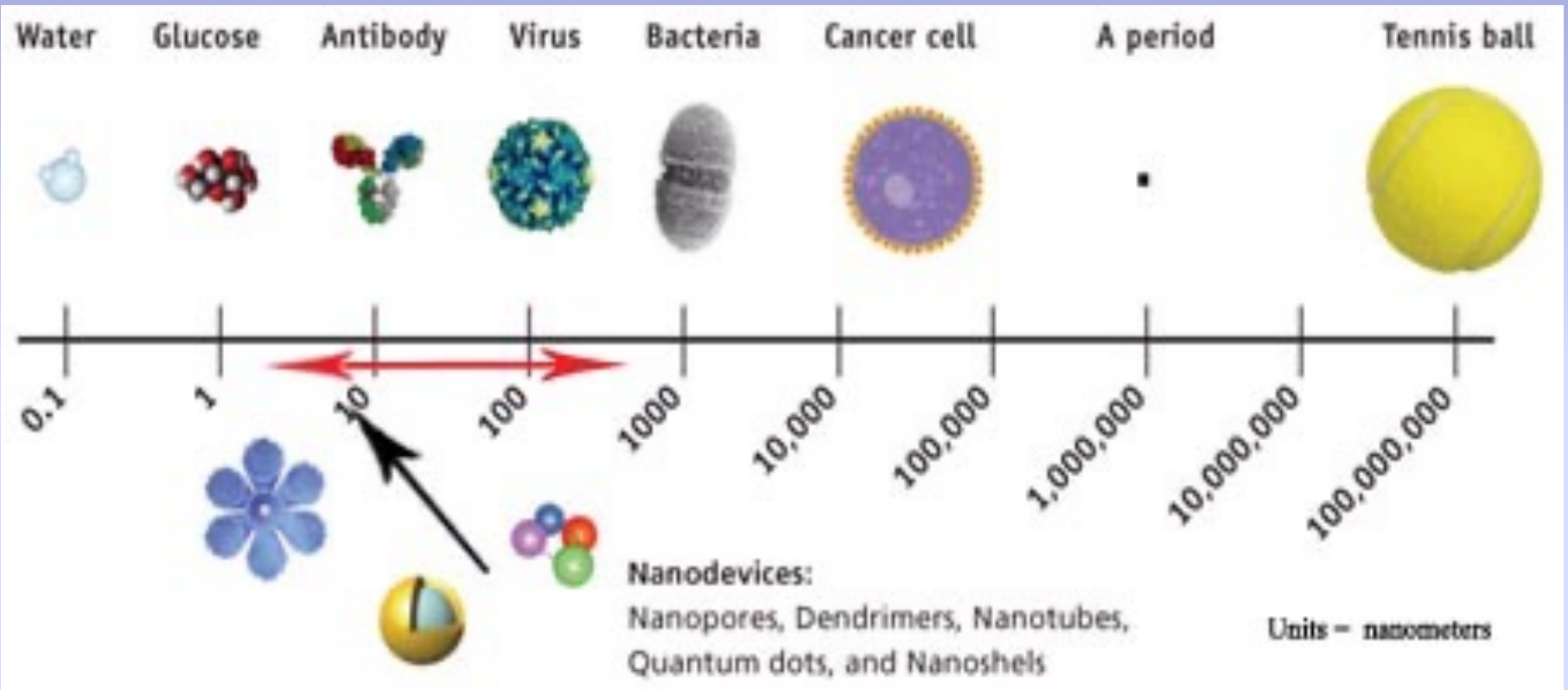
Nanomaterials

Nanotechnology

- is already making **today's** products:
 - Lighter
 - Stronger
 - Faster
 - Smaller
 - More Durable

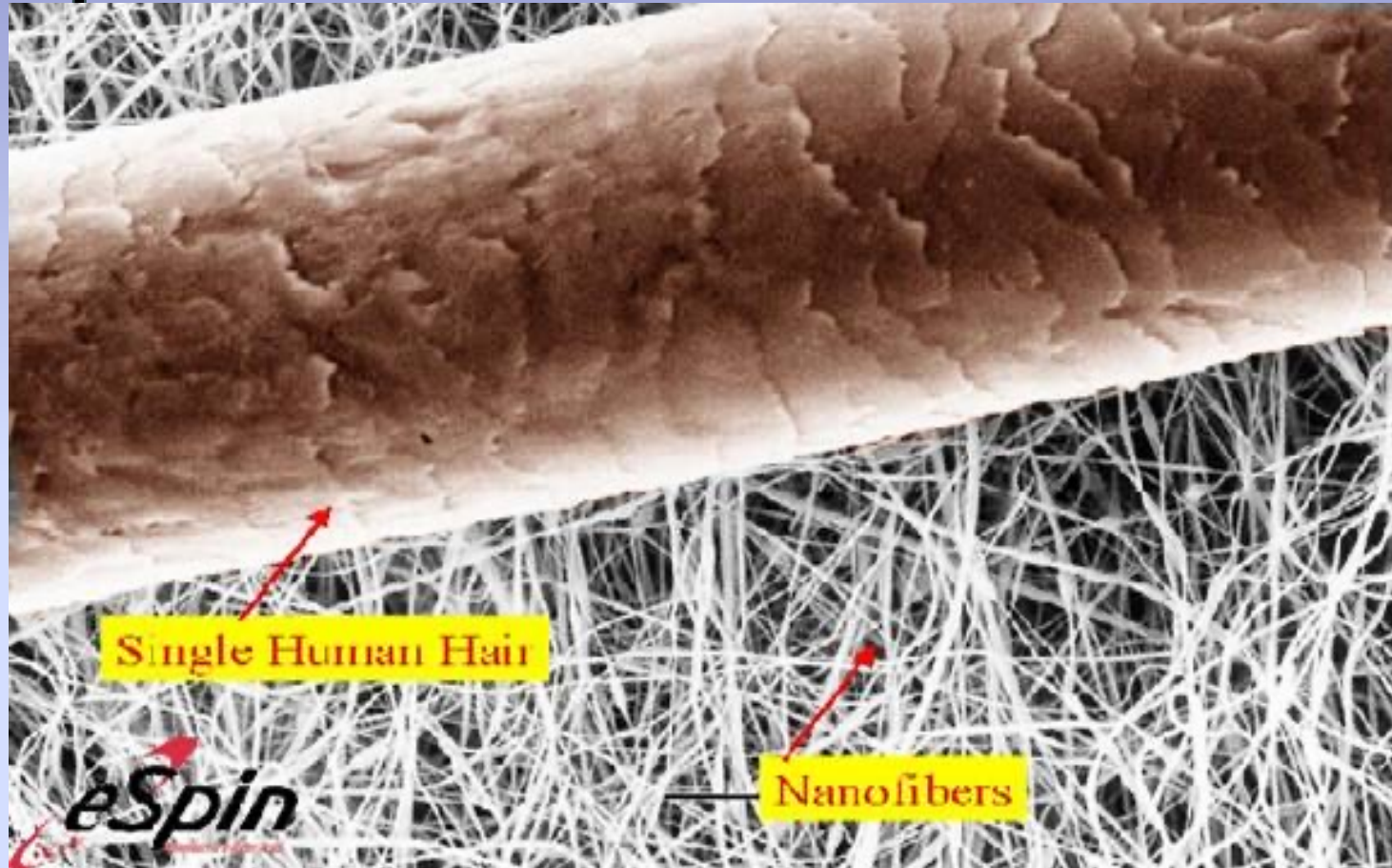


How small is Nano - small?



Units in nanometers (μm)

Compared to Human Hair



A Human Hair is about 100,000 μm wide

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers.

A nanometer is one millionth of a millimeter- approximately 100,000 times smaller than the diameter of a human hair.

Properties of Nanomaterials-

- (i) large fraction of surface atoms;
- (ii) high surface energy;
- (iii) spatial confinement;
- (iv) reduced imperfections,

Two principle factor causing properties of nanomaterials to differ significantly from bulk materials.

❖ **Relative surface area**

❖ **Quantum effects**

These property can change or enhance property such as reactivity, strength, electric and magnetic behaviour.

Surface Effect

- **As the size of particle decreases greater proportion of atom are found at the surface for e.g.**
 - Size 30 nm- 5% of atom on its surface**
 - Size 10 nm- 20% of atom on its surface**
 - Size 3 nm- 50% of atom on its surface**

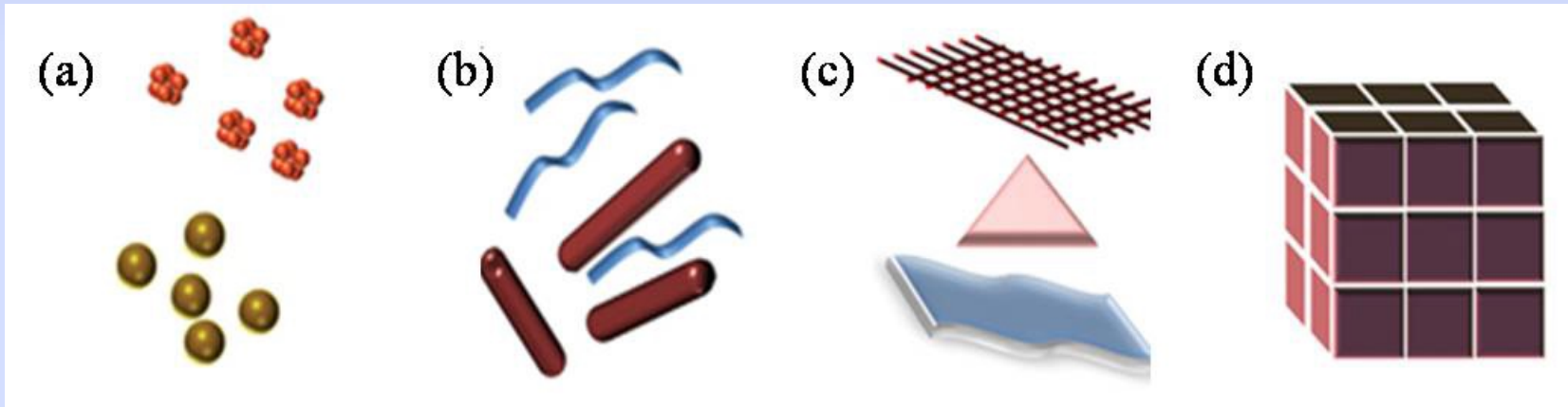
To understand the effect of particle size on surface area, consider an American Silver Eagle coin. This silver dollar contains 31 grams of coin silver and has a total surface area of approximately 3000 square millimeters. If the same amount of coin silver were divided into nanoparticles— say 10 nanometer in diameter— the total surface area of those particles would be 7000 square meters (which is equal to the size of a soccer field)

Quantum Effect

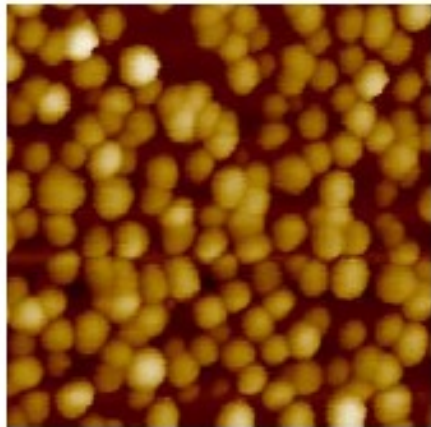
- The quantum confinement effect can be observed once the diameter of particle is of the same magnitude as the wavelength of electron
- Quantum confinement effect is responsible for increase of energy gap between energy state and band gap.
- When particles are small there electric, optical and magnetic properties differ significantly from bulk materials

Classification of Nano Materials

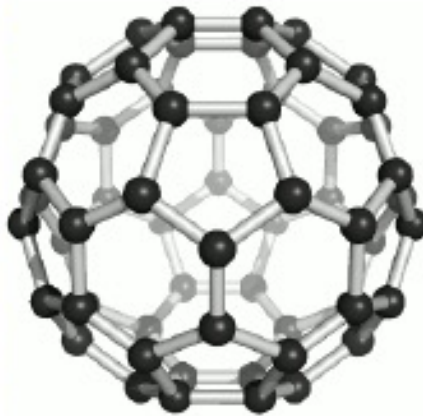
- Zero dimension (quantum dots)
- One dimension (quantum wires, rods)
- Two dimension (plates, network, quantum wells)
- Three dimension (fullerenes- C₆₀, haeckelites)



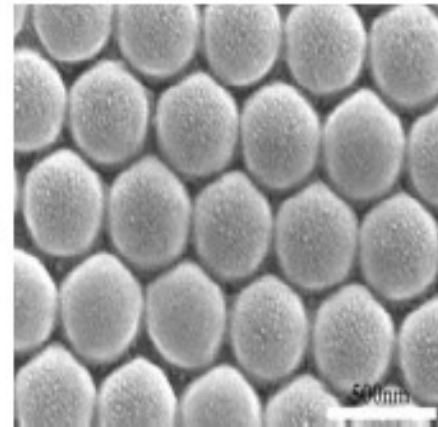
Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.



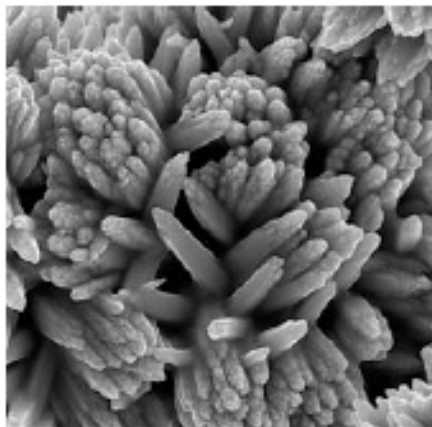
Au nanoparticle



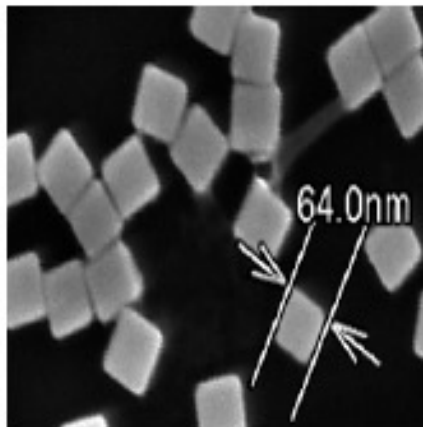
Buckminsterfullerene



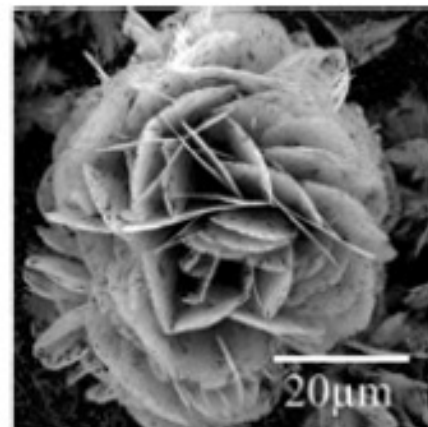
FePt nanosphere



Titanium nanoflower



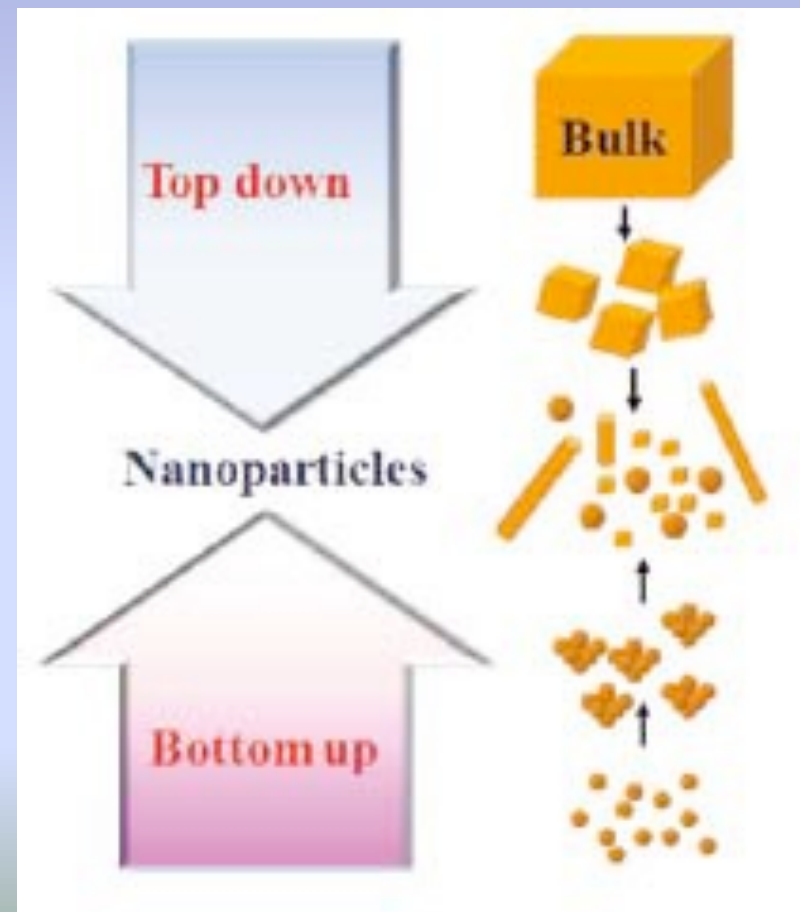
Silver nanocubes



SnO₂ nanoflower

- **Nanomaterial - synthesis and processing**
- Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the 'bottom up' or the 'top down' approaches to synthesize nanomaterials.

Schematic illustration of the preparative methods of nanoparticles.



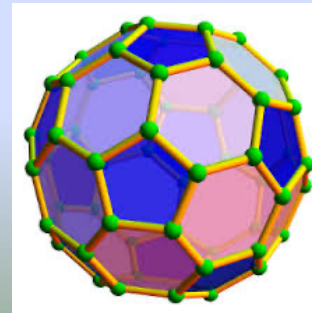
- **Bottom up**
- assemble atoms (*sol-gel method, precipitation etc.*)
- *Example, synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures)*

- **Top down**
- dis-assemble
- *For example, the synthesis of porous silicon by electrochemical etching*

- This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering upto medicine.

Fullerenes

- **Fullerenes** are spherical carbon-cage molecules with sixty (C₆₀) or more carbon atoms. The molecule was named after R. Buckminster Fuller, who confirmed structural formula . A hollow pure carbon molecule in which atom lies at the vertices of polyhedron with **12 pentagonal** faces and any number of hexagonal faces.
- Each carbon is bound to other three carbon in pseudo spherical arrangement of alternating pentagonal and hexagonal rings in the manner of soccer ball . Hence the nick name Bucky ball. They measure about **0.7-1.5 nm** in diameter. They are fascinating for scientists because they show unusual properties for carbon materials. Fullerenes are studied for potential medical use: they are strong antioxidants; one could also bind specific antibiotics to the structure to target resistant bacteria and even target certain cancer cells such as melanoma. Heat resistance and superconductivity are some of the more heavily studied properties of fullerenes in mechanical engineering.

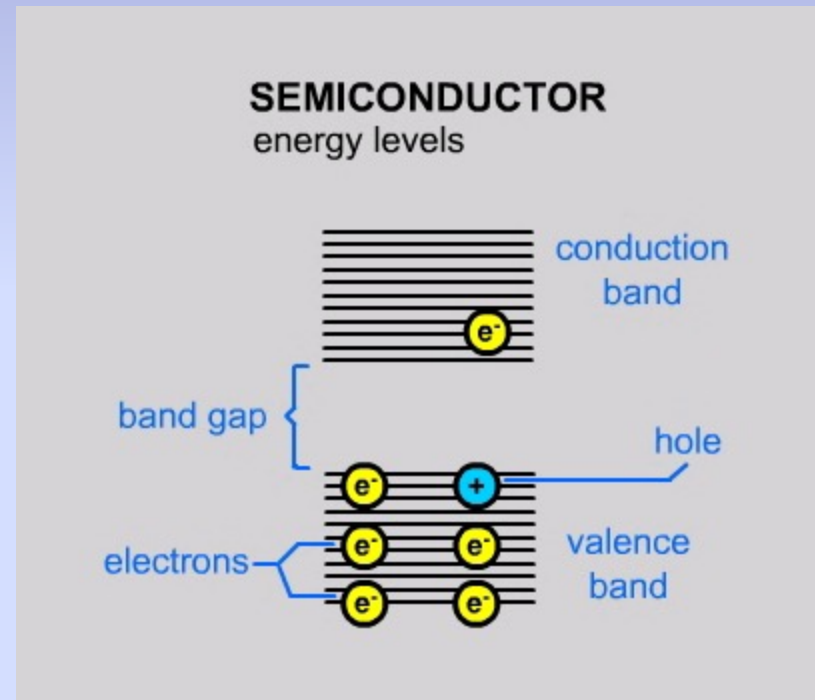


Quantum dot:

In two words, a **semiconductor nanocrystal**.

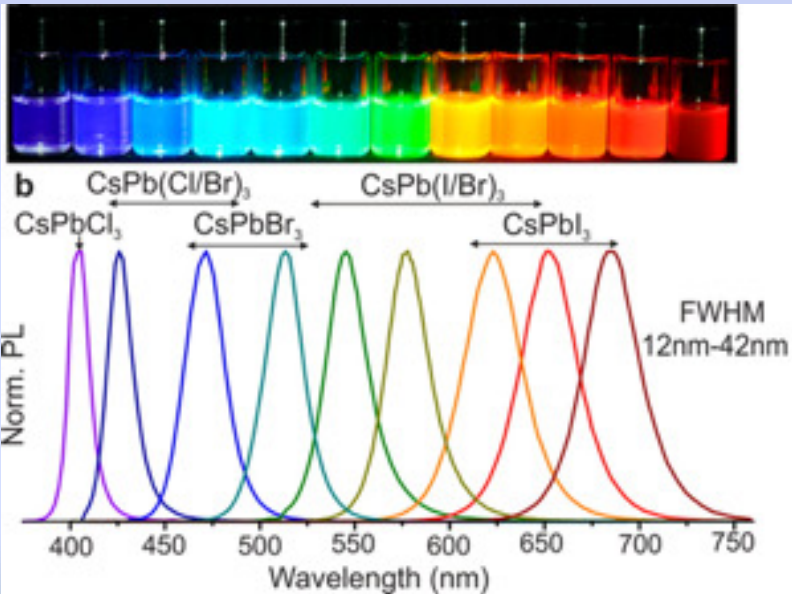
Easily tunable by changing the size and composition of the nanocrystal

- The average distance between an electron and a hole in an exciton is called the Excited Bohr Radius.
- When the size of the semiconductor falls below the Bohr Radius, the semiconductor is called a quantum dot.

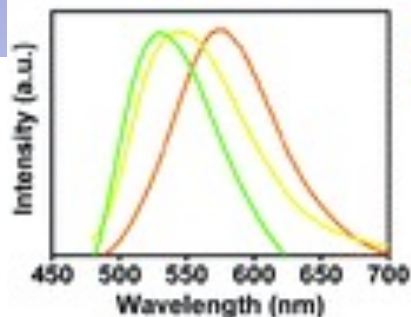
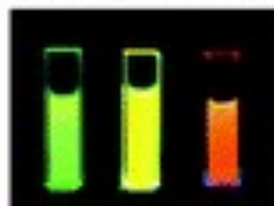


Tuning Quantum Dots

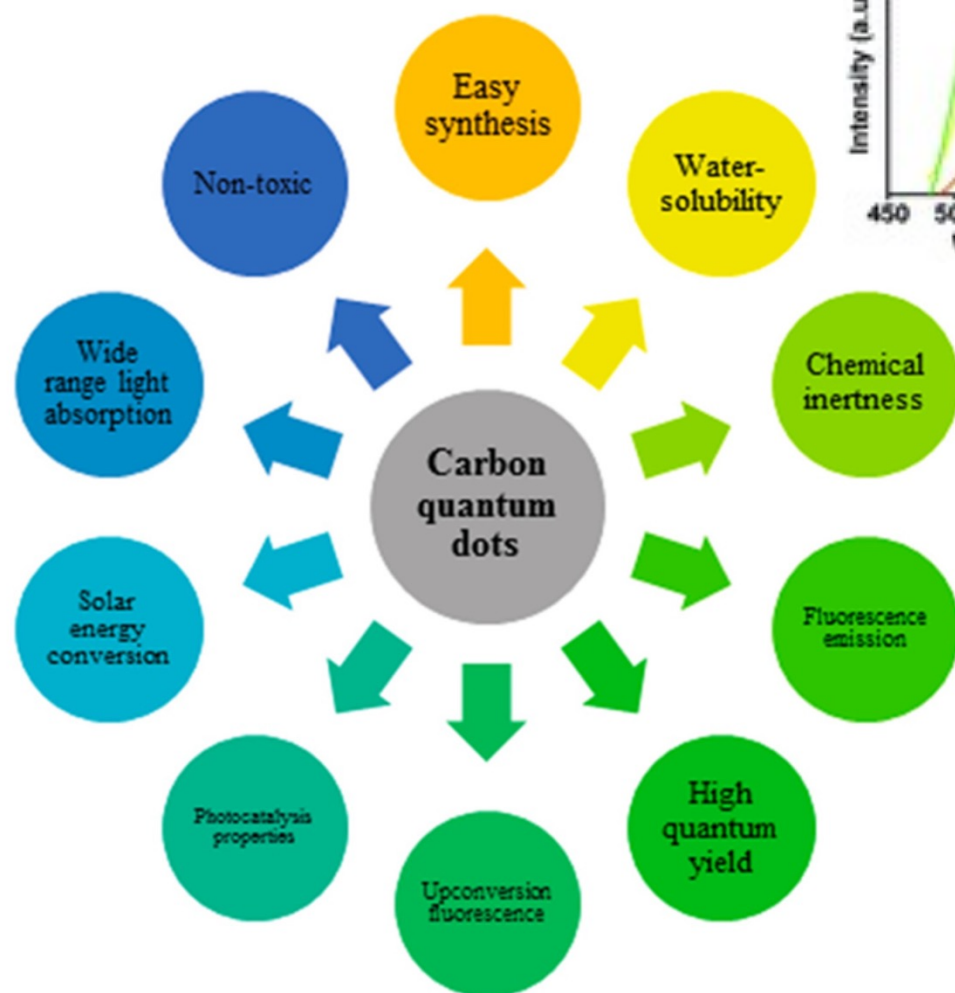
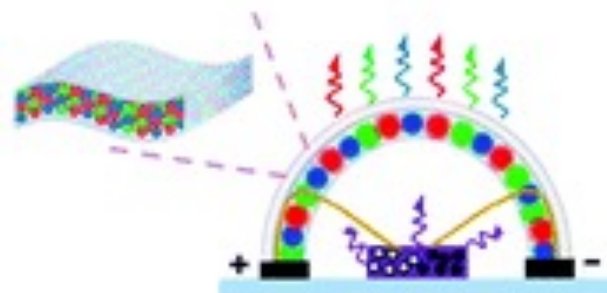
- By changing size, shape, and composition, quantum dots can change their absorptive and emissive properties dramatically



Multicolor Fluorescent Carbon Quantum Dots



White Light Emitting Diodes



Applications:

- **Medicine-**
- Can be set to any arbitrary emission spectra to allow labeling and observation of detailed **biological processes**.
- Quantum Dots can be useful tool for monitoring **cancerous cells** and providing a means to better understand its evolution.
- In the future, Qdots could also be armed with tumor-fighting toxic therapies to provide the **diagnosis and treatment** of cancer.
- Qdots are much more resistant to degradation than other optical imaging probes such as organic dyes, allowing them to **track cell processes** for longer periods of time.
- Quantum dots offer a wide **broadband absorption** spectrum while maintaining a distinct, static emission wavelength.

- **LED-**
- Used to produce inexpensive, industrial quality **white light**.
- Marked improvement over traditional LED–phosphor integration by dot’s ability to absorb and emit at **any desired wavelength**.
- Produce white light by **intermixing** red, green, and blue emitting dots homogenously within the phosphor difficult to accomplish with the traditional LED-phosphor set up.

Solar Cells and Photovoltaics

- Traditional solar cells are made of semi-conductors and expensive to produce. Theoretical upper limit is 33% efficiency for conversion of sunlight to electricity for these cells.
- Utilizing quantum dots allows realization of third-generation solar cells at **~60% efficiency** in electricity production while being **\$100 or less per** square meter of paneling necessary.
- Effective due to quantum dots' ability to preferentially absorb and emit radiation that results in optimal generation of electric current and voltage.

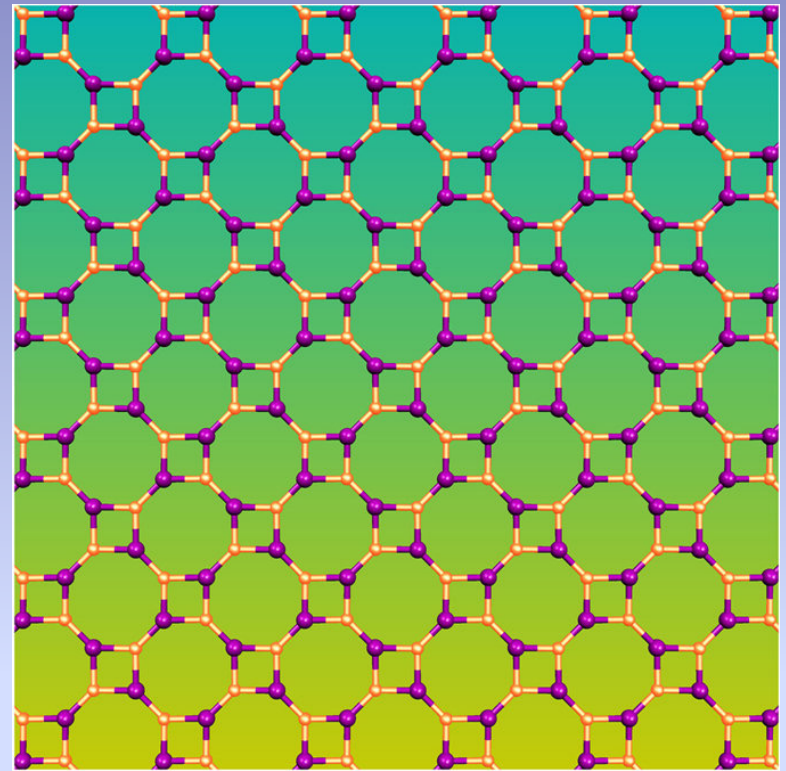
- **Other Future Quantum Dot Applications...**

- **Anti-counterfeiting capabilities:** inject dots into liquid mixtures, fabrics, polymer matrices, etc. Ability to specifically **control absorption** and emission spectra to produce **unique validation signatures**. Almost impossible to mimic with traditional semi-conductors.
- **Counter-espionage / Defense applications:** Integrate quantum dots into dust that **tracks enemies**. Protection against friendly-fire events.
- Research continues. The possibilities seem endless...

The name 'Haeckelite' has been proposed to designate a three-fold coordinated network generated by a periodic arrangement of pentagons, hexagons and heptagons

Starting from a planar Haeckelite array, tubular structures are obtained by applying the same wrapping procedure as for the usual nanotubes, which are rolled up sheets of graphene.

The Haeckelite nanotubes may adopt various shapes, among which coiled structures, doublescrew molecules, corrugated cylinders, and pearl-necklace-like nanotubes are the most spectacular.



GaN Haeckelite 8-4

- A planar structure containing square and octagonal rings which is called Haeckelites 8-4

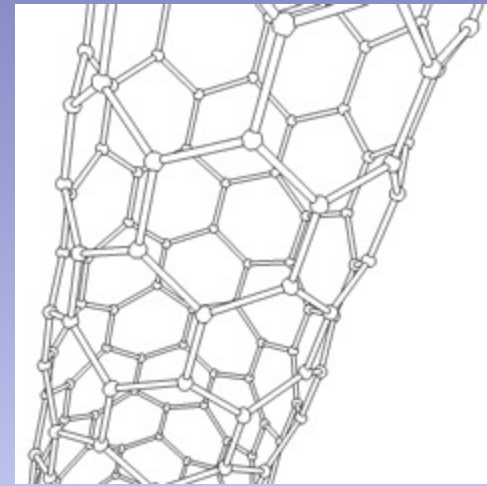
Properties:

- * Regular coiled nanotubes exhibit exceptional mechanical, electrical, and magnetic properties due to the combination of their peculiar helical morphology and the fascinating properties of nanotubes.**
- * For straight nanotubes with small diameter, it has been demonstrated that they exhibit either metallic or semiconducting electrical conduction depending on their chiral vectors and independent of the presence of dopant or defects.**
- * coiled nanotubes can show even semimetallic characteristics, in addition to the metallic and semiconducting behaviors, which could not be manifested in straight nanotubes.**
- * Straight carbon nanotubes as discontinuous reinforcement for polymer matrices is regarded as the ultimate carbon fiber with break strengths as high as 200 GPa and elastic moduli in the 1 TPa range.**
- * Carbon nanotubes also have aspect ratios of around 10³, w500 times more surface area per gram, and possess extraordinary capability of returning to their original, straight structure following deformation**

Applications of haeckelites:

- * Potential to be incorporated in various nano-technology devices as mechanical components in the form of **resonating elements or nano-springs** and in novel **reinforcement composites**.
- * carbon-based material that can be used as **carbon fillers** in reinforcement composites.
- * **tactile sensors** incorporating carbon micro-coils had better discrimination abilities when compared to conventional sensors, making haeckelites novel tactile sensors.
- * ability to **inhibit the breeding of keloid fibroblast**, i.e., cancer cells associated with leukaemia of the uterus.
- * useful as **electromagnetic nano-transformers or nano-switches**.
- * useful as a tool to **detect mass change** as small as a few tens of attograms.

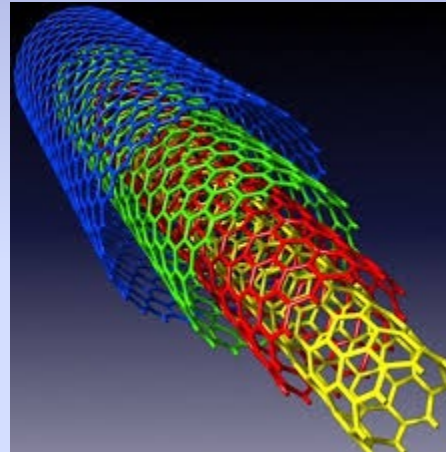
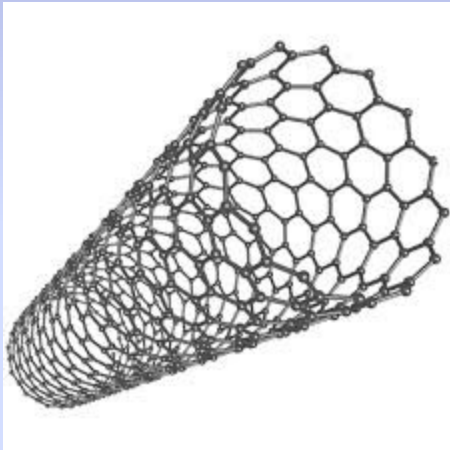
Carbon nanotubes(CNT)



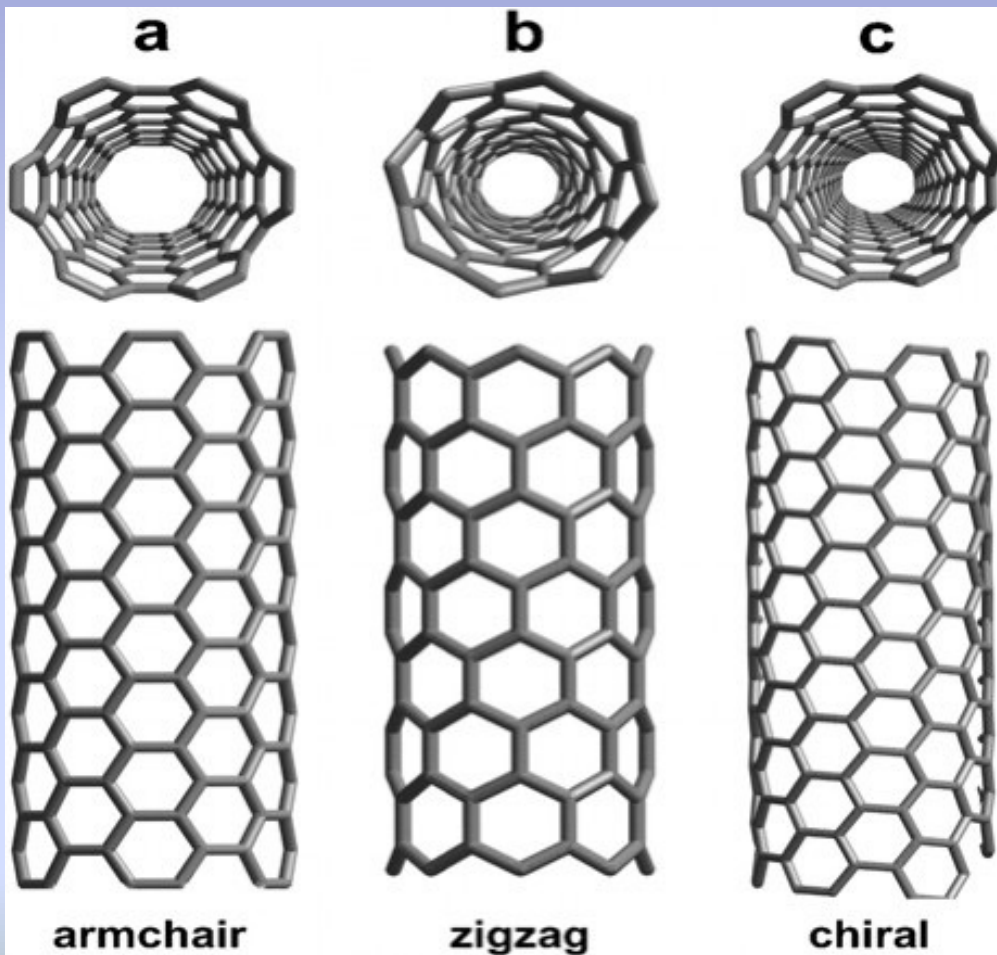
- Their name is derived from long hollow structure with wall formed by one atom thick sheets of carbon called graphene. These sheets are rolled at specific and discrete (chiral) angle. The combination of rolling angle and radius decides the nano tubes properties For e.g. Whether nano tube shell is metal or semi conductor.
- They have outstanding mechanical and electronic properties and are good thermal conductors. The tensile strength, or breaking strain of CNTs is 6-7 times that of steel. They are among the stiffest and strongest fibers known. CNTs can be metallic or semiconducting depending on their structure. Some CNTs are the most efficient electrical conductors ever made, while others behave more like silicon. These properties, coupled with the lightness of carbon nanotubes, give them great potential for use in reinforced composites, nanoelectronics, sensors and nanomechanical devices.

Classification of Carbon nanotubes

- Carbon nano tubes are categorized as,
Single walled nano tubes (**SWNT**) Multi walled nano tubes (**MWNT**)



Nanotubes have been constructed with length-to-diameter ratio of up to **132,000,000 :1** significantly larger than for any other material. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology



Single-walled

carbon nanotubes:

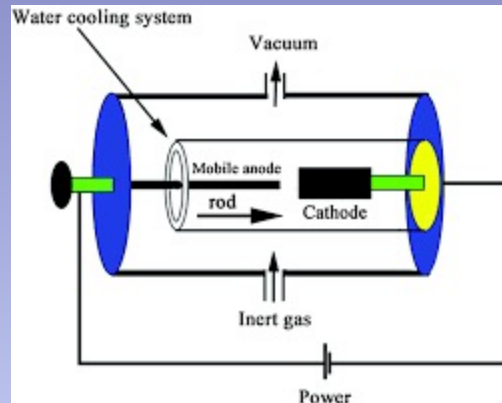
- armchair - metallic
- zigzag - semiconducting
- chiral - semiconducting

- multi-walled - metallic

Method of Preparation

- Arc Method
- Laser Method
- Chemical deposition method

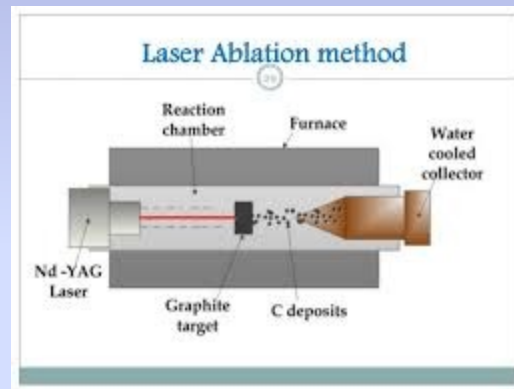
Arc Method



- The carbon arc discharge method, initially used for producing C₆₀ fullerenes, is the most common and perhaps easiest way to produce CNTs, as it is rather simple. However, it is a technique that produces a complex mixture of components, and requires further **purification**- to separate the CNTs from the soot and the residual catalytic metals present in the crude product. This method creates CNTs through arc-vaporization of **two carbon rods placed** end to end, separated by approximately **1mm**, in an enclosure that is usually filled with **inert** gas at low pressure. Recent investigations have shown that it is also possible to create CNTs with the arc method in liquid nitrogen. A direct current of **50 to 100A**, driven by a potential difference of approximately **20V**, creates a **high temperature discharge** between the two electrodes. The discharge **vaporizes the surface** of one of the carbon electrodes, and forms a small **rod-shaped deposit** on the other electrode. Producing CNTs in **high yield depends on the uniformity of the plasma arc, and the temperature** of the deposit forming on the carbon electrode.

Laser Method

- In 1996 CNTs were first synthesized using a **dual-pulsed laser**. Samples were prepared by laser vaporization of **graphite rods** with a **50:50 catalyst mixture of Cobalt and Nickel** at **1200°C** in **flowing argon**, followed by **heat treatment in a vacuum at 1000°C** to remove the C₆₀ and other fullerenes. The **initial** laser vaporization pulse was followed by a **second pulse**, to vaporize the target more uniformly. The use of **two successive** laser pulses **minimizes** the amount of carbon deposited as **soot**.



- The second laser pulse breaks up the larger particles ablated by the first one, and feeds them into the growing nanotube structure. The material produced by this method appears as a **mat of "ropes"**, **10-20nm in diameter and up to 100µm or more in length**. Each rope is found to consist primarily of a bundle of **single walled** nanotubes, aligned along a common axis. By **varying** the growth **temperature**, the **catalyst** composition, and other process **parameters**, the average nanotube **diameter and size** distribution can be varied.

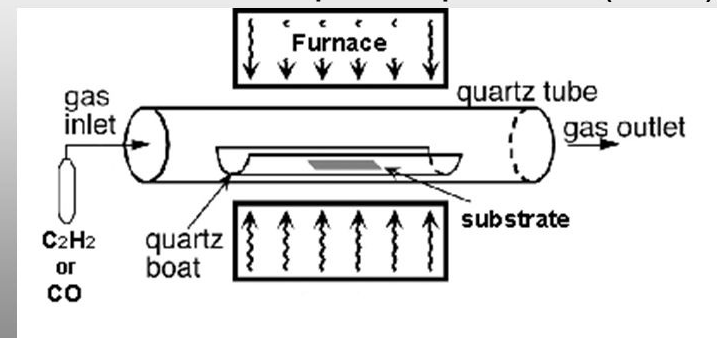
Chemical Vapor Deposition

- The simplest method to produce nanoparticles is by heating the desired material in a furnace containing the desired material.
- Large amounts of CNTs can be formed by **catalytic CVD of acetylene over Cobalt and iron catalysts supported on silica or zeolite**. In this method gases like CH_4 and C_2H_6 are cracked under the pressure of 10^4 Pa in presence of catalyst like Fe, Co, Ni, Pt .
- Catalyst plays very important role in formation of carbon nanotubes.
- Both **MWNT** and **SWNT** can be obtained by this method. **SWNT** can be produced at $600-1150^\circ\text{C}$ and **MWNT** are produced at low temperature of $300-800^\circ\text{C}$.

Synthesis Method of CNT



III. Chemical Vapor Deposition (CVD)



MWCNT	SWCNT
600-800 °	900-1000 °
$\text{C}_2\text{H}_2 \rightarrow 2\text{C} + \text{H}_2$	$2\text{CO} \rightarrow \text{C} + \text{CO}_2$

Main properties of carbon nanotubes

- Electrical Conductivity
- Strength and Elasticity
- Thermal Conductivity
- High aspect ratio and Field emission

Electrical Conductivity

- The conductivity of CNT have been found to be function of their **chirality**, degree of **twist** as well as **diameter**. CNTs can be either metallic or semi conductor. The **resistivity** of single walled nanotubes ropes was of the order of 10^{-4} ohm-cm at 27°C . This means they are the most **conductive** carbon fiber known. The current **density** that was possible to achieve was 10^9 A/cm² (while copper burn at 10^6 A/cm²) It has been reported that SWNT may contain some defects. This defects allow the SWNT to act as **transistors, rectifying diodes**. It has also been reported that single wall nanotubes can route **electrical speed** up to 10 GHz.

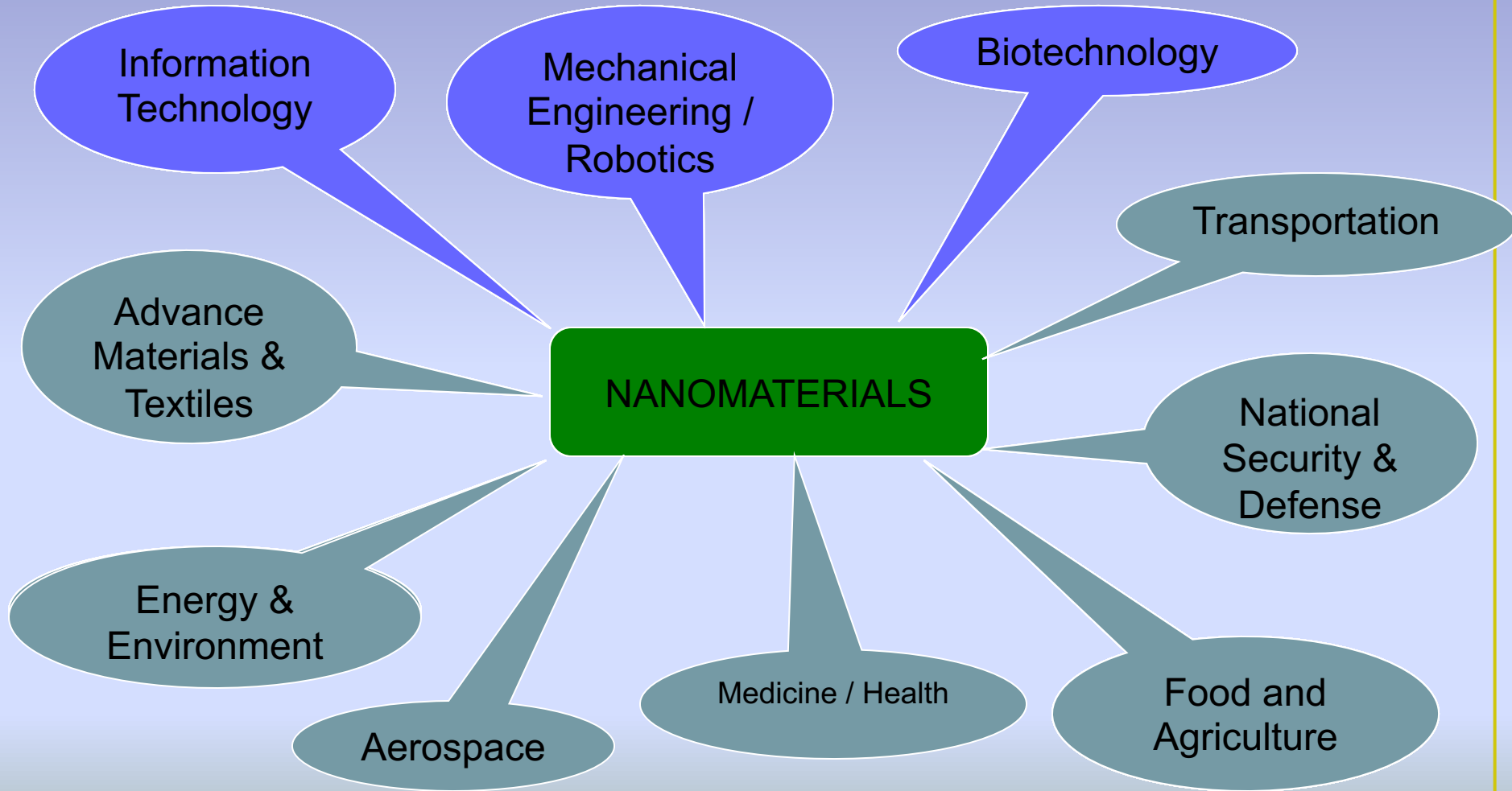
Strength and Elasticity

- CNTs are expected to be ultimate **high strength** fiber. Single walled nanotubes are **stiffer than steel** and are **resistant** to damage from physical forces. Pressing on the tip of nanotubes will cause it to **bend without damage** to the tip. This property make CNTs very useful as probe tip for **high resolution scanning** probe microscopy. The current **Young's modulus** value for single walled nanotubes is about 1 teraPascal but this value is highly disputed and a value as **high** as 1.8 TPa(tera Pascal). Young modulus depend on **size and chirality** of single walled nano tube.

Thermal conductivity and High aspect ratio

- CNTs have been shown to exhibit **superconductivity** below 20°K. Preliminary experiments and simulation studies on thermal property of CNT show very **high thermal conductivity**. It is expected therefore nanotube **reinforcement** in polymeric materials may also significantly improve the **thermal and thermo mechanical properties** of composites. CNTs represent very **high aspect ratio**. The high aspect ratio means that **lower loading** of CNTs is needed than to other conductive material. CNTs have proven to be **excellent additives** to impart electric conductivity in plastics.

Application of nanomaterials



Nano mechanics and lubricants

Carbon nanotubes are **stiff and hard** like diamond but **flexible** due to this they find several **mechanical application**. Cutting tools made up of Nano crystalline materials such as tungsten carbide titanium carbide are more **wear resistant** than convectional counter parts. They find application in **drill, helmets, bullet proof cloth**, etc. At present fastest known **oscillators** are made up of nanotubes. Nanotubes develop material which are **slicker** than Teflon and also **waterproof**. Membrane made up of CNTs allow **liquid flow** up to five times faster than conventional membrane.

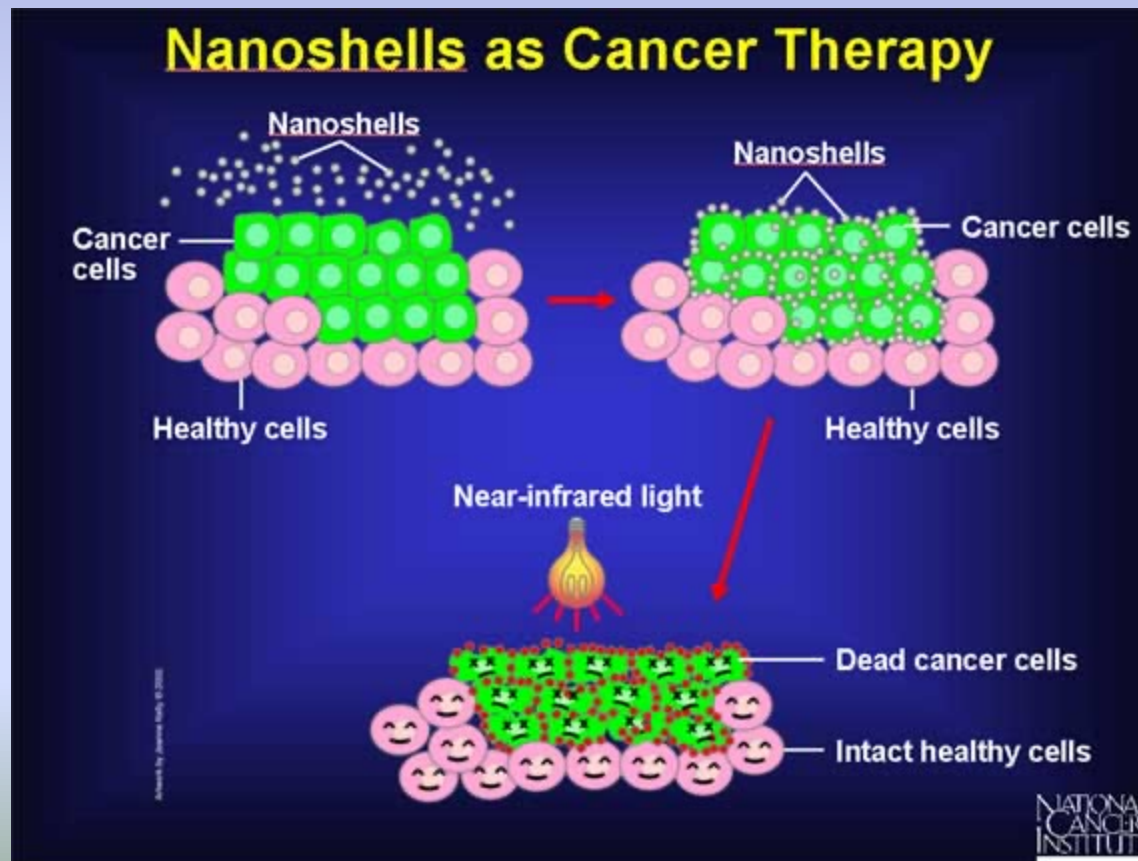
Nano sphere of inorganic material can act as **nano sized ball bearing**. They also find application in **high performance engine and drivers**.

Medicine

- Nanomaterials are of the size 10^{-9} . Hence they are smaller or comparable than **single cell, virus, protein**. Thus materials can freely **move through tissue or bind to biological system**. Endothelium layers are porous thus nano particle can **penetrate** through them and can be used as medicine or **carrier**. Many of magnetic nano particles have been used in **cancer therapy** like hyperthermia. Magnetic particles are also used for **tagging** cancer cells, bacteria red blood cells. They are also used in **contrast enhancing** agent in MRI. Thus they can be used to **detect** brain tumor liver tumor and lymph nodes.

Nano shells as Cancer Therapy

Nano shells are **injected** into cancer area and they **recognize** cancer cells. Then by applying **near-infrared light**, the heat generated by the light-absorbing Nano shells has successfully **killed** tumor cells while leaving neighboring cells intact.



Environment & Catalyst

- With nano technology it is possible to synthesize metal nano particles of highly ordered mono dispersed film. These nano catalyst **greater activity and specific in action**. It is possible to achieve **specific or selective activity**. This will reduce huge requirement of all **rare earth metal** in the production of catalyst
- Nano porous aluminum silicates(zeolites) are used in **water treatment**. Nano porous membrane with definite and desired pore are used as **nano filters** for dust and impurities from air and water. Gold nano particles are used for **degradation of toilet odor**. Nano ZnO is used for **degradation of chlorinated phenol**. Nano photo catalyst are used for **degradation of pollutant** present in waste water. Nanomaterials are used as
- catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in **automobile catalytic converters** and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

Electronics

- Traditional electronic circuits are built by etching individual
- components into silicon wafers. Rapid technological progress was first predicted in 1965 by Gordon Moore who stated that integrated circuit(IC) **density and performance** would double every 18 months. **Electronic miniaturization** has been the true driving force for nanotechnology research and applications. *Nano electronics* can help us to improve the **capabilities** of electronics devices while we **reduce their weight and power consumption**. Nanotechnologies are therefore expected to enable the production of smaller, cheaper devices with **increasing efficiency**. CNTs are being used for **low voltage** field emission displays. Nano crystalline nickel and metal hydrides are envisioned to require **less frequent recharging and last longer**. Nano scale fabricated magnetic material find application in **data storage**. Nanowires for junctionless transistors.

Importance of Nanomaterials-

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

(i) Nano-phase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.

(ii) Nano-structured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.

(iii) Nano-sized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.

(iv) Single nano-sized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the super-paramagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration.

(v) Nano-structured metal clusters and colloids of mono- or plurimetallic composition

have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Core-shell-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical

transformations and electro-catalysis (fuel cells). Enantioselective catalysis was also

achieved using chiral modifiers on the surface of nanoscale metal particles.

(vi) Nano-structured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NO_x, CO, CO₂, CH₄ and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO₂) finds application for rechargeable batteries for cars or consumer goods. Nano-crystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.

(vii) Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

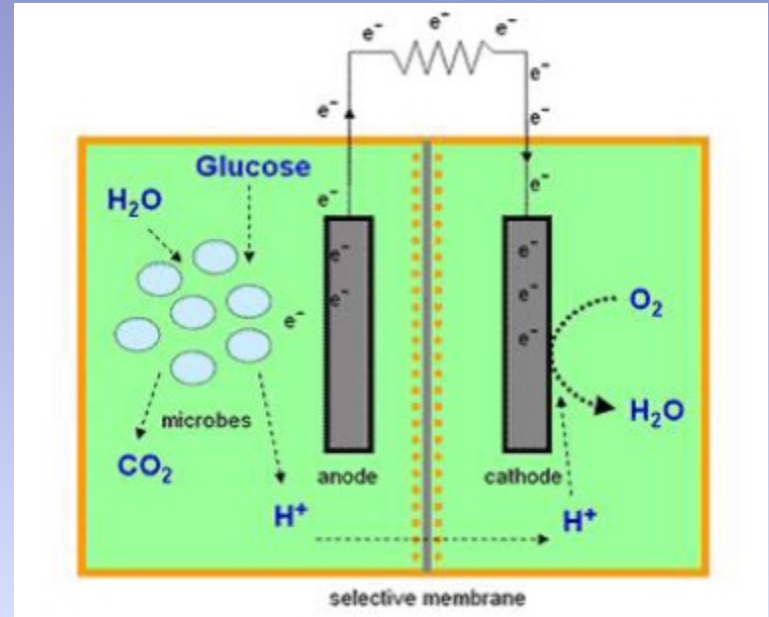
- Nano-Aluminium is used as solid fuel in rocket propulsion.
- Sun-screen lotions containing nano-TiO₂ provide enhanced sun protection factor (SPF) by blocking UV radiation while eliminating stickiness.

Carbon nanotubes- Microbial fuel cell

Microbial fuel cell is a device in which bacteria consume water-soluble waste such as sugar, starch and alcohols and produces electricity plus clean water. This technology will make it possible to generate electricity while treating domestic or industrial wastewater.

Microbial fuel cell can turn different carbohydrates and complex substrates present in wastewaters into a source of electricity.

The efficient electron transfer between the microorganism and the anode of the microbial fuel cell plays a major role in the performance of the fuel cell. The organic molecules present in the wastewater possess a certain amount of chemical energy, which is released when converting them to simpler molecules like CO₂. The microbial fuel cell is thus a device that converts the chemical energy present in water-soluble waste into electrical energy by the catalytic reaction of microorganisms.



Schematic representation of microbial fuel cell

- Carbon nanotubes (CNTs) have chemical stability, good mechanical properties and high surface area, making them ideal for the design of sensors and provide very high surface area due to its structural network. Since carbon nanotubes are also suitable supports for cell growth, electrodes of microbial fuel cells can be built using of CNT.
- Due to three-dimensional architectures and enlarged electrode surface area for the entry of growth medium, bacteria can grow and proliferate and get immobilized.
- Multi walled CNT scaffolds could offer self-supported structure with large surface area through which hydrogen producing bacteria (e.g., *E. coli*) can eventually grow and proliferate. Also, CNTs and MWCNTs have been reported to be biocompatible for different eukaryotic cells. The efficient proliferation of hydrogen producing bacteria throughout an electron conducting scaffold of CNT can form the basis for the potential application as electrodes in MFCs leading to efficient performance.

Disadvantages of Nanomaterials

(i) **Instability of the particles** - Retaining the active metal nanoparticles is highly challenging, as the kinetics associated with nanomaterials is rapid. In order to retain nanosize of particles, they are encapsulated in some other matrix. Nanomaterials are thermodynamically metastable and lie in the region of high-energy local-minima. Hence, they are prone to attack and undergo transformation. These include poor corrosion resistance, high solubility, and phase change of nanomaterials. This leads to deterioration in properties and retaining the structure becomes challenging.

(ii) **Fine metal particles act as strong explosives** owing to their high surface area coming in direct contact with oxygen. Their exothermic combustion can easily cause explosion.

(iii) **Impurity** - Because nanoparticles are highly reactive, they inherently interact with impurities as well. In addition, encapsulation of nanoparticles becomes necessary when they are synthesized in a solution (chemical route). The stabilization of nanoparticles occurs because of a non-reactive species engulfing the reactive nano-entities. Thereby, these secondary impurities become a part of the synthesized nanoparticles, and synthesis of pure nanoparticles becomes highly difficult.

Formation of oxides, nitrides, etc can also get aggravated from the impure environment/ surrounding while synthesizing nanoparticles. Hence retaining high purity in nanoparticles can become a challenge hard to overcome.

(iv) **Biologically harmful** - Nanomaterials are usually considered harmful as they become transparent to the cell-dermis. Toxicity of nanomaterials also appears predominant owing to their high surface area and enhanced surface activity. Nanomaterials have shown to cause irritation, and have indicated to be carcinogenic. If inhaled, their low mass entraps them inside lungs, and in no way they can be expelled out of body. Their interaction with liver/blood could also prove to be harmful (though this aspect is still being debated on).

(v) **Difficulty in synthesis, isolation and application** - It is extremely hard to retain the size of nanoparticles once they are synthesized in a solution. Hence, the nanomaterials have to be encapsulated in a bigger and stable molecule/material. Hence free nanoparticles are hard to be utilized in isolation, and they have to be interacted for intended use via secondary means of exposure. Grain growth is inherently present in nanomaterials during their processing. The finer grains tend to merge and become bigger and stable grains at high temperatures and times of processing.

(vi) **Recycling and disposal** - There are no hard-and-fast safe disposal policies evolved for nanomaterials. Issues of their toxicity are still under question, and results of exposure experiments are not available. Hence the uncertainty associated with affects of nanomaterials is yet to be assessed in order to develop their disposal policies.