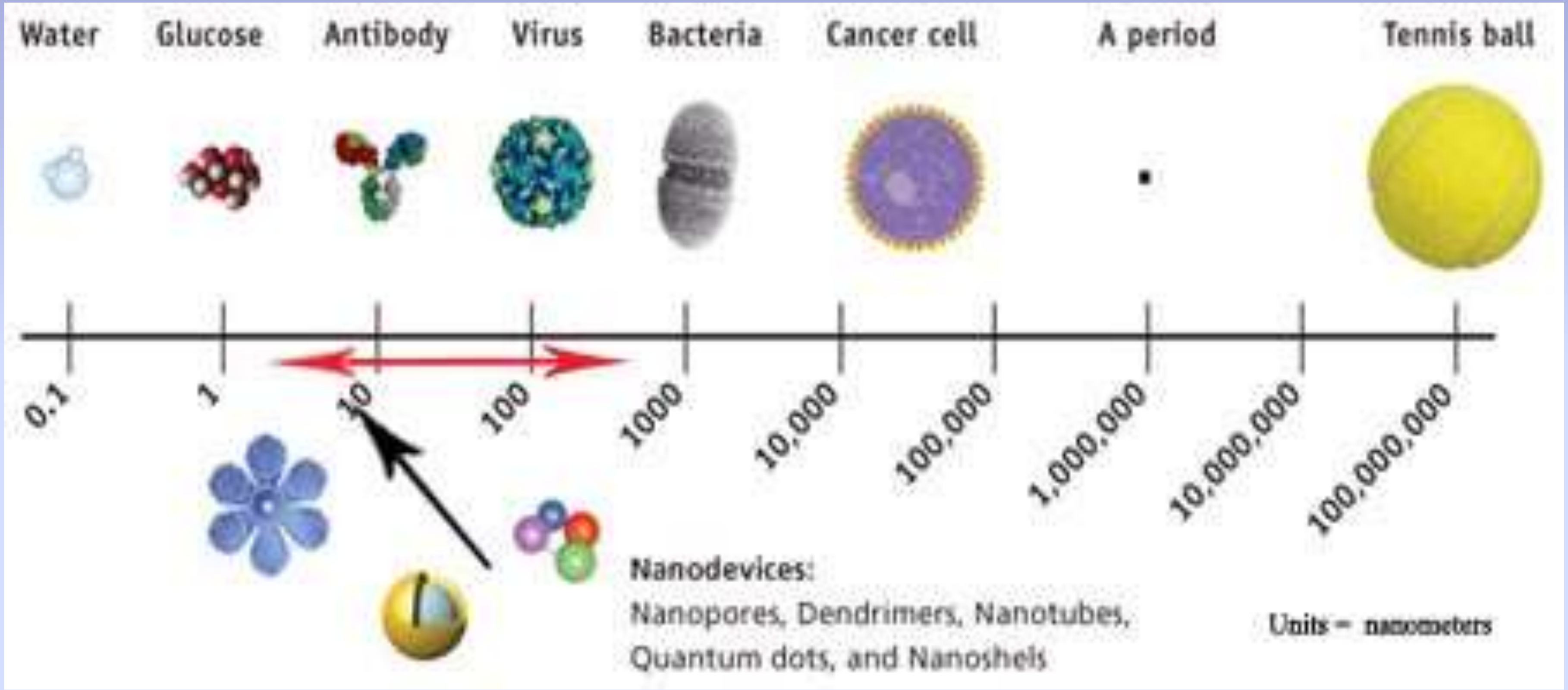
Nanomaterials

Nanotechnology

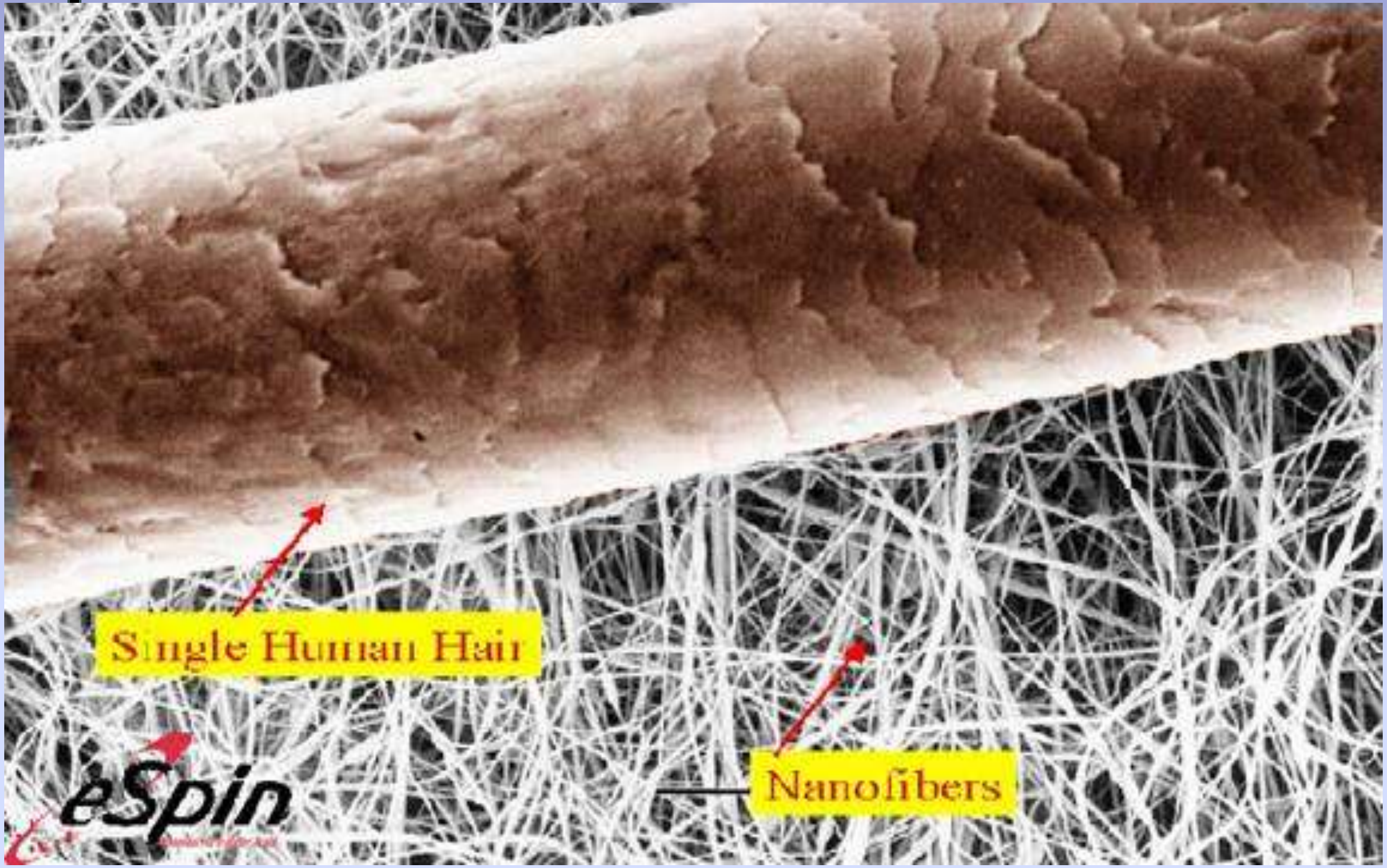
- is already making **today's** products:
  - Lighter
  - Stronger
  - Faster
  - Smaller
  - More Durable

How small is Nano - small?



Units in nanometers (nm)

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.

1. **Relative surface area**

2. Quantum effects

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

1. Surface Area 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

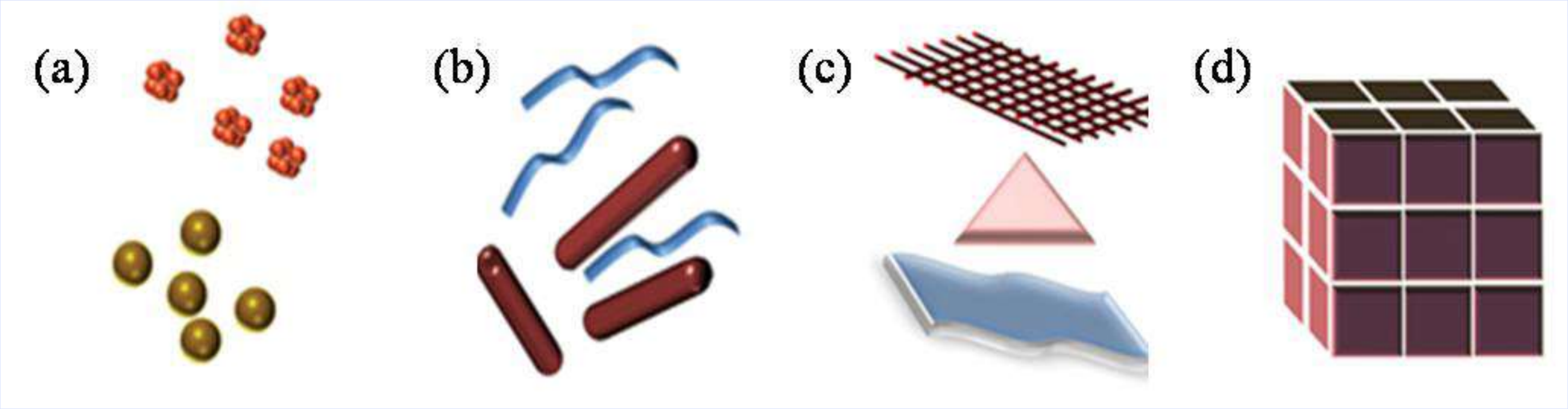
To understand the effect of particle size on surface area, consider an American Silver Eagle coin. This silver dollar contains 31 grams of coin silver and has a total surface area of approximately 3000 square millimeters. If the same amount of coin silver were divided into nanoparticles– say 10 nanometer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

2. Quantum Effect

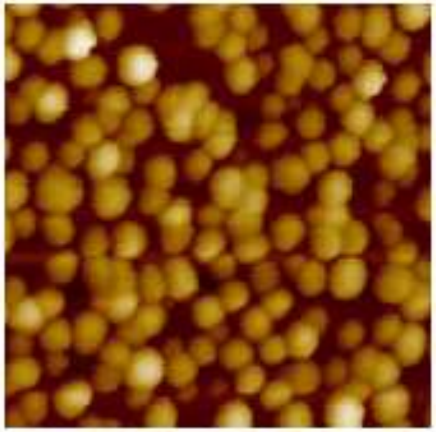
- The quantum confinement effect can be observed once the diameter of particle is of the same magnitude as the wavelength of electron
- Quantum confinement effect is responsible for increase of energy gap between energy state and band gap.
- When particles are small there electric, optical and magnetic 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 (Poly-crystals, Dendrimers)

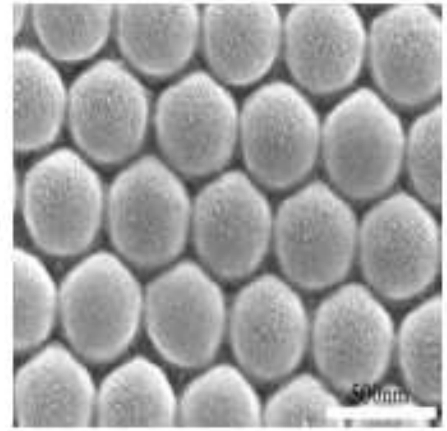


Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

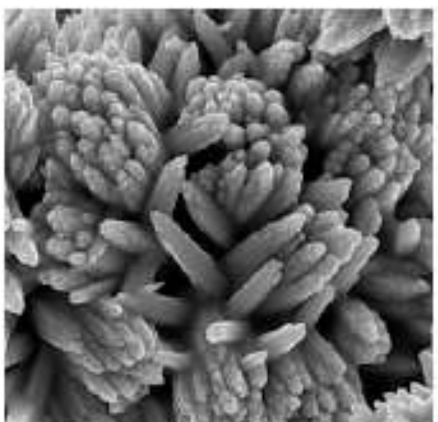


Au nanoparticle

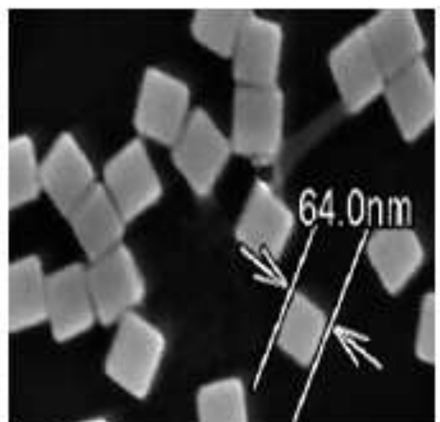
Buckminsterfullerene



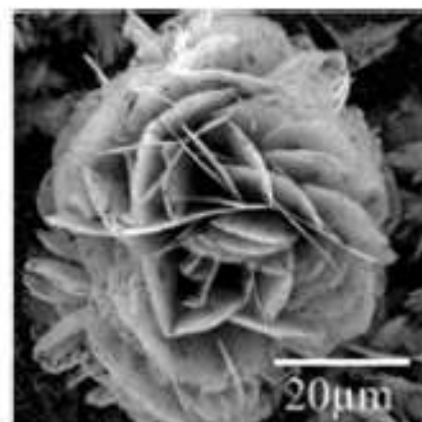
FePt nanosphere



Titanium nanoflower



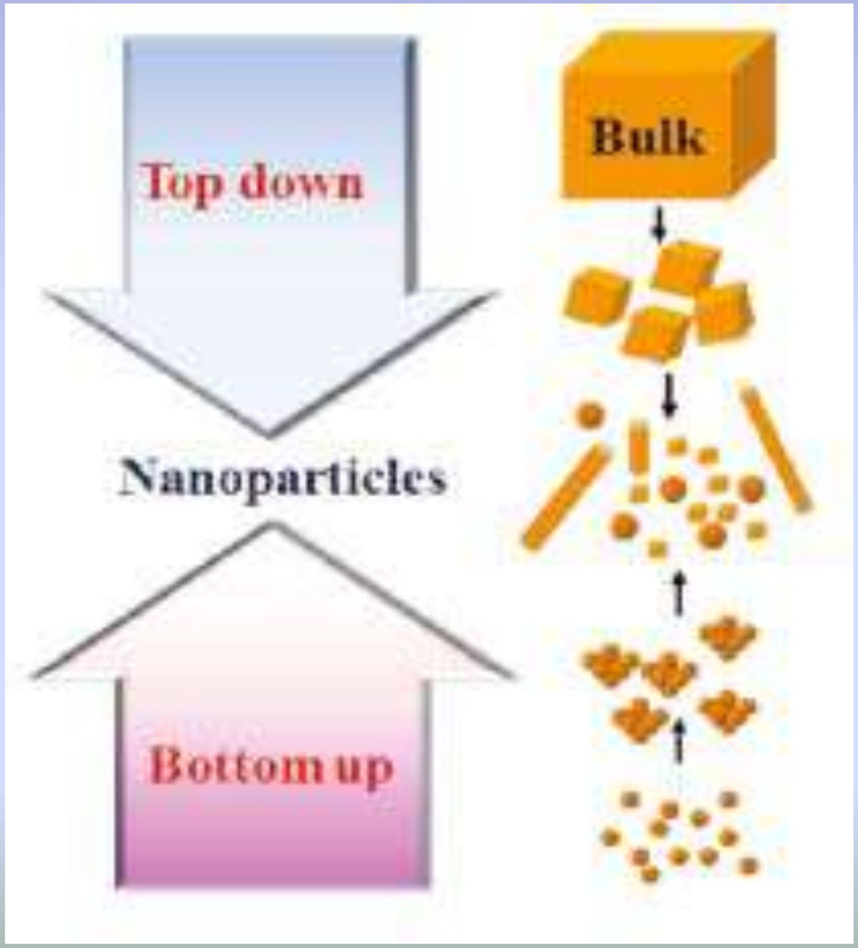
Silver nanocubes



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*

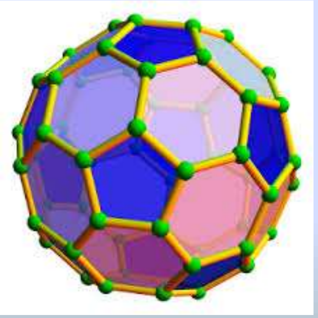
- This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering upto medicine.

Fullerenes

Fullerenes are spherical carbon-cage molecules with sixty (C60) or more carbon atoms.

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.



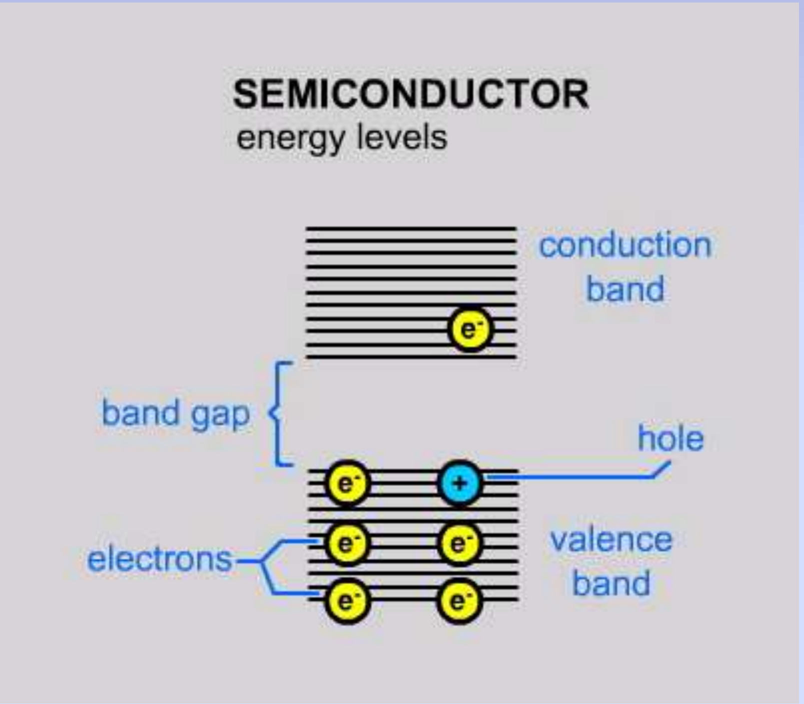
Quantum dot (QD):

In two words, a semiconductor nano-crystal

Easily tunable by changing the size and composition of the nanocrystal

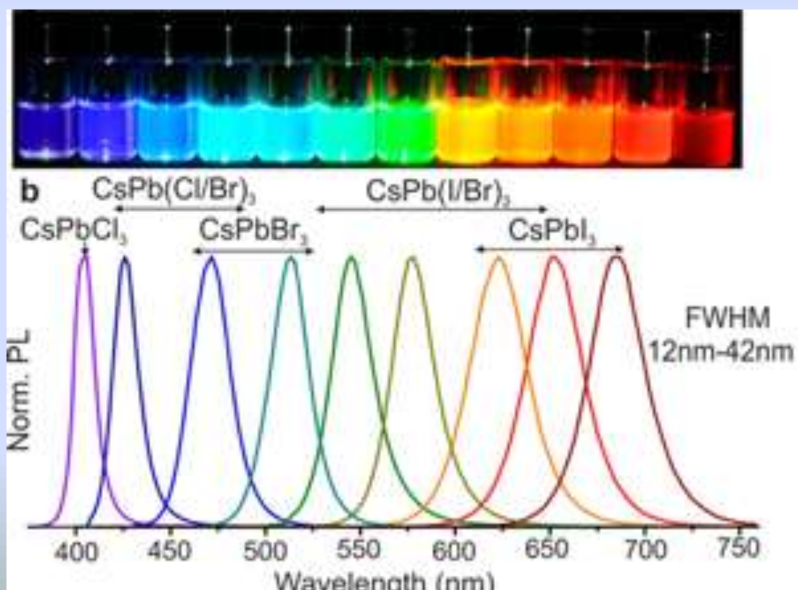
The average distance between an electron and a hole in an exciton is called the Excited Bohr Radius.

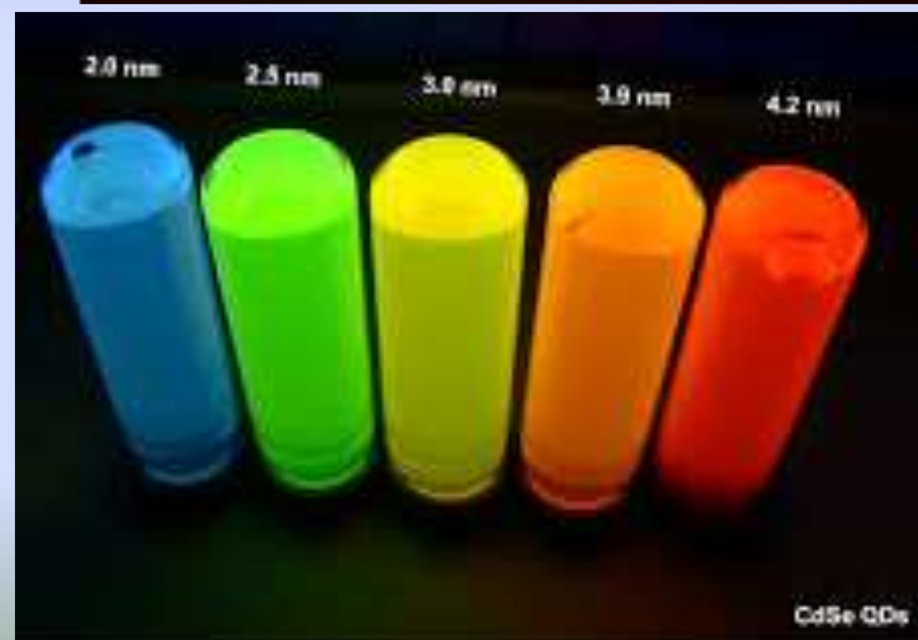
When the size of the semiconductor falls below the Bohr Radius, the semiconductor is called a quantum dot.



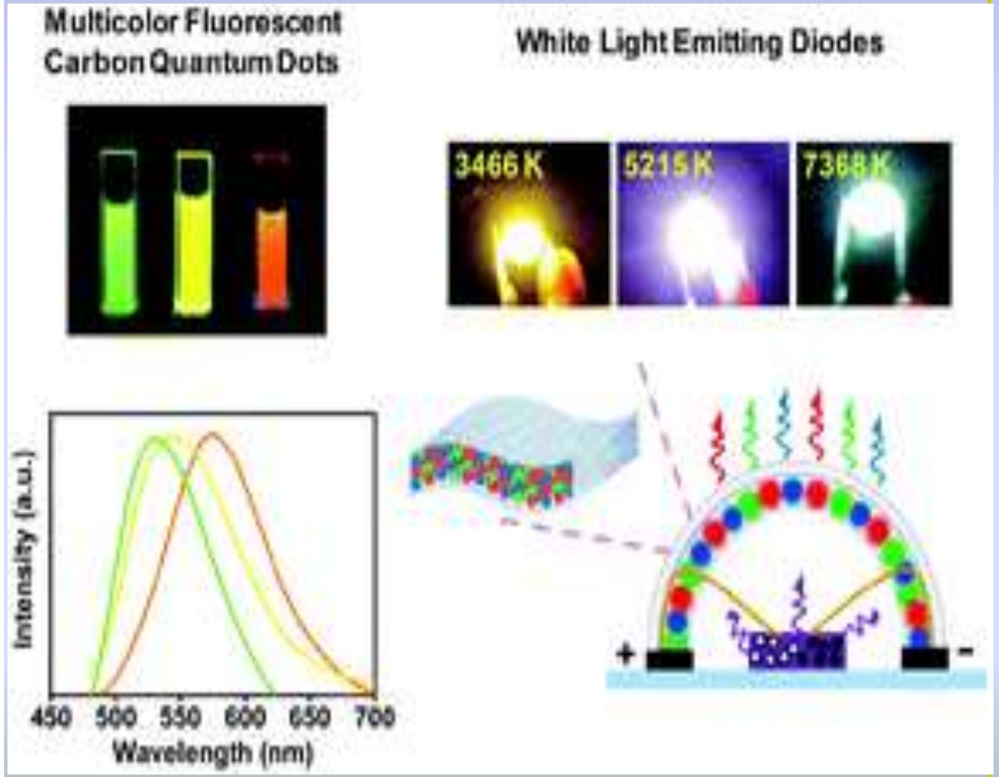
Tuning Quantum Dots

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





Quantum dots have properties intermediate between bulk semiconductors and discrete atoms or molecules. Their optoelectronic properties change as a function of both size and shape. Larger QDs of 5–6 nm diameter emit longer wavelengths, with colors such as orange or red. Smaller QDs (2–3 nm) emit shorter wavelengths, yielding colors like blue and green. However, the specific colors vary depending on the exact composition of the QD.



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, Q-dots could also be armed with tumor-fighting toxic therapies to provide the diagnosis and treatment of cancer.
- Q-dots 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 Photo-voltaics

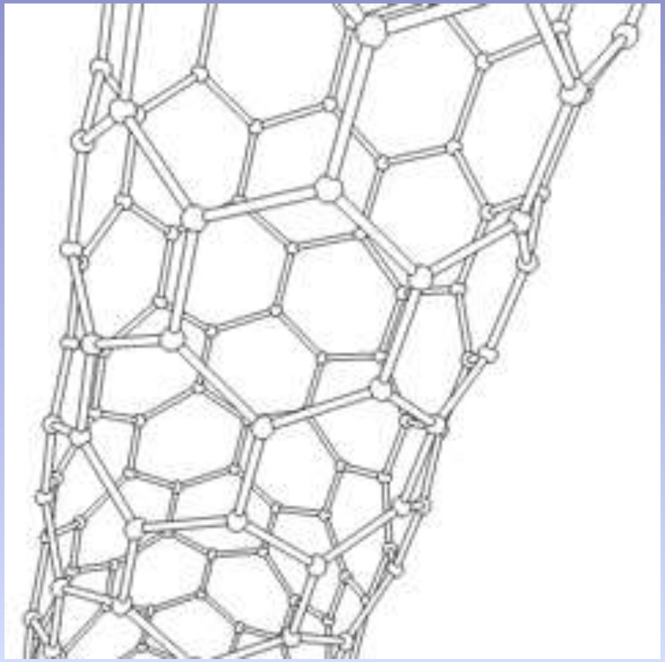
- Traditional solar cells are made of semi-conductors and expensive to produce. Theoretical upper limit is 33% efficiency for conversion of sunlight to electricity for these cells.
- Utilizing quantum dots allows realization of third-generation solar cells at ~60% efficiency in electricity production 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…

Carbon nanotubes(CNT)

There 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.

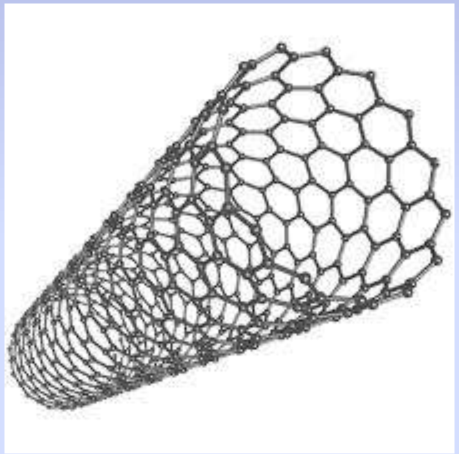


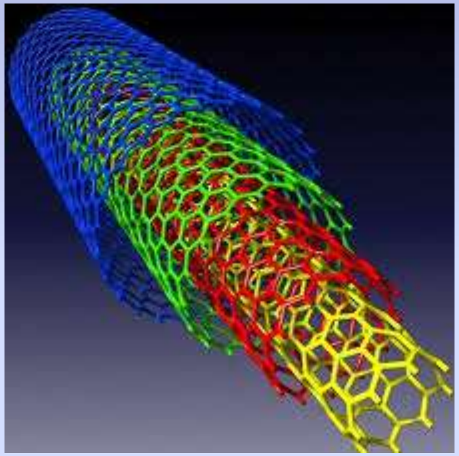
They have outstanding mechanical and electronic properties and are good thermal conductors. The tensile strength, or breaking strain of CNTs is 6-7 times that of steel. They are among the stiffest and strongest fibers known. CNTs can be metallic or semiconducting depending on their structure. Some CNTs 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

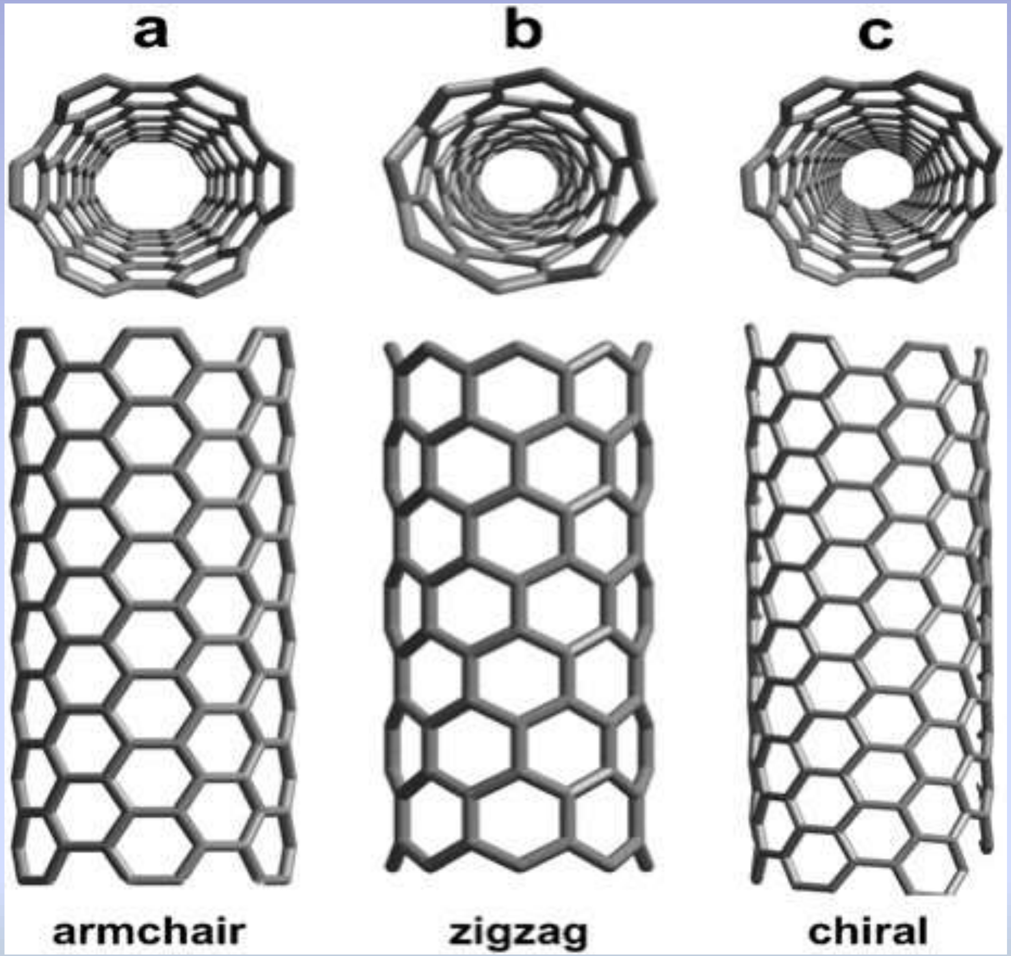
- Carbon nano tubes are categorized as,

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:

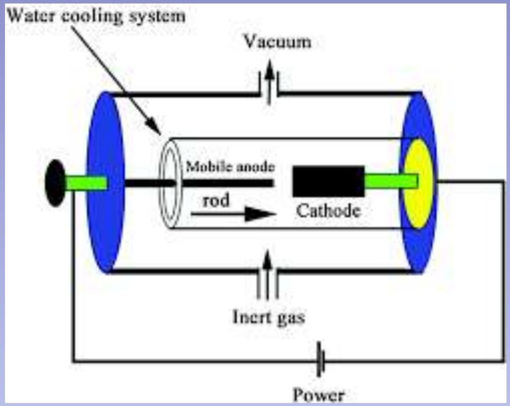
- armchair - metallic
- zigzag - semiconducting
- chiral - semiconducting

- multi-walled - metallic

Method of Preparation

- Arc Method
- Laser Method
- Chemical deposition method

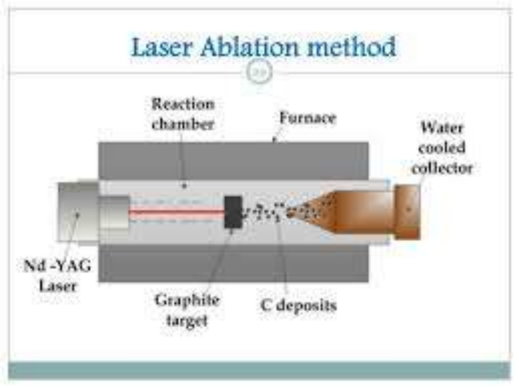
Arc Method



- 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.

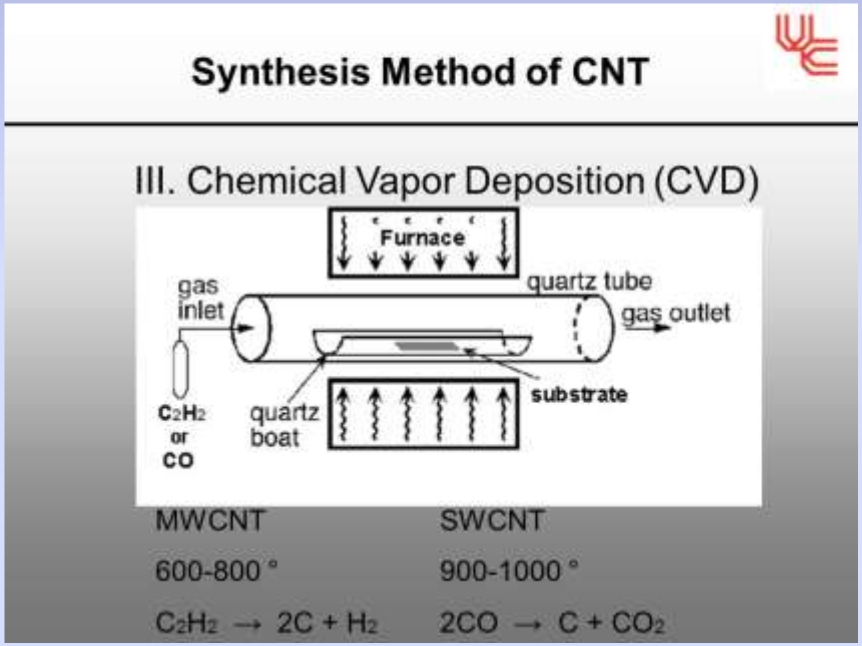
Chemical Vapor Deposition

The simplest method to produce nanoparticles is by heating the desired material in a furnance 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 $600\text{-}1150^0C$ and MWNT are produced at low temperature of $300\text{-}800^0C$.

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 the 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/cm^{2} (while copper burn at 10^{6} A/cm^{2}).
- 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.

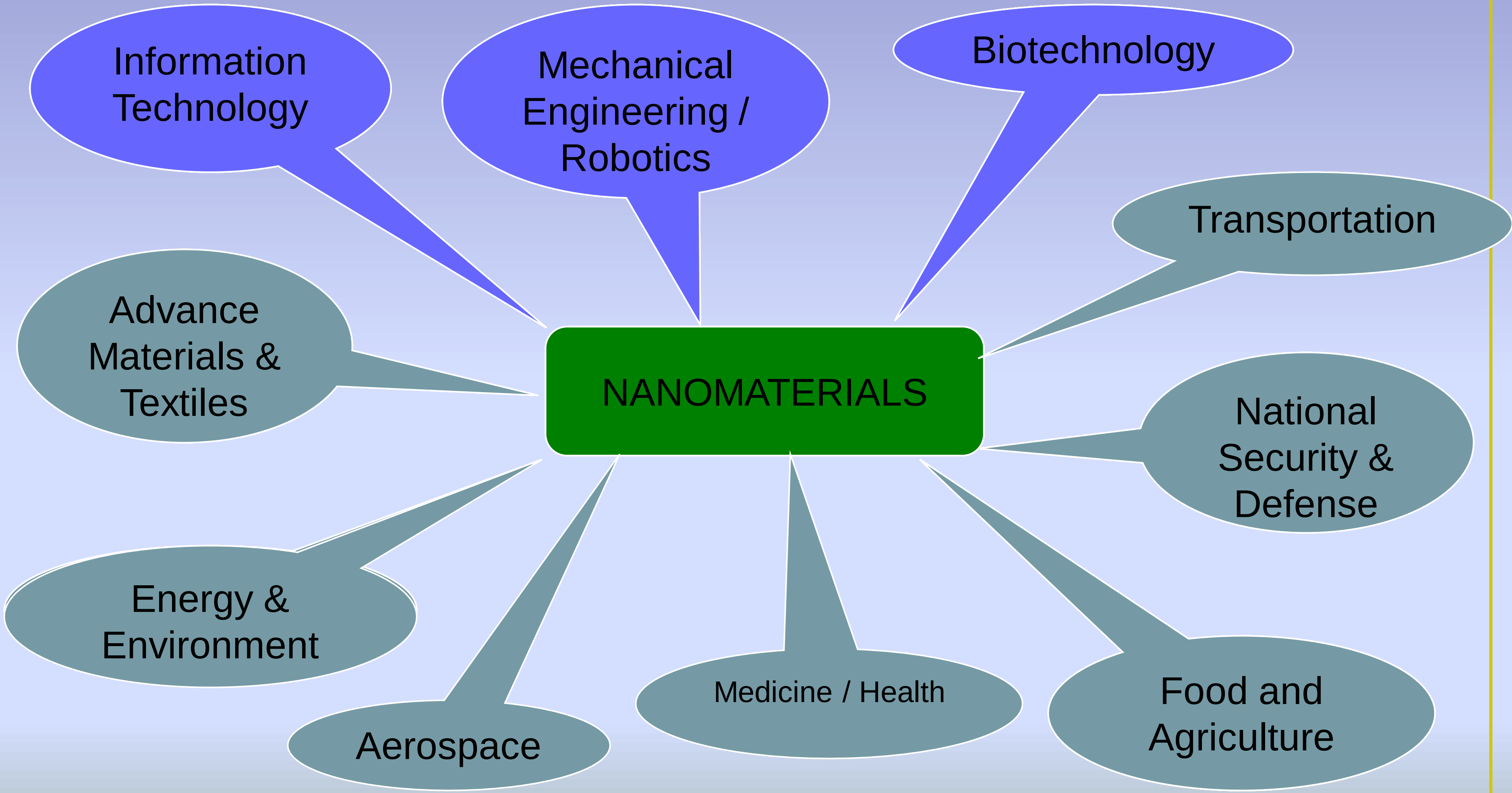
Strength and Elasticity

- 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 Tpa (TeraPascal) but this value is highly disputed and a value as high as 1.8 Tpa (tera Pascal) can be achieved. 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 electrical conductivity in plastics.

Application of nanomaterials



Nano mechanics and lubricants

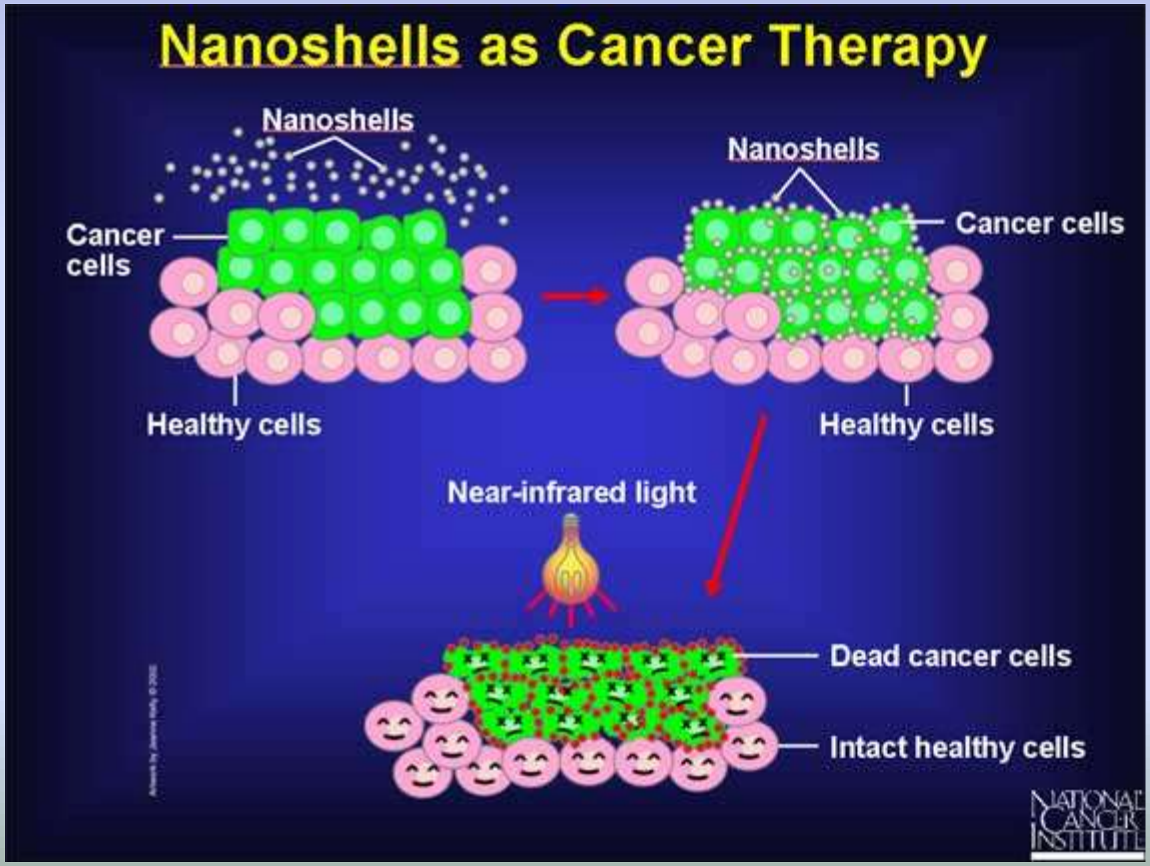
- Carbon nanotubes are stiff and hard like diamond but flexible due to this they find several mechanical application.
- Cutting tools made up of Nano crystalline materials such as tungsten carbide titanium carbide are more wear resistant than convectional counter parts.
- They find application in drill, 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.

Medicine

- Nanomaterials are of the size 10^{-9}. Hence they are smaller 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 particle are also used for tagging cancer cells, bacteria red blood cells. They are also used in contrast enhancing agent in MRI.
- Thus they can 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 possess greater activity and are 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 toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution.

Electronics

- Traditional electronic circuits are built by etching individual components into silicon wafers.
- 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 junction-less transistors.

General applications of Nano-materials

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-paramagnetic behavior.

(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 (Cortex-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 (NOx, 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.

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 nanomateirals 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.