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M. Sc. Inorganic Chemistry III Semester Chemistry of materiels Bv

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What is Nanotechnology?

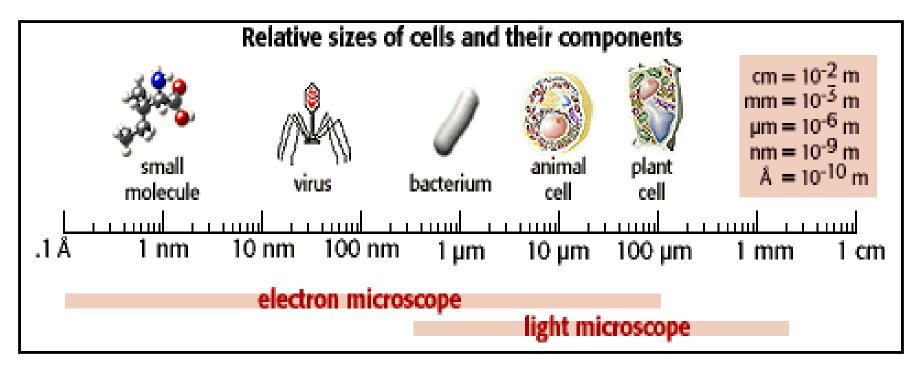
Field of applied science whose theme is the control of matter on an atomic and molecular scale.

NANOMETER.....(nm)

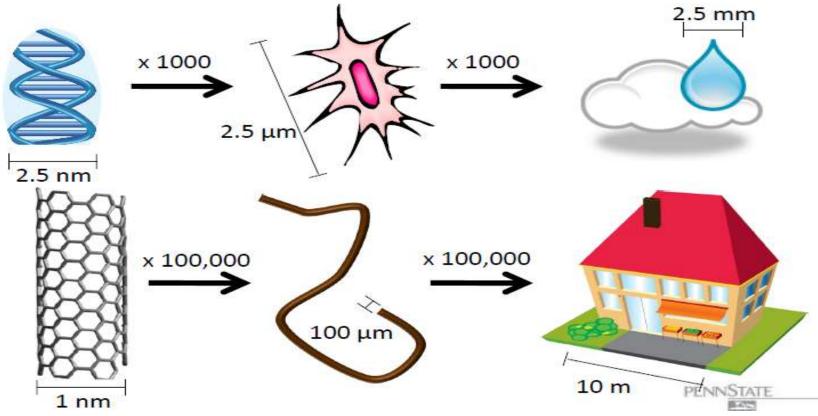
•A nanometer is one billionth of a meter (10⁻⁹ m). This is roughly ten times the size of an individual atom.

Nanoparticles :

Objects with at least one of their dimensions in the range 1-200 nm



How small is the nanoscale?



One human hair (cross section) is about 100,000 nm. Larger than nanoscale is the microscale and smaller than that is the atomic scale.

Gold Colloids: Historical Perspective



Roman Era Cup: Red color is due to gold nanoparticles



Czech glass colored yellow with silver and red with gold

- Absorbance in visible region : Bright red color allows direct visualization
- High extinction coefficients: Three to four order of magnitude as compared to organic chromophores.
- Easily prepared as monodisperse particle by chemical synthesis
- Excellent stability and can be easily functionalized.



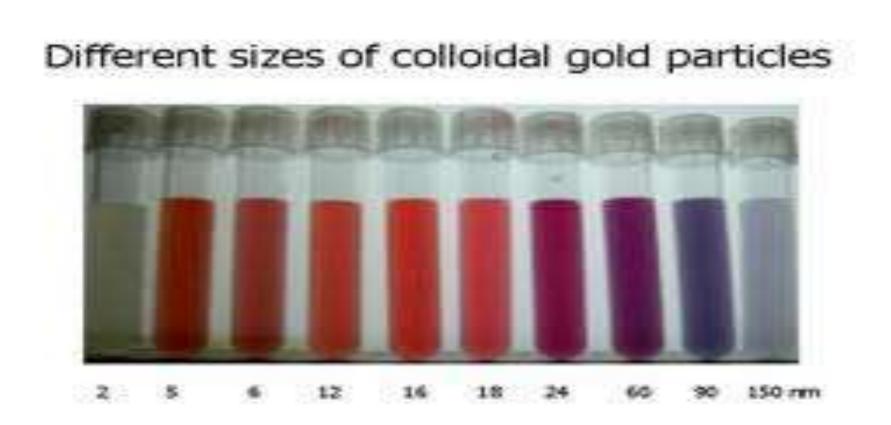
This <u>cranberry glass</u> bowl was made by adding <u>gold(III) oxide</u> to molten glass.



Known since ancient times, the synthesis of colloidal gold was originally used as a method of <u>staining glass</u>. Colloidal gold has been used since <u>Ancient Roman</u> times to colour glass intense shades of red or mauve, depending on the concentration of gold, and in <u>Ancient Indian Chemistry</u>, for various potions.

In the 16th century, the <u>alchemist</u> <u>Paracelsus</u> claimed to have potion called created a Aurum *Potabile*(Latin: potable gold). In *The newe* iewell of health, 1576, translator George <u>Baker</u> promoted the use and preparation of potable gold, along with other "most excellent secretes of phisicke and philosophie".

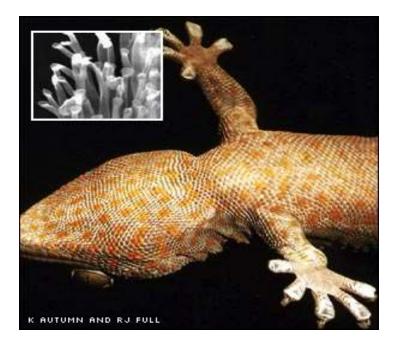
The newe iewell of health, 1576, trans. George Baker. Chemical Heritage Foundation



Modern scientific evaluation of colloidal gold did not begin until <u>Michael</u> <u>Faraday's</u> work of the 1850s. <u>Paracelsus</u>' work is known to have inspired <u>Michael Faraday</u> to prepare the first pure sample of colloidal gold, which he called 'activated gold', in 1857. He used <u>phosphorus</u> to reduce a solution of <u>gold chloride</u>.

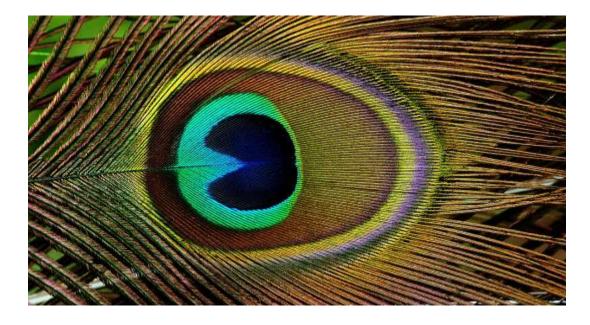


Natures are working at nano level far before scientists knew about it. The **lotus effect** refers to the very high water repellence (<u>superhydrophobicity</u>) exhibited by the leaves of the lotus flower (<u>Nelumbo</u>). The lotus leaf observe under microscope exhibits some bumps of micrometer size. The bumps are decorated with nanometer size structure. This can help a water drop stay on the lotus leaf without spreading on it. When the water drop rolls on the leaf, it collects the dirt on the surface and make the surface clean. The self-cleaning property of water repellent plant gives us the idea to make water repellent fabric.





The gecko can walk up glass and even hang upside down. The hairs (spatulae) on its feet are so small they can exploit forces that pull molecules together, sticking the gecko to the ceiling. Nanotech can make sticky tape lined with gecko-like synthetic hairs that do the same job.



There is something stunning about the colours of a peacock feather. It's not just a simple matter of the sort of coloured pigments an artist mixes up on a palette. The colours in the feathers almost glow in their iridescence, changing subtly with angle to catch the eye. To produce this effect, the feather contains a natural nanotechnology that has the potential to transform optics when this remarkable approach is adapted for use in human technology. In the peacock feathers it's the internal structure of the feather (or to be precise the tiny 'barbules' on the feather) that produce the hue. The colouration is primarily due to internal reflections off the repeated structure of the barbule, similar to the way the lattice arrangement of a crystal can produce enhanced reflection.

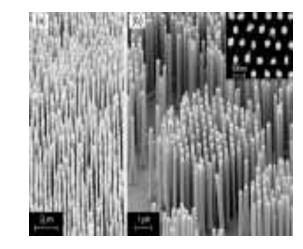
ORIGIN OF NANOTECHNOLOGY

Richard Feynman first conceived the idea of molecular manufacturing in his 1959 speech, "There's Plenty of Room at the Bottom." in which he described the possibility of synthesis via direct manipulation of atoms.

MILESTONES IN NANOTECHNOLOGY

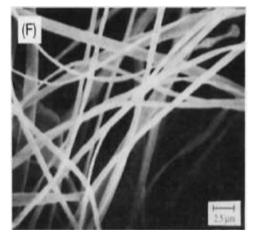
- 1857 Michael Faraday synthesized gold colloids of nanosize
- 1915 W. Ostwald, a famous chemist, wrote a book 'World of Neglected
- Dimensions' in German
- 1931 E. Ruska and M. Knoll developed the first electron microscope
- 1951 E. Müller developed the Field Ion Microscope which enabled the imaging of atoms from the tip of metallic samples
- 1959 R. Feynman delivered his now very famous talk 'There is Plenty of Room at the Bottom' pointing out to the scientists that reduced dimensionality of materials would create fascinating materials
- 1968 A.Y. Cho and J. Arthur developed Molecular Beam Epitaxy technique for layer by layer growth of materials
- 1970 L. Esaki demonstrated the quantum size effect (QSE) in semiconductors
- 1980 A.I. Akimov showed QSE in CdS and CdSe particles dispersed in glass, triggering the research on nanoparticles
- 1981 G. Binnig and H. Rohrer developed the scanning tunnelling microscope (STM) by which atomic resolution could be obtained. This was also followed by a family of scanning probe microscopes of various types 1985 - R.F. Curl, H.W. Kroto and R.F. Smalley synthesized sixty atom carbon
- molecule, later named as 'Fullerene'
- 1989 D.M. Eigler wrote letters 'IBM' using xenon atoms
- 1991 S. lijima discovered 'carbon nanotubes'
- 1999 C.A. Mirkin developed the 'Dip Pen Lithography'
- 2000 D.M. Eigler devised 'Quantum Mirage' using Fe atoms on the copper
- substrate.

NANOMATERIALS

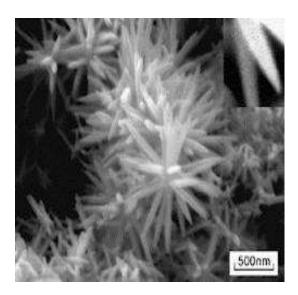


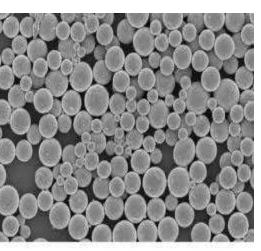
Nanorods





Nanowire





Nanoparticles

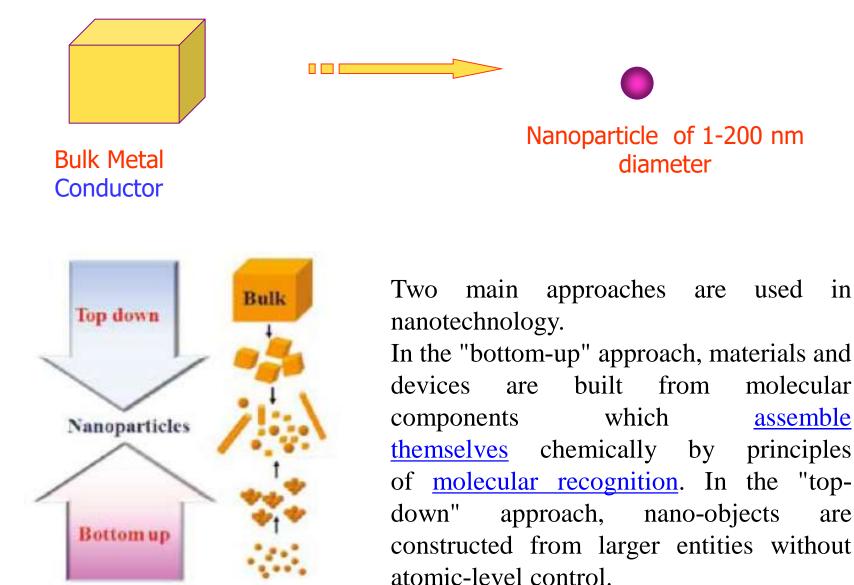


Nanotubes

Nanodots

Nanoflowers 13

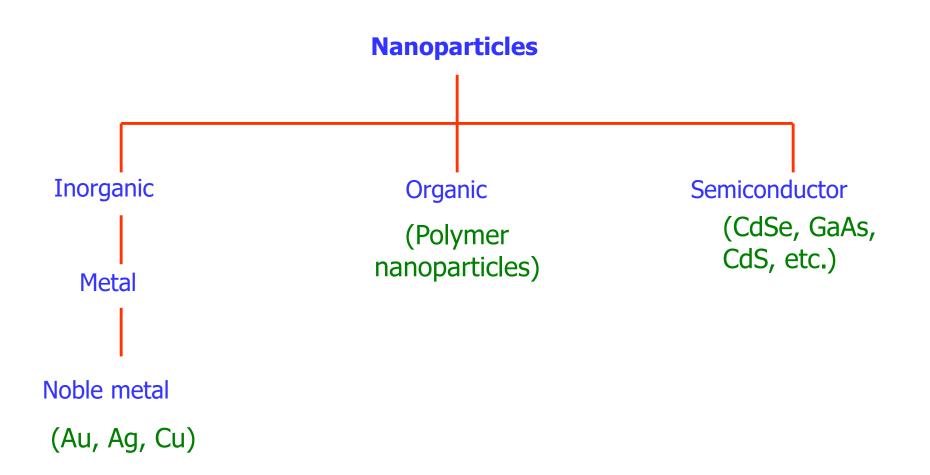
Unique properties : Different from bulk as well as molecules

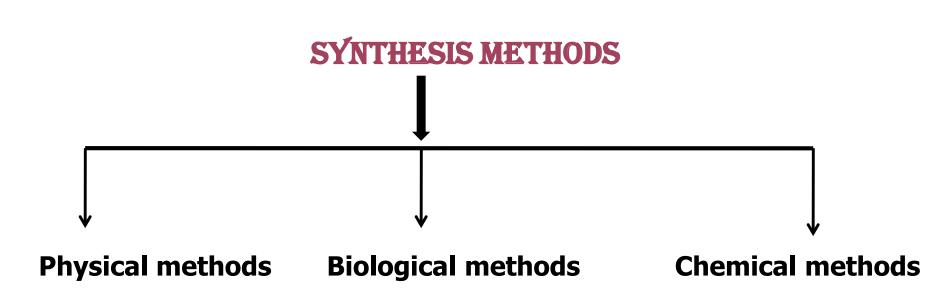


Schematic illustration of the preparative methods of nanoparticles.

are

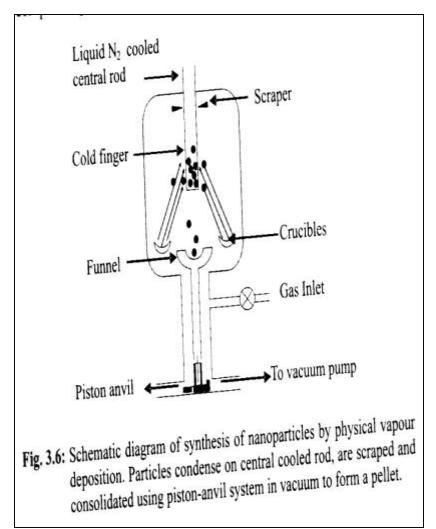
in





PHÝSICAL METHODS

Physical vapour deposition method



This method involves source of evaporation, an inert gas or reactive gas for collisions with material vapour.

Processes are carried out in vacuum chamber to get purity of desired end product.

High vapour pressure metal oxides are evaporated. The rate of evaporation and the pressure of gases inside the chamber determine the particle size and their distribution.

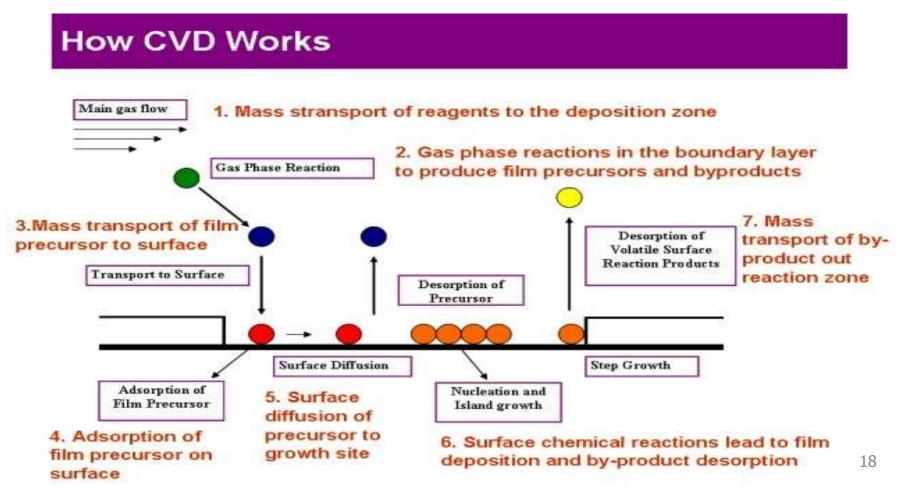
Clusters or nanoparticles condensed on the cold finger can be scraped off inside the vacuum system.

Chemical Vapor Deposition

➤ In CVD technique, the vaporized precursors are introduced into a CVD reactor and adsorb onto a substance held at an elevated temperature.

These adsorbed molecules will either thermally decompose or react with other gases/ vapors to form crystals.

 \succ Another key feature of chemical vapor synthesis is that it allows formation of doped or multi-component nanoparticles by use of multiple precursors.



Laser Ablation

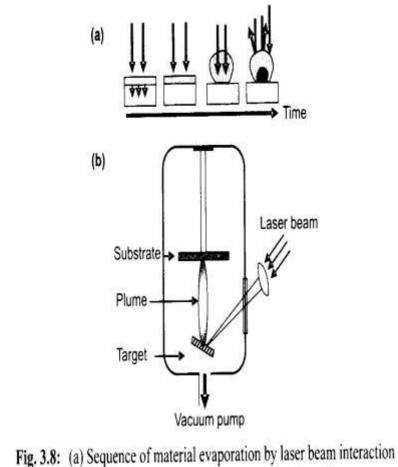


Fig. 3.8: (a) Sequence of material evaporation by laser beam interaction with a target material. (b) Laser deposition schematic apparatus.

Table 3.1: Wavelengths of some commonly used excimer lasers

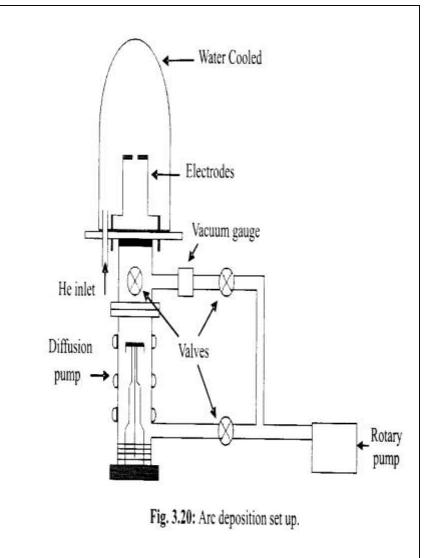
Gas	F,	ArF	KrCl	KrF	XeCl	XeF
λ, nm	157	193	222	249	308	350

In this method, vaporization of the material is effected using pulses of laser beam of high power. The set up is an Ultra High Vaccum (UHV) equipped with inert or reactive gas introduction facility, Laser beam, solid target and cooled substrate.

Clusters of any material of which solid target can be made are possible to synthesize. A powerful beam of laser evaporates the atoms from a solid source and

atoms collide with inert gas atoms and cool on them forming clusters.

Electric arc deposition



This method leads to mass scale production of Fullerenes, carbon nanotubes and some other nanomaterials.

It required basically water cooled vacuum chamber and Electrodes to strike an arc between them. Inert gas pressure is maintained in the vacuum system.

The adjustment of the electrode gap without breaking the vacuum becomes essential, as one of the electrode burns and gap increases.

BIOLOGICAL METHODS Synthesis using micro-organism

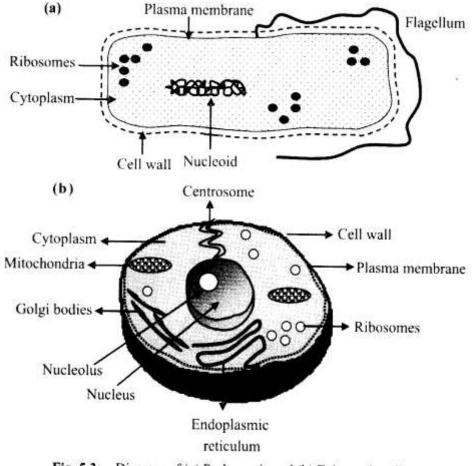


Fig. 5.3: Diagram of (a) Prokaryotic and (b) Eukaryotic cells.

Microorganisms are capable of interacting with metals coming in contact with them through their cells and form nanoparticles.

Some microorganisms produce hydrogen sulfide. It can oxidize organic matter forming sulphate, which in turn acts like an electron acceptor for metabolism. This H₂S can in presence of metal salt convert metal ions into metal sulphide, which deposit extracellularly.

Cells are also capable of reacting with metals or ions by processess like oxidation, reduction, methylation, demethylation etc.

Using Plant Extracts

This is truly green chemistry technique but comparative to other techniques

Use of plant extracts is relatively less investigated.

There are few examples which suggest that plant extract can be used in nanoparticles synthesis.

e.g. live alfalfa plants and geranium are found to produce gold nanoparticles from solids.

Procedure:-

Finely crushed leaves are put in Erlenmeyer flask and boiled in water just for a minute. Leaves get ruptured and cells release intracellular material. Solution is cooled and decanted. This solution is added to HAuCl₄ aqueous solution, and nanoparticles of gold start forming within a minute.

CHEMICAL METHODS

Microemulsion method

The preparation of metal nanoparticles using the microemulsion system, where ionic and non ionic surfactants are used has been well reported.

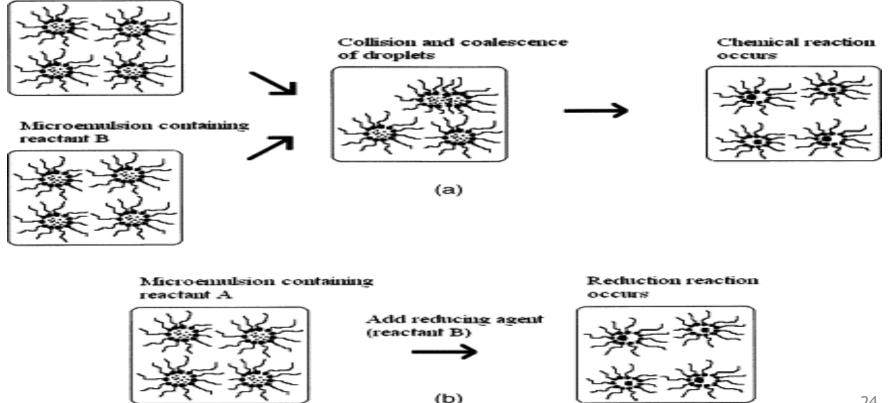
Whenever two immiscible liquids are mechanically agitated they form emulsion. The tendency of the liquids is such that the liquid in smaller quantity tries to form small droplets, coagulated droplets or layers so that they are all separated from the other liquid. (e.g. fat droplets in milk).

Microemulsions are transparent and droplet sizes are in range of 1-100 nm required for syntheses of nanoparticles. Microemulsions are stabilized by surfactants. Nanoparticles of Co, Cu, CdS, ZnS can be synthesized.

Micelles

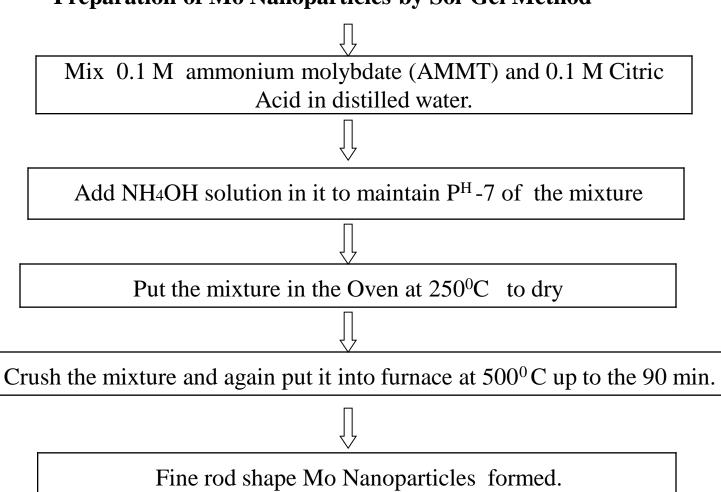
Then the two reverse micelles are mixed with continuous stirring. A change in the color occurred almost immediately after mixing the two reverse micelles. The size of the nanoparticles was in the range of 5 to 50 nm. Example-One solution should have Cobalt bis92ethylhexyl) sulfosuccinate[Co(AOT)2] and other sodium borohydride $(NaBH_4).$

Microentaining reactant A



Sol Gel method

✓ The sol-gel method is based on inorganic polymerization reactions. The sol-gel process includes four steps: hydrolysis, polycondensation, drying and thermal decomposition.
✓ The size of the sol particles depends on the solution composition, pH and temperature.

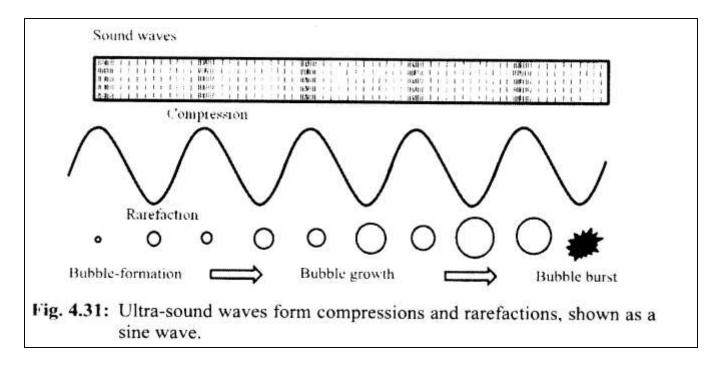


Preparation of Mo Nanoparticles by Sol-Gel Method

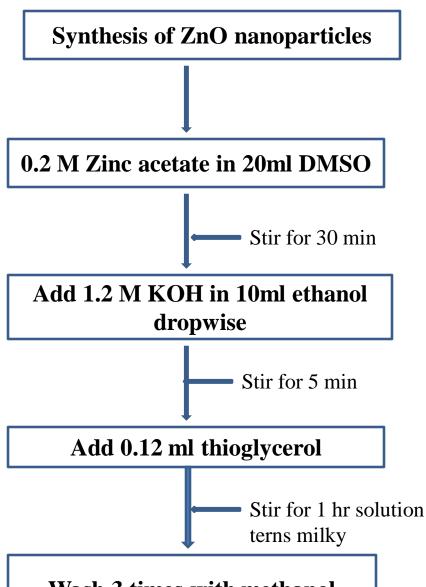
Examples; Synthesis of SiO2 nanoparticles

 $\begin{array}{l} Si(OC_{2}H_{5})_{4} + H_{2}O \\ & \xrightarrow{hydrolysis} Si(OC_{2}H_{5})_{3}OH + C_{2}H_{5}OH \\ \equiv Si - O - H + H - O - Si \equiv \\ & \xrightarrow{water \ condensation} \equiv Si - O - Si \equiv + H_{2}O \\ \equiv Si - OC_{2}H_{5} + H - O - Si \equiv \\ & \xrightarrow{alcohol \ condensation} \equiv Si - O - Si \equiv + C_{2}H_{5}OH. \end{array}$

Sonochemical method



In this method the precursors is enhanced by taking the advantage that large amount of energy can be released when bubbles burst in a liquid. Bubbles are formed by using ultrasonic waves. In the range of 20kHz to 2MHz. The Ultrasonic wave passing through the liquids create very small bubble which keeps on growing until it reaches a critical size and then bursts releasing very high energy to locally reach a temperature of 5000 ° C and pressure of few 100 times of atmosphere. Cooling rates can be as high as 10¹¹⁰ C per sec. such high cooling rates give rise to nanoparticles. Example. ZnS CeO₂, WO₃.



Wash 3 times with methanol Disperse the particles in methanol

Chemical Reduction Method:

□It is the most widely used method for nanoparticles synthesis.

□Metal ion in aqueous solution is reduced by reducing agents such as thioglycerol, hydroquinone, sodium borohydride, hydrazine, sodium citrate, ascorbic acid etc. to produce nanoparticles.

□An electric charge on the reductant particle was found to exert large effect on the process of nanoparticles formation.

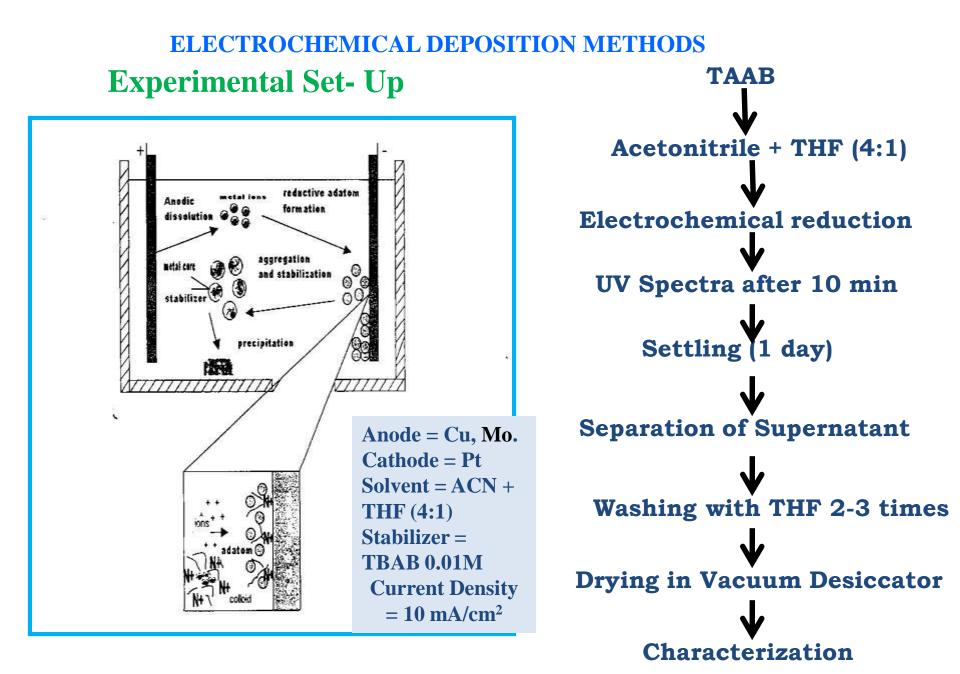
The most highly dispersed and stable colloidal nanoparticles are formed by using anionic reductant.

Specially designed Instrumental setup for synthesis of Nanoparticles





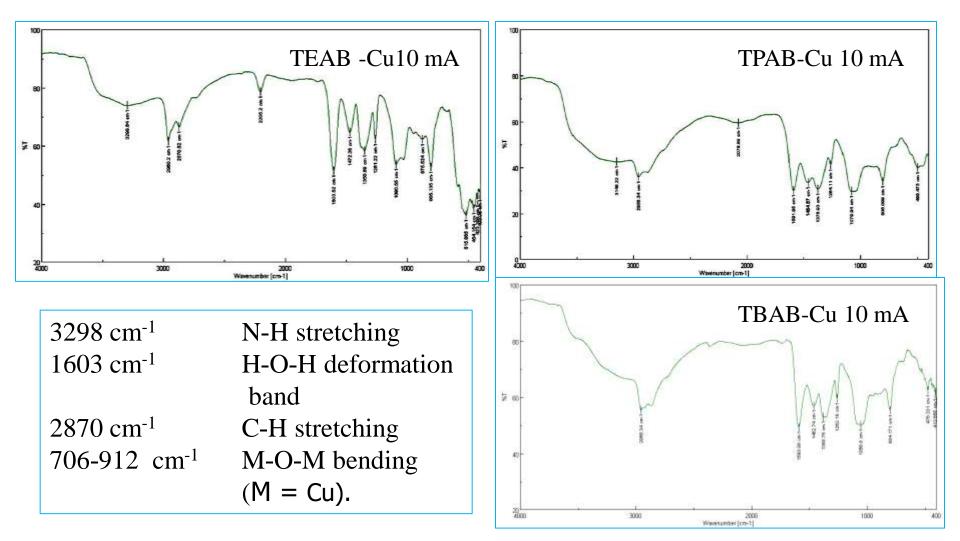




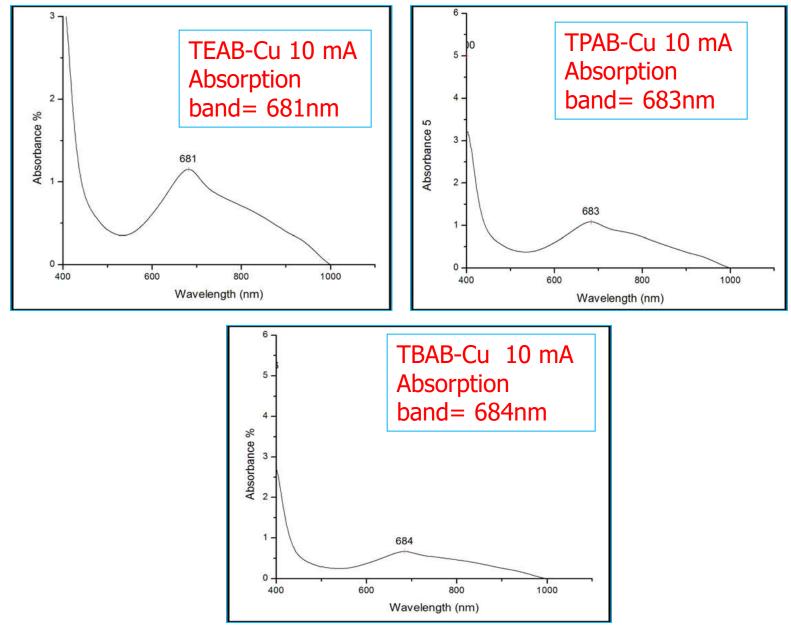
AUTOLAB PGSTAT instrument used for Synthesis of Nano Particles and Electro-analytical Technique



Characterization of CuO Nanoparticles FT-IR SPECTROSCOPY

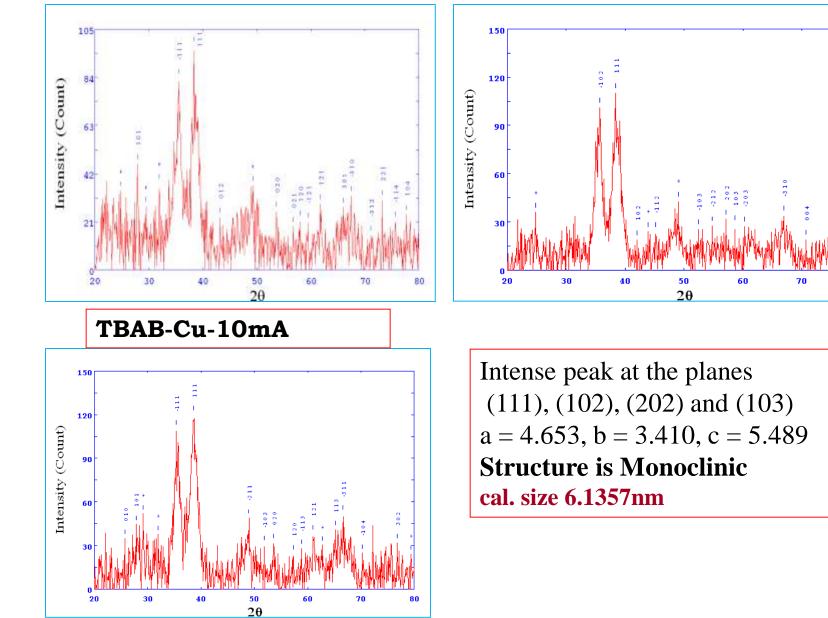


UV-VISIBLE SPECTROSCOPY

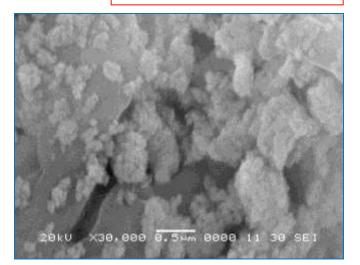


XRDTEAB-Cu-10mA

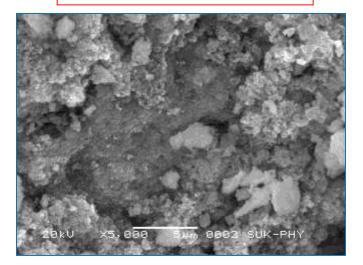




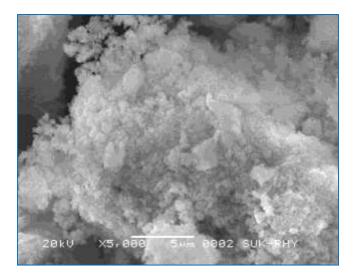
SEM-EDS TEAB-Cu-10mA

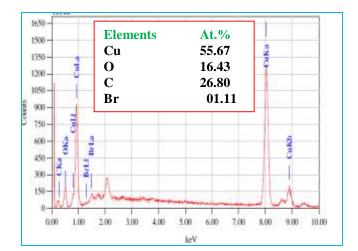


TPAB-Cu-10mA



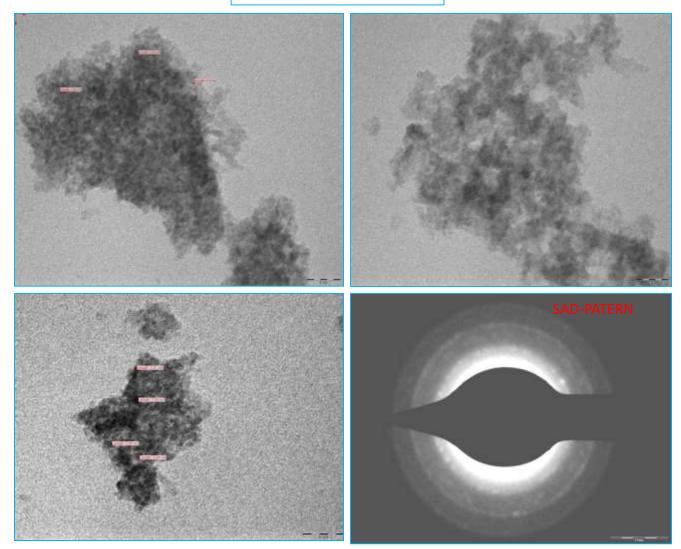
TBAB-Cu-10mA





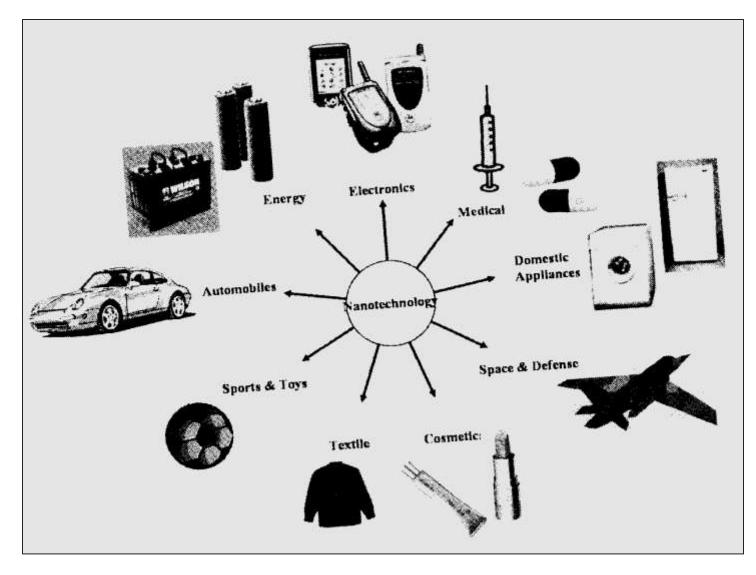


TBAB-Cu-10mA



Calculated particle size of TBAB-Cu-10mA 2-4 nm. From SAED pattern the ring shows high crystallinity of nanoparticles .

APPLICATIONS





Any material to show good catalytic activity must possess high surface area.

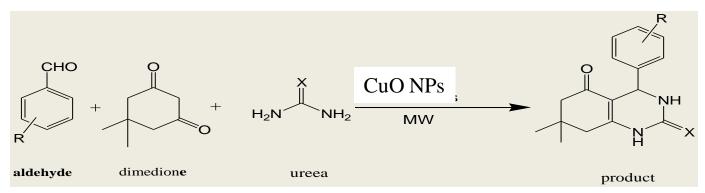
Nanomaterials have tremendous implications in catalysis since the surface area of nanomaterials markedly increases with the reduction of their size.

✤ For example, a nanocrystal of 10 nm diameter will have ~15 % of its atoms on the surface while nanocrystal of 1 nm diameter will have ~100 %.

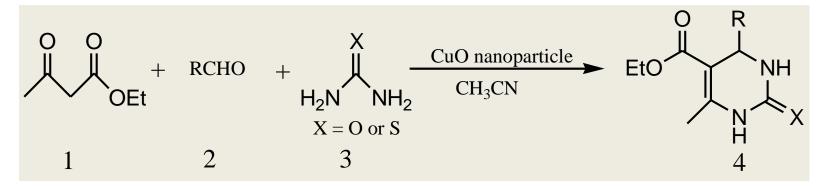
Thus, a small nanocrystal with a higher surface area would be more catalytically active.

Nanoparticles catalysis has been investigated for both homogenous and heterogeneous systems.

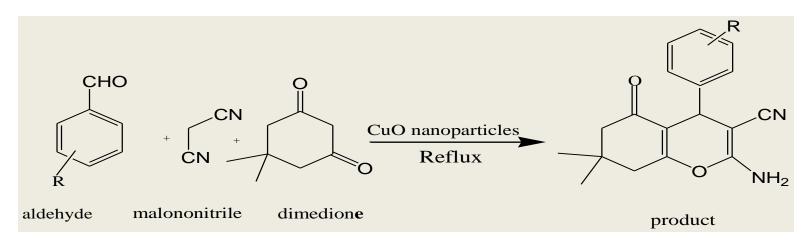
A. Synthesis of Octahydroquinazolinone Derivatives



B. Synthesis of 3, 4-Dihydropyrimidin-2 [1*H*] – Ones using CuO NPs as a catalyst



C. Synthesis of Tetrahydrobenzo[b]pyran Derivatives





□Nanoparticles are also becoming quite popular in cosmetics.

□Zinc oxide and titanium oxide nanoparticles of fairly uniform size are able to absorb ultraviolet light and protect the skin.

□Nanoparticles based creams gives smooth appearance.

□Nano based dyes and colours are quite harmless to skin and can be used in hair creams or gels.

Domestic Appliances



Silver nanoparticles are used in refrigerators. Food in refrigerators can remain fresh and prevent fungal growth for longer time than ordinary refrigerators.

➢Air purifiers or air conditioners and water purifiers with silver nanoparticles are claimed to have advantages.

The clothes washed in silver nanoparticles lined washing machines are claimed to stay sterile for about a month.

Some of the building blocks like window materials are made by nanomaterials. One can maintain the inside temperature of the houses reducing heating/cooling effects due to outside weather using appropriate window materials like aerogels which are highly insulating and transparent.



Scientists and engineers have been able to recreate some of the effects of nanotechnology in commercial products, such as stain- and water-resistant fabric, and iridescent security images on currency.

Nanotechnology is working to enhance security for currency as well as many other applications including authenticating legal documents, merchandise, concert tickets, tax-paid stamps, medical & credit transactional cards, visas & passports.

Modern Nano Fabric is the result of a new technological breakthrough in fabric's enhancement and health concept. It has Exceptional antibacterial effect, Anti UV ray, Heat conductive, Improve blood circulation, Anti-inflammatory and anti allergic. Nano Health Fabric fibers are made with composites polymeric material, which emit infrared rays and negative Ions. The combination of Infrared rays and Negative Ions help improve blood circulation, aid in stress relief, increase mental alertness, and assist faster recovery from fatigue and injuries.

Automobiles



 \checkmark Even a simple car is made up of a large number of parts and materials.

- \checkmark Nanotubes composites have mechanical strength better than even steel.
- ✓ Nanoparticles paints provide smooth, thin, attractive coating.
- ✓ Window glass material i.e. self cleaning so that it is not necessary to wash the windows with water.
- ✓ By using nanoparticles clay better, light weight rubber consuming thinner tyres are possible.
- ✓ Nanomaterials catalysts converts emission of particles and poisonous gases like CO and NO from cars into less harmful gases.
- \checkmark Hydrogen gas can be stored in nanocylinders i.e. carbon nanotubes.

Semiconductor Nanoparticles

The small size of semi conductor nanoparticles can provide high efficiency of detrapping of light generated electrons and holds the increasing probability of the photocatalytic process on the surface of the conductor.

The idea of using nanoparticles for photocatalytic water decomposition was first proposed by Henglein and Duonghong who demonstrated the possibility of photoredution of methylviologen in colloidal solutions of semi-conductors.

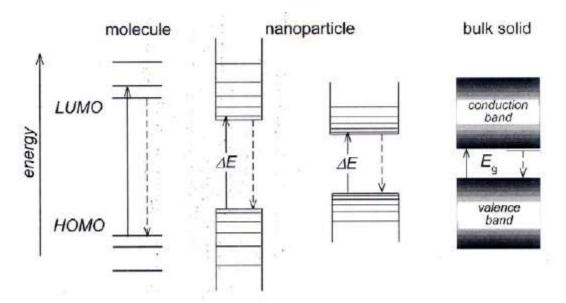


Fig. 2.1 Schematic energy diagrams illustrating the situation for a nanoparticle, in between a molecule and a bulk semiconductor.

Nanomedicines

Ancient cultures in Egypt, India and China have used gold to treat diseases like smallpox, skin disorders, syphilis and measles.

In India, Ayurved an ancient medical science makes use of various Bhasma. One of them Suvarna Bhasma (Gold Ash) is a therapeutic form of gold metal nanoparticles.

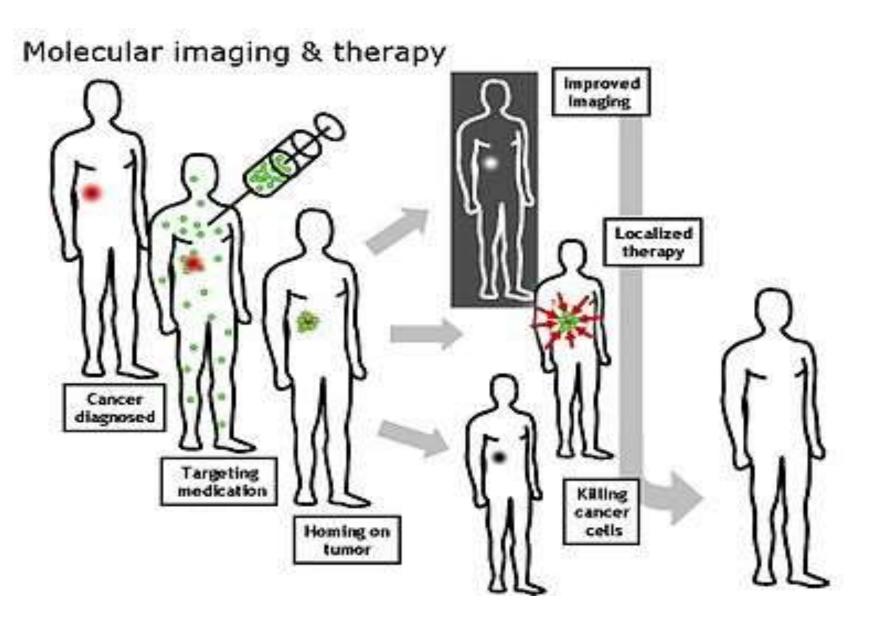
In the past few decades, several organogold complexes have emerged with antitumor, antimicrobial, antimalarial and anti-HIV activities.

Proteins grafted into gold nanoparticles have also been used to kill cancer cells.

The antibacterial effects of Ag salts have been noticed since antiquity and Ag is currently used to control bacterial growth in a variety of applications including dental work, catheters and burn wounds.

Drug Delivery

- Nanocapsusles and nanospheres surrounded by a polymer matrix into which the drug is physically and uniformly dispersed are used as drug delivery devices.
- These have the ability to circulate for a prolonged period of time, target a particular organ as carriers of DNA in gene therapy and have the ability to deliver proteins, particles and genes.
- Particle size and surface characteristics can be easily manipulated to achieve passive and active drug targeting after parental administration.
- They control and sustain release of the drug during transportation and at the site of localization, altering organic distribution of the drug and subsequent clearance of the drug so as to achieve increase in drug efficiency and avoid side effects.
- Drug loading is relatively high and drugs can be incorporated into the system without any chemical reaction thus preserving drug activity. Site specific targeting can be achieved by attaching targeting ligands to the surface of the particles or use of magnetic guidance.
- The system can be used for various routes of administration including oral, parental, intra-ocular etc.
- The delivery of the drug Doxorubcin into the mononuclear phagocytic system rich organs/tissues like liver, spleen and lungs is helpful for treatment of hepatic-carcinoma, hepatic metastasis, gynecological cancers, bronco pulmonary tumors, myeleoma and leukemia. Bioactive molecules and vaccines based on peptides and₄₆ protein can also be encapsulated and delivered.

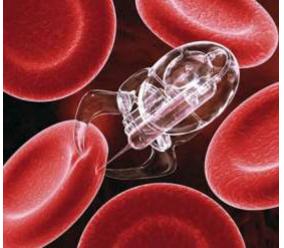


A schematic illustration showing how nanoparticles or other cancer drugs might be used to treat cancer. Scientist may now be able to destroy tumors without killing healthy cells at the same time.

Nano Robots.



http://i.telegraph.co.uk/telegraph/multimedia/ archive/01518/nano-robot_1518042i.jpg

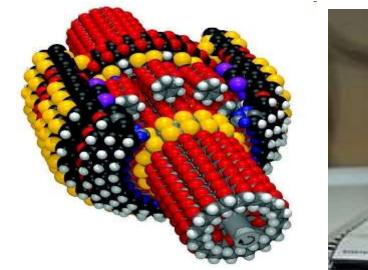


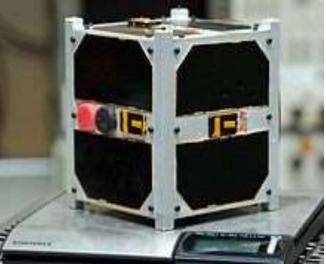
Nano robotics is the technology of creating machines or robots at or close to the microscopic scale of nanometers. (10^{-9}) .

Microscopic robots made from DNA molecules can walk, follow instructions and work together to assemble simple products on an atomic-scale assembly line, mimicking the machinery of living cells.

Nano-materials have been exploited in hundreds of products, but this is the first time production was achieved by "exotic man-made DNA objects" so small that their instructions had to be encoding in the world around them (e.g., chemical markers that direct their movements).







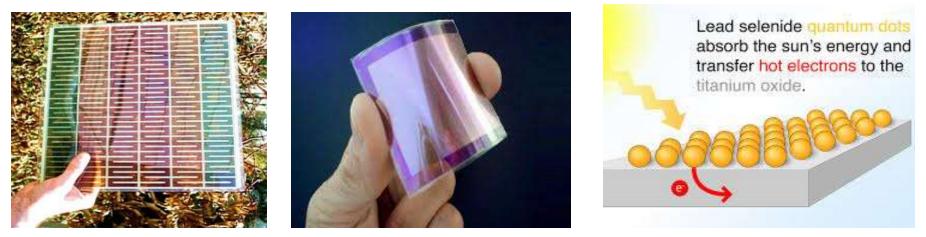
ESTCube-1 1U CubeSat



3 microsatellites of <u>Space</u> <u>Technology 5</u>

Cost and performance of space travel will be improve significantly. Improvements in shuttles with cheaper space flights benefits to the Astronauts. Nano satellites will be 90% lighter with much greater strength. Greater safety margin due to the use of Diamondiod fibers that Nanotechnology can produce.

Solar Energy



A new technique that not only reduces the cost of solar cells to a quarter but also makes them beautiful. These solar cells come in pink and are called Dye Sensitive Solar Cells of DSSCs.

These solar cells make use of a mixture of ruthenium or lead selenide and either titanium of zinc oxide particles to absorb sunlight. This material absorbs sunlight but there is no way by which they can transfer this power. Here is where nanotechnology comes in. Nanowires are implanted in the cells which serve as connections between the cells on the panel.

In space solar energy is used to power the satellites or space crafts.

Solar cells currently in use have reached an efficiency ~30% at air mass zero(AM0). Some solar cell are approaching an efficiency of ~40%.

However there is still a concern in reducing weight of materials used in solar cells

Columbia Tragedy



Feb. 1, 2003 columbia space shuttle disintegrated on its descend back to earth.

Ist indication was the loss of temperature sensors on the left wing.

Foam struck the left wing.

There was loss of tire pressure warning on the left main gear. Indication of excessive structural heating.

Solution to Columbia space shuttle.

Biosensors-

Sensing device with a biological or biologically derived sensing element which is integrated with a physical transductor.

Fabrication of overall space shuttle material –That can withstand 1000°c

Nanosensors and nanorovers with enhanced monitoring and efficient control of propulsion systems, Life supports and higher mission success rates.

Nano food ? !!!

Preservation of food without refrigeration. Protection of food from bacteria and diseases. Lighter foods.!!!



Interactive Nanotech Food

Nanotechnology isn't just protecting your food - it's in your food. Scientists are manufacturing nano-sized vitamins that are easier for our bodies to absorb. In the future they hope to create 'interactive' food - food and drink that could change color, flavor or nutrients on demand.

Defense

Aerogels are very low density materials used to reduced the weight. Even some special light weight suits, jackets can be made by using aerogels as poor conductor of heat.

Quick detection of biological weapons is urgent need of defense department to 'on the spot check' the dangerous traffic of harmfull biological weapons or epidemic. Example to detect the Anthrax Or SARS patients immediately.



Nanotech in Electronics.



Nanoelectronics refer to the use of nanotechnology on electronic components, especially transistors. **Nanoelectronics** often refer to transistor devices that are so small that inter-atomic interactions and quantum mechanical properties. Present transistors (such as CMOS90 from TSMC or Pentium 4 Processors from Intel) do not fall under this category, even though these devices are manufactured under 90nm or 65nm technology.

Improving display screens on electronics devices.

Memory chips with a projected density of one tera byte of memory per square inch or greater.

Reading the size of transistors used in integrated circuits.

Carbon Nanotubes in Display Devices.



Replacement of cathode ray tube (CRT) technology by electron producing CNT.

Carbon nanotubes are also likely to be used in IT. These tubes can be either conducting or semiconducting and have the potential for memory and strage as well.



