

Introduction to Nanotechnology

IUPAC Definition: a nanoparticle is a particle of any shape with dimensions in the range of 10^{-9} to 10^{-7} m (1-100 nm).

Nanotechnology: A more generalized description of nanotechnology was subsequently established by the National Nanotechnology Initiative, which defines nanotechnology as the manipulation of matter with at least one dimension sized from 1 to 100 nanometers.

Brief History



Stained glass windows.

Dr. Richard P. Feynman

- “*Why cannot we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?*”

"There's Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics" was a lecture given by physicist Richard Feynman at the annual American Physical Society meeting at Caltech on December 29, 1959.

Birth of Nanotechnology

In 1974, Professor Taniguchi of Tokyo Science University used the word “nanotechnology” to describe the science and technology of processing or building parts with nanometric tolerances.

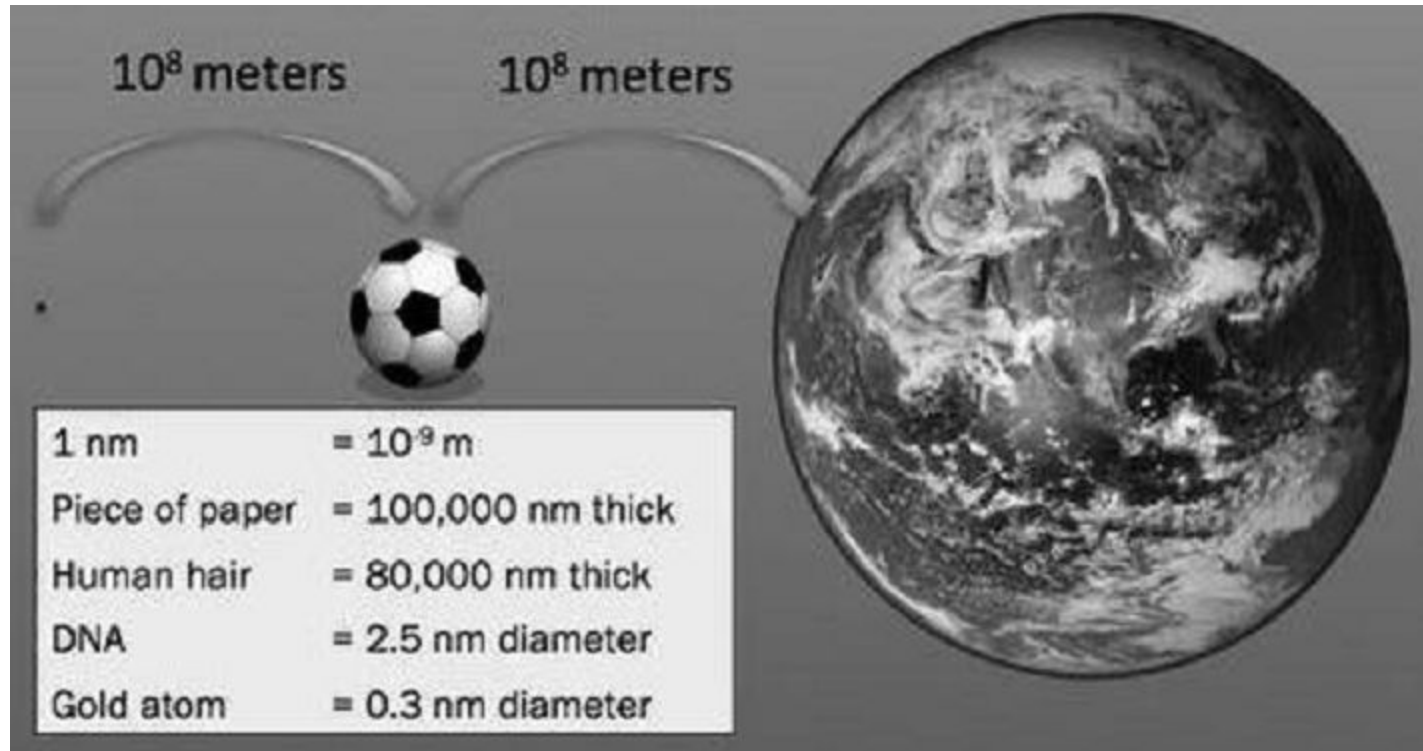
To date, nanotechnology has become an interdisciplinary bridge due to unique properties of nanomaterials, widely applied to pharmacy, therapeutics, electromagnetics and catalysis.

Long back ago

As far back as the fourth century, nanoparticles were used by artisans for generating a glittering effect on the surface of pots. One the left is a famous artefact called the Lycurgus Cup resides in the British Museum in London. What makes this cup unique is that its color changes from green (when illuminated from the outside) to red (when illuminated from within) due to nanoparticles of gold and silver in the glass.

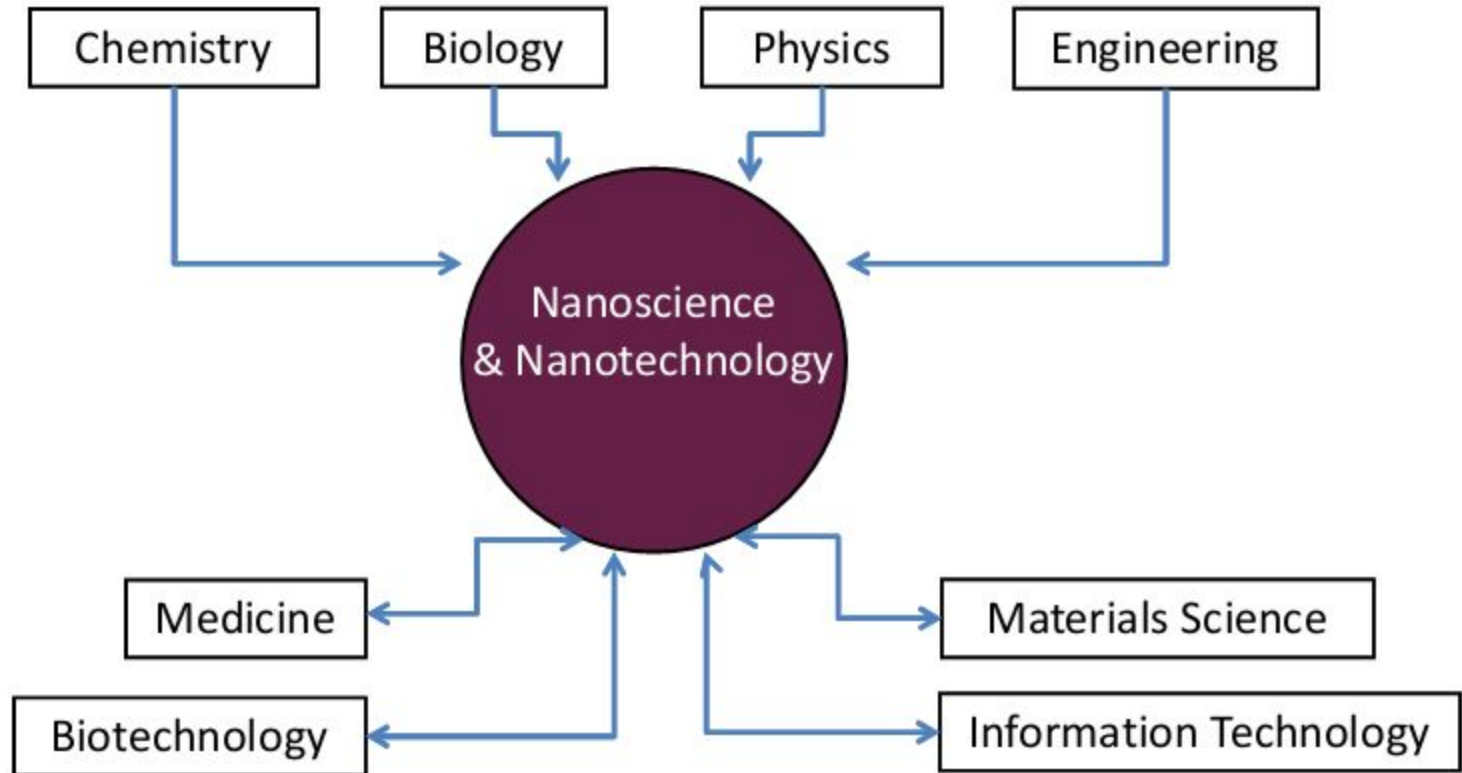


How small is “nano”?



On this scale, interatomic (coulombic) forces become large, and must be considered when undertaking studies to characterize, experiment, and model the behaviors of nanomaterials

An Interdisciplinary Endeavor



Three (of several) Senses of Small

What do we mean by small particle and why does their chemistry change?

Size and surface area effects

1 nm –100 nm **Fundamental materials properties remain** the same but size, shape and surface area alter some behaviors work function, solubility, chemical potential, contaminate sorption.

Critical Size and Characteristic Length Scale

Interesting or unusual properties because the **size of the system approaches some critical length** (includes quantum effects). **Many characteristics** of material may have normal or nearly normal behaviour

New (Non-extensive) Properties

Systems not large enough to have extensive properties. Particles become effectively polymorphs of “bulk” materials and statistical homogeneity may not be valid.

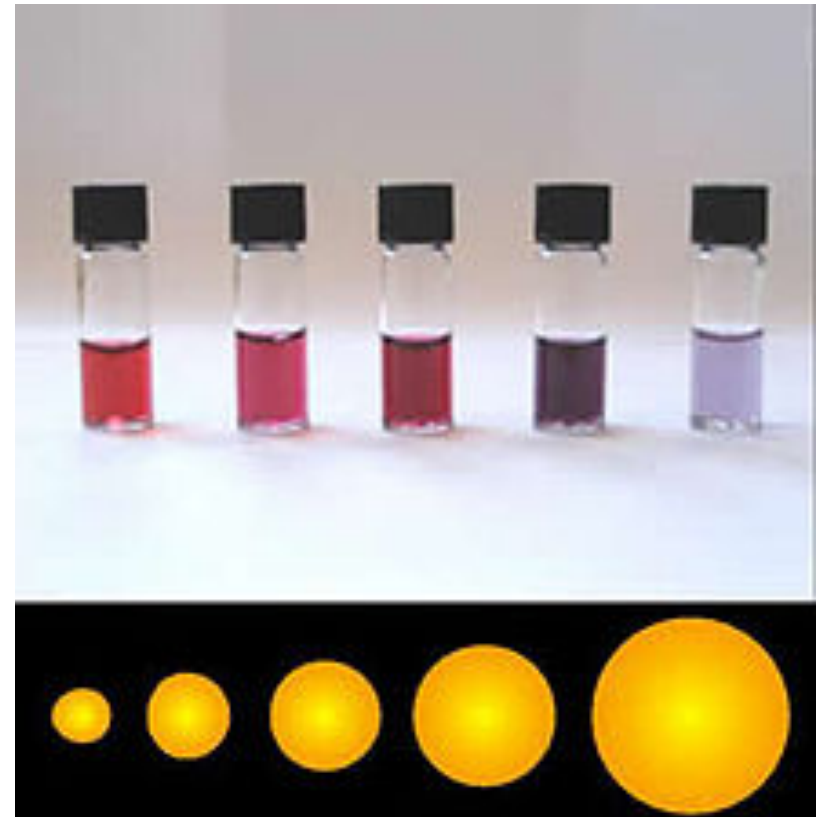
Some examples

Size decreases ---- \square Surface energy increases ---- \square Thus Melting point decreases.
Eg.: 3 nm CdSe nanocrystal melts at 700K compared to bulk CdSe at 1678 K.

Reactivity
Melting point
Strength
Conductivity
Color

Suspensions of gold nanoparticles of various sizes. The size difference causes the difference in colors.

Size and Shape Matter

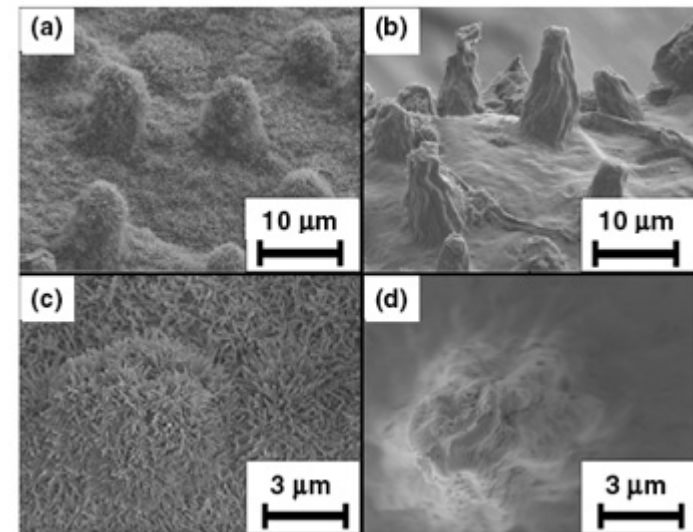
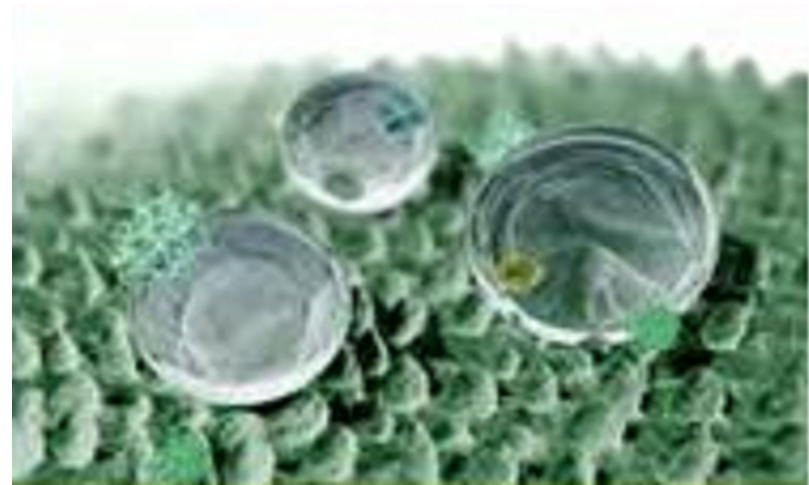


Where does the inspiration comes from ?

and the answer is nature.....

Lotus-Inspired Nanotechnology Applications

1. The Lotus effect



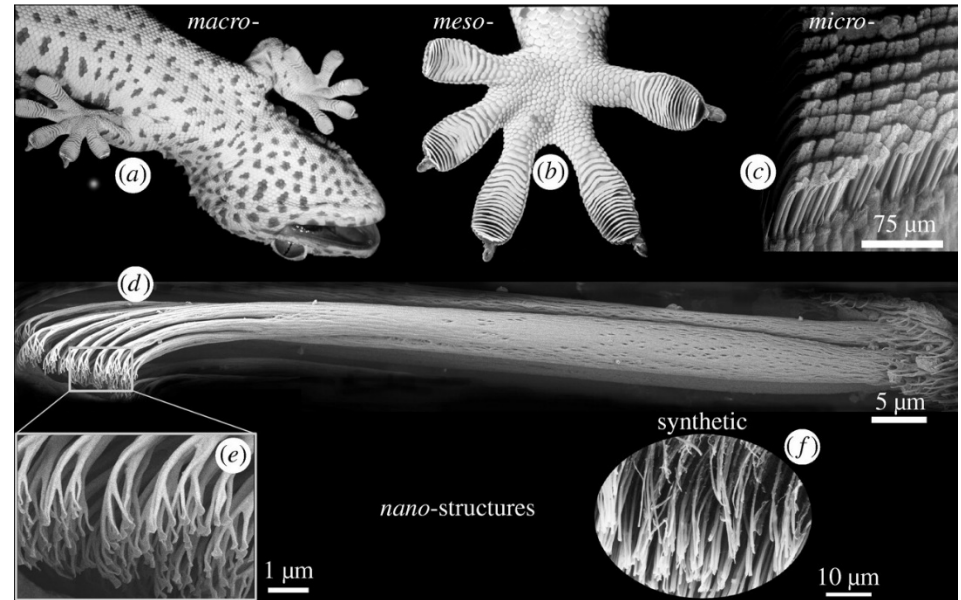
<http://iopscience.iop.org/0957-4484/17/5/032>

Where does the inspiration comes from ?

2. Gecko adhesion: If geckos had not evolved, it is possible that humans would never have invented adhesive nanostructures.

Applications for gecko-inspired adhesive nanostructures

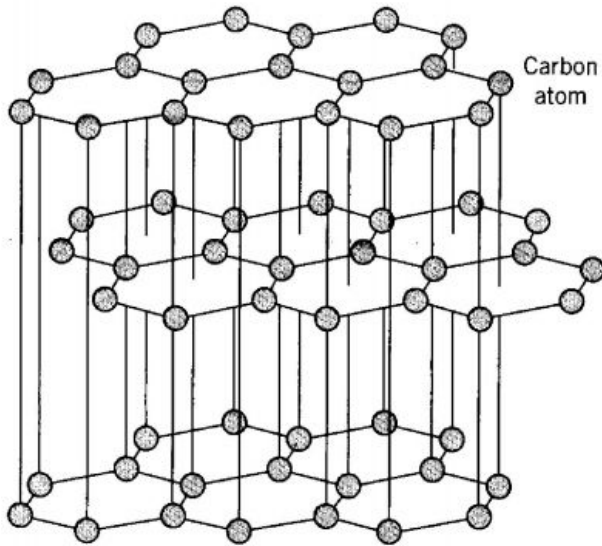
- dry self-cleaning adhesive
- Biomedical applications such as endoscopy and tissue adhesives
- MEMS switching
- wafer alignment
- micromanipulation
- robotics



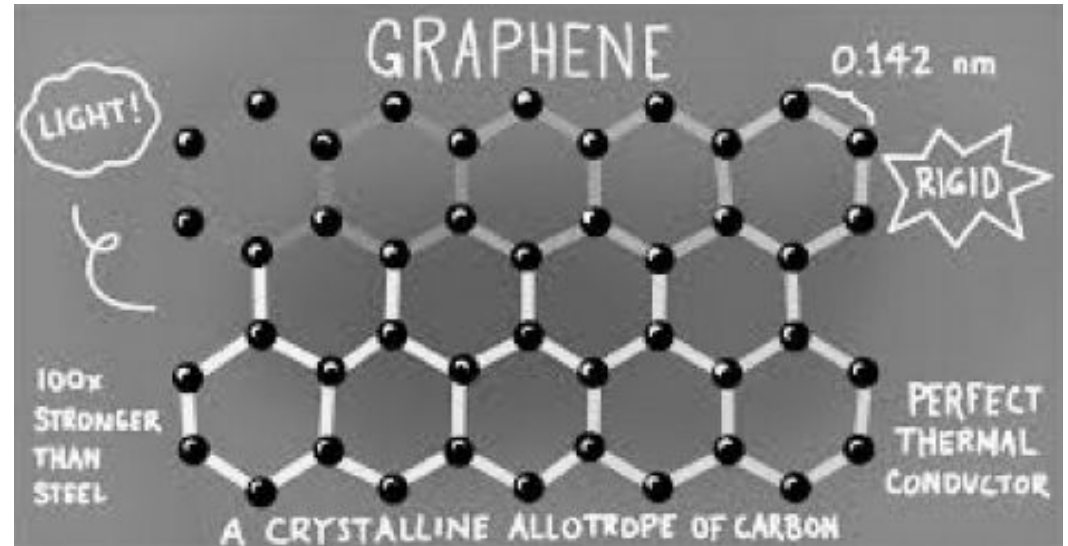
Sports applications such as fumble-free football gloves or rock climbing aids (Irving 1955) could be revolutionary. Using gecko technology to climb is not a new idea. In a seventeenth century Indian legend, Shivaji and his Hindu warriors used adhesive lizards from the Deccan region as grappling devices to scale a sheer rock cliff and mount a surprise attack on a Maharashtrian clifftop stronghold (Ghandi 2002). The legendary climb was even depicted in a 1923 historical film, *Sinhagad* (although in this version of the legend it was Shivaji's military commander, Tanaji, who used geckos to assail the fortress; Varma 2005).

<https://doi.org/10.1098/rsta.2007.2173>

Difference between bulk and nanomaterials



BULK carbon as graphite



Nano carbon as graphene

Two principal factors cause the properties of nanomaterials to differ significantly from bulk materials:

- Increased relative surface area
- quantum effects

These factors can change or enhance properties such as reactivity, strength and electrical characteristics.

Confinement in nanomaterials

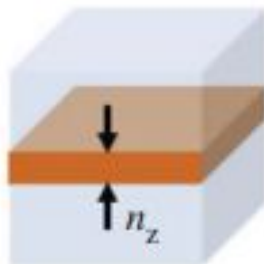
If two dimensions are so reduced and one remains large, the resulting structure is referred to as **quantum wire**. Quantum wires, which are confined in two dimensions, can be thought of as nanometer-sized cylinders that can measure several microns in length.

Finally, the **quantum dot** is a zero-dimensional nanometre-sized sphere, confined in all three dimensions.

no confinement
bulk
(3D materials)

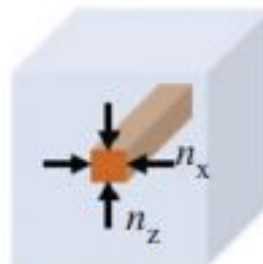


1D confinement
Q-well/ultrathin film
(2D materials)



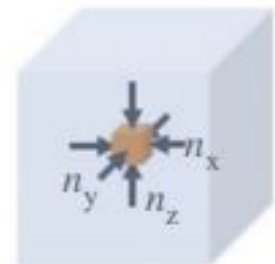
Thin films
Quantum wells

2D confinement
Q-wire
(1D materials)



Nanorods
Nanowires
nanotubes

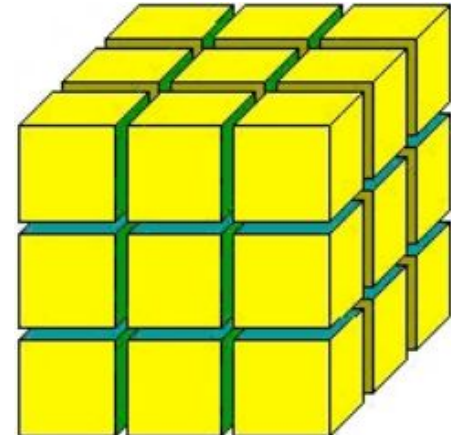
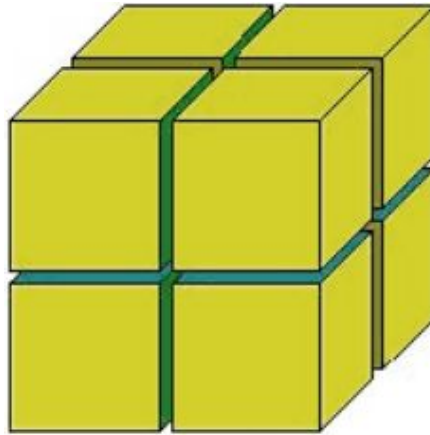
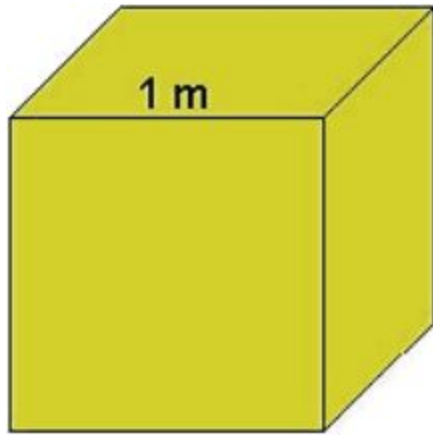
3D confinement
Q-dot
(0D material)



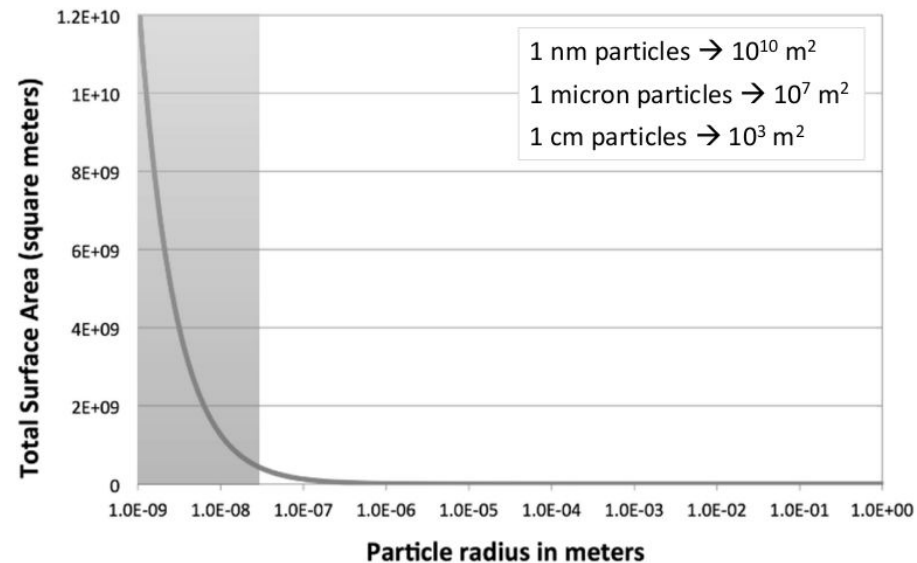
Nanoparticles
Quantum dots

<https://royalsocietypublishing.org/doi/10.1098/rsos.180387>

What is the Big Deal About Nanoscience



The drastic increased ratio of surface area to volume makes interactions between the surfaces of particles very important. If something has more surface area, there are more places for other chemicals to bind or react with it. For example, fine powders offer greater reaction speed because of the increased surface area. Think about how much faster you can cool a glass of water if you put crushed ice in it rather than ice cubes.



Nanoscale particles maximize surface area, and therefore maximize possible reactivity.

Surface area to volume ratio

Macro-scale

A typical material possesses:

$\sim 10^{23}$ atoms/cm³ (volume density); $\sim 10^{15}$ atoms/cm² (surface density)

Assume that, we've a cube of unit length

Total number of atoms $\sim 10^{23}$ atoms/cm³ x (1 cm)³ $\sim 10^{23}$

Total number of surface atoms $\sim 10^{15}$ atoms/cm² x 6 x (1 cm)² $\sim 6 \times 10^{15}$

So, the ratio of surface to total atoms will be $\sim 6 \times 10^{-8}$.

Nano-scale

A typical material possesses:

$\sim 10^{23}$ atoms/cm³ (volume density); $\sim 10^{15}$ atoms/cm² (surface density)

Assume that, we've a cube of length = 10 nm = 10^{-7} cm

Total number of atoms $\sim 10^{23}$ atoms/cm³ x (10^{-7} cm)³ ~ 100

Total number of surface atoms $\sim 10^{15}$ atoms/cm² x 6 x (10^{-7} cm)² ~ 60

So, the ratio of surface to total atoms will be ~ 0.6 .

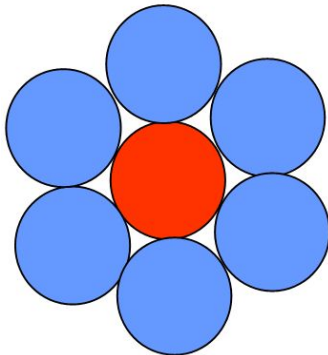
Nanoscale objects have a greater surface area than volume.

Very important property

Nanoparticles: their properties

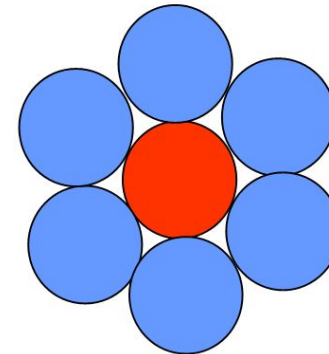
HOW and WHY do these large numbers of surface atoms compared to interior atoms make nanoparticles so different?

Interior Atoms



Attracted to lots of nearest neighbors
High Coordination Numbers

Surface Atoms



Attracted to few nearest neighbors
Low Coordination Numbers

Surface atoms have Higher energy!

$$E_{\text{surface atoms}} - E_{\text{interior atoms}} = E_{\text{surface}} \text{ (Surface Energy)}$$

Effect on the rate of chemical reactions

- Size of the particles taking part in a reaction and surface area
- Concentrations of reactants
- Temperature
- Presence of a catalyst

As the size of nanoscale particles decreases, the surface area to volume ratio increases. Therefore, the surface energy increases!

Increases the rate of some chemical reactions.

Effect on the melting point

Assume the change in internal energy (ΔU) and change in entropy per unit mass during melting are independent of temperature.

$$\Delta\theta = \frac{2T_0\sigma}{\rho Lr}$$

$\Delta\theta$ = deviation of melting point from the bulk value

T_0 = bulk melting point

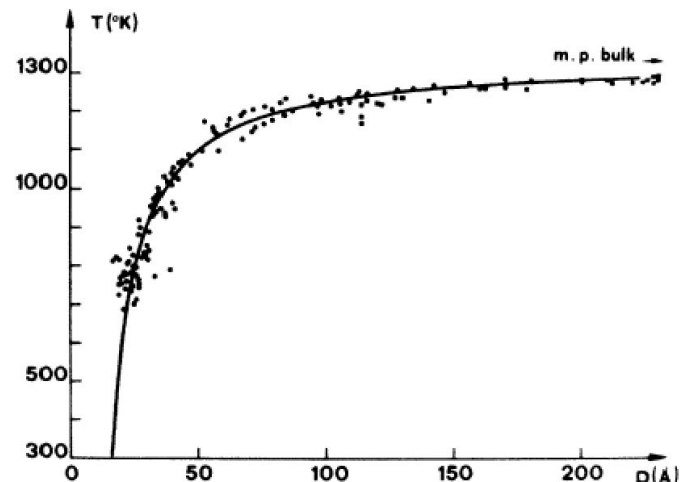
σ = surface tension coefficient for a liquid-solid interface

ρ = particle density

L = Latent heat of fusion

r = particle radius

- Lowering of the melting point is proportional to $1/r$.
- $\Delta\theta$ can be as large as couple of hundred degrees when the particle size gets below 10 nm!!
- Most of the time, σ the surface tension coefficient is unknown; by measuring the melting point as a function of radius, σ can be estimated.
- For nanoparticles embedded in a matrix, melting point may be lower or higher, depending on the strength of the interaction between the particles and matrix.
- Nanoparticles have a lower melting point than their bulk counterparts.



Melting point of gold nanoparticles as a function of size. Phys. Rev. A 13, 2287–2298 (1976).

Effect on mechanical properties

- The mechanical properties of nanomaterials increase with decrease in size, because smaller the size, lesser is the probability of finding imperfections such as dislocations, vacancies, grain boundaries.
- Strength of material improves significantly as the particle size decrease due to perfect defect free surface.
- Hardness and yield strength of material also increases as particle size decreased.
- Elastic modulus and toughness of material also increases as the particle size decreased.

Lower number of defects

Fewer surface defects

Effect on the Electronic Properties

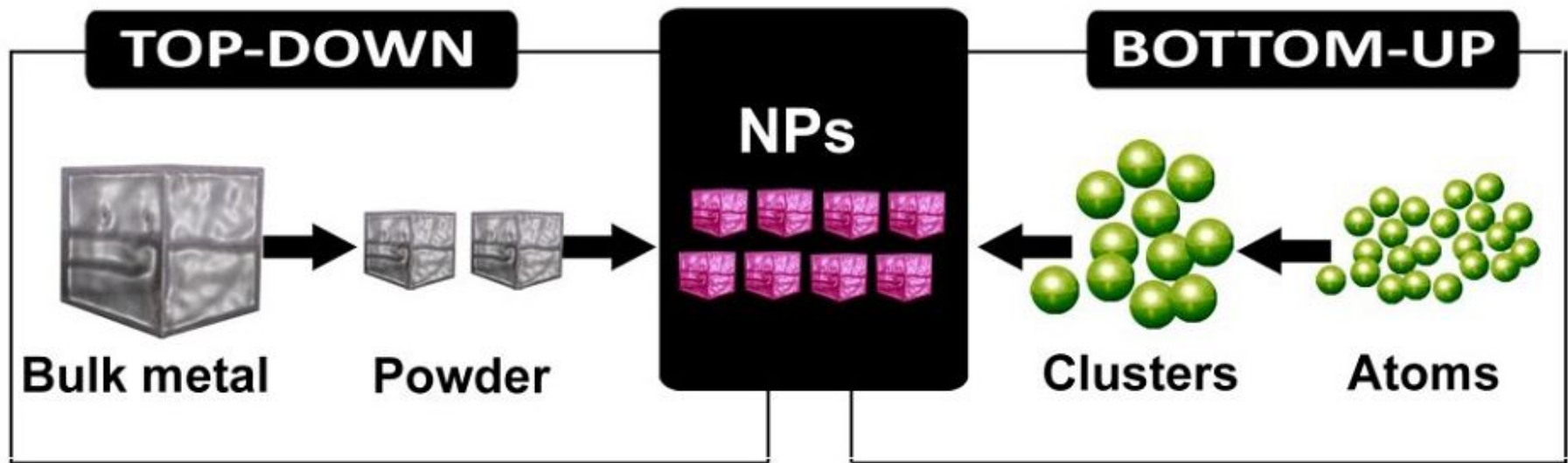
Size plays an important role in electrical properties and is based on mainly following mechanisms:

- Surface scattering
- Change of electronic structure
- Quantum Transport
- Change of microstructure
- Discrete Charging

Change of Electronic Structure

- Reduction in characteristic dimension below de-Broglie wavelength results in change of electronic structure, leading to widening of bandgap. Such a change results in reduced electrical conductivity.
- Some metal nanowires undergo transition to become semiconductor and semiconductors might become insulators when their diameters are reduced below a critical diameters.

Synthesis of Nanoparticles



Uses macroscopic structures, which can be externally-controlled in the processing of nanostructures. Slicing or successive cutting of a bulk material to get nano-sized particle.

Typical examples are etching through the mask, ball milling.

Build up of a material atom by atom, molecule by molecule. Physical forces operating at nanoscale are used to combine basic units into larger stable structures.

Typical examples are quantum dot formation during epitaxial growth and formation of nanoparticles from colloidal dispersion.

Top-Down approach

In Top-down techniques, the starting material is solid state

Physical processing methods

Mechanical methods:

cutting, etching, grinding, ball milling

Lithographic techniques:

Photo Lithography

Electron Beam Lithography

Bottom-up approach

All the Bottom-up techniques, the starting material is either gaseous state or liquid state of matter

Physical and chemical processing methods

Physical Vapor Deposition (PVD):

- Involves condensation of vapor phase species
- Evaporation (Thermal, e-beam) sputtering
- Plasma Arcing
- Laser ablation

CVD: Deposition of vapor phase of reaction species

Self-assembled Monolayer

Electrolytic deposition

Sol-gel method

Ball Milling

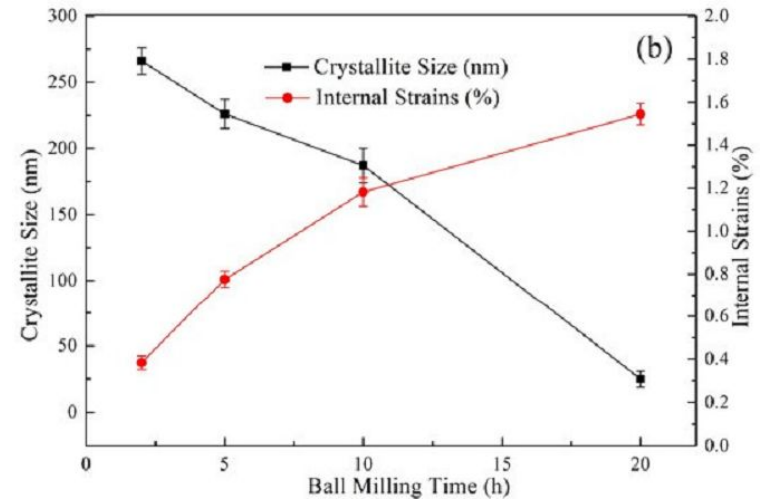
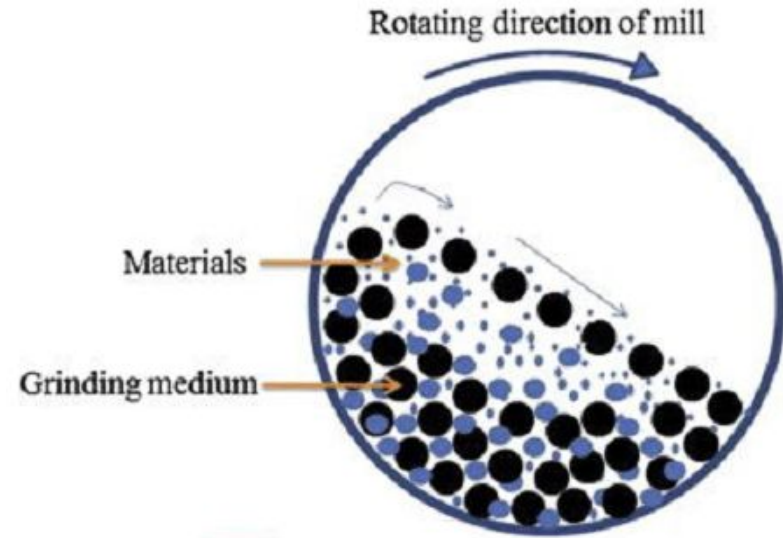
Simplest method of making nanoparticle in powder form Begin with bulk materials (top) that are subsequently reduced to nano-size (down) by the way of physical, chemical and mechanical processes.

e.g. Mechanical-ball milling, grinding *etc.*

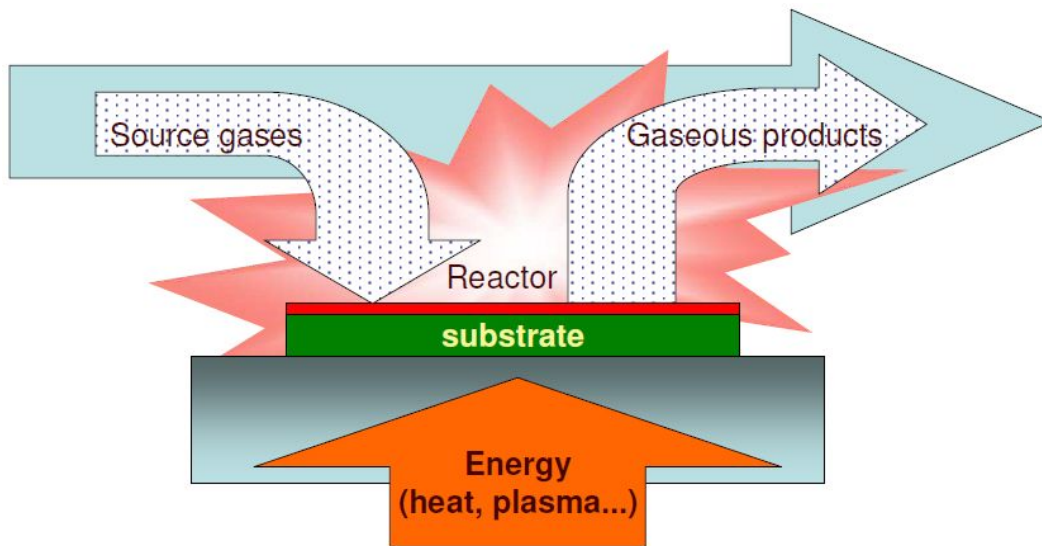
- Macro or micro scale particles are ground in a ball mill, a planetary ball mill, or other size reducing mechanism.
- 2:1 mass ratio of balls to materials
- Material is forced to the walls and pressed against the walls.
- The resulting particles are separated by filters and recovered.
- Broad size distribution and varied particle geometry
- May contain defects and impurities from the milling process.
- Metallic and ceramic nanomaterials are produced, generally.

Ball Milling

- ❑ A hollow steel cylinder containing tungsten balls rotates about its central axis (partially filled with the material to be grounded plus the grinding medium).
- ❑ Particle size is reduced by brittle fracturing resulting from ball-ball and ball-wall collisions.
- ❑ Milling takes place in an inert gas atmosphere to reduce contamination.
- ❑ Control the speed of rotation and duration of milling-grind material to fine powder(few nm to few tens of nm).



Chemical Vapour Deposition



Reactant gases introduced in the chamber, chemical reactions occur on wafer surface leading to the deposition of a solid film.

e.g. APCVD, LPCVD, PECVD, MOCVD
most commonly used for dielectrics and Si.

CVD major steps:

- Introduce reactive gases to the chamber. One or more than one gas may be used plus carrier gases (nonreactive gases)
- Activate gases (decomposition) by heat or plasma.
- Gas absorption by substrate surface .
- Transport of volatile byproducts away from substrate.
- Exhaust waste.

Deposition of film through chemical reaction and surface absorption.

Chemical Vapour Deposition

Advantages

- High coating hardness
- Good adhesion (if the coating is not too thick)
- Good uniformity of coating

Disadvantages

- High temperature process (distortion)
- Sharp edge coating is difficult (thermal expansion mismatch stresses)
- Limited range of materials can be coated
- Environmental concerns about process gases

- Gaseous compounds react to form a dense layer on a heated substrate.
- The most widely deposited wear resistant coatings are TiC, TiN, chromium carbide and alumina.
- Deposition temperatures are generally in the range 800-1000°C which restricts the range of materials that can be coated and can also lead to component distortion.

Characteristics of a CVD coating process

- Applied at elevated temperature to facilitate reaction.
- Typically applied under vacuum.
- Contaminants must be removed from the part surface before coating application.
- Process may limit the base materials that can be coated, *i.e.* temperature limitations or reactivity limitations.
- Process may limit the ability to mask specific target areas.
- Unlike most PVD (physical vapor deposition) processes, the CVD Process is not limited to line-of-site application. Coating gas will coat all areas of a part including threads, blind holes, and interior surface.
- Film thickness is limited due to coating stress.
- Coating is bonded to the surface during the reaction which creates a superior adhesion when compared to typical PVD or low temperature applied spray coatings.

CVD Benefits

- Can be applied to a wide variety of base materials including ceramics, glass, metals and metal alloys.
- Can coat precision surfaces and intricate surfaces including seal areas and internal surfaces.
- Can withstand exposure to low and high temperature and extreme temperature variation.
- A durable coating to substrate bond means the coating remains bonded in high stress environments, even when the substrate surface flexes or bends.
- Precursor gas can be optimized for chemical inertness, high lubricity, corrosion resistance, fouling resistance, high purity, or wear resistance.

Coating Drawbacks

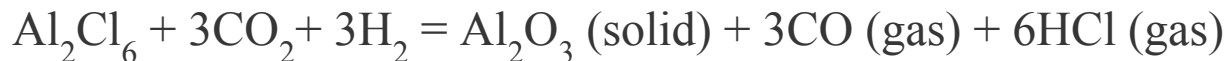
- Typically applied at higher temperatures (depending on the precursor).
- Difficult to mask surface. Usually an all or nothing coating.
- Size limited to reaction chamber capacity.
- Parts must be broken down into individual components
- Not an "on site" process, parts must be shipped to a coating center.

Typical example: CVD

The simplest CVD process involves the pyrolytic decomposition of a gaseous compound on the substrate to provide a coating of a solid reaction product. For example, the following reactions are used to produce solid coatings of tungsten metal (W), titanium carbide (TiC) and titanium nitride (TiN) respectively:



Alumina may be deposited by the reaction:



Application of CVD technique

CVD has applications across a wide range of industries such as:

Coatings – Coatings for a variety of applications such as wear resistance, corrosion resistance, high temperature protection, erosion protection and combinations thereof.

Semiconductors and related devices – Integrated circuits, sensors and optoelectronic devices.

Optical Fibres – For telecommunications.

Composites – Preforms can be infiltrated using CVD techniques to produce ceramic matrix composites such as carbon-carbon, carbon-silicon carbide and silicon carbide-silicon carbide composites.

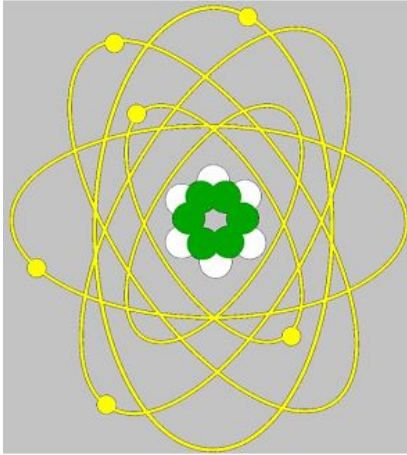
Powder production – Production of novel powders and fibres

Catalysts

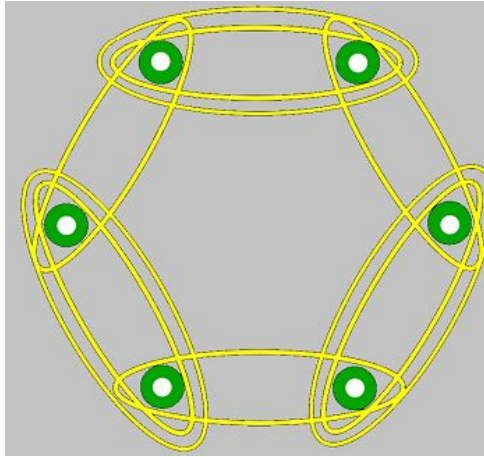
Nanomachines, Nanomedecine, Nanofiber, *etc.*

Carbon based materials

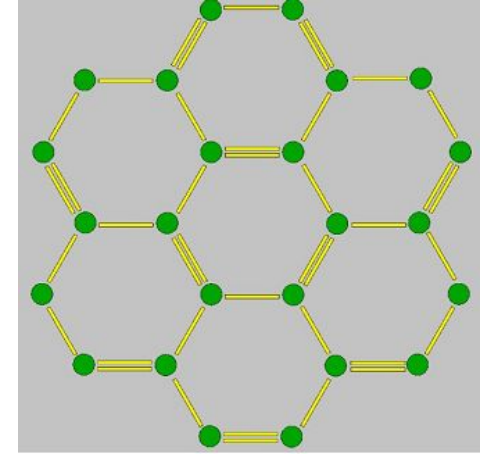
Carbon is a unique material, and can be a good metallic conductor in the form of graphite, a wide band gap semiconductor in the form of diamond, or a polymer when reacted with hydrogen.



Carbon atom



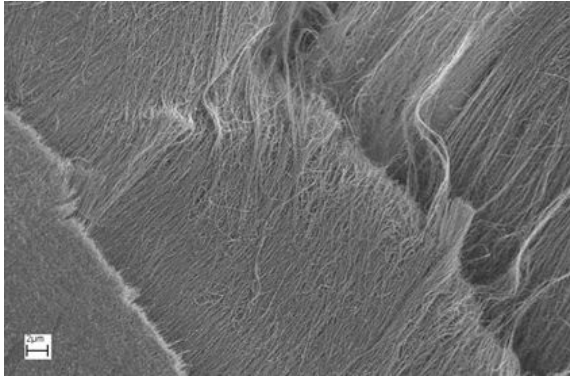
Aromatic ring



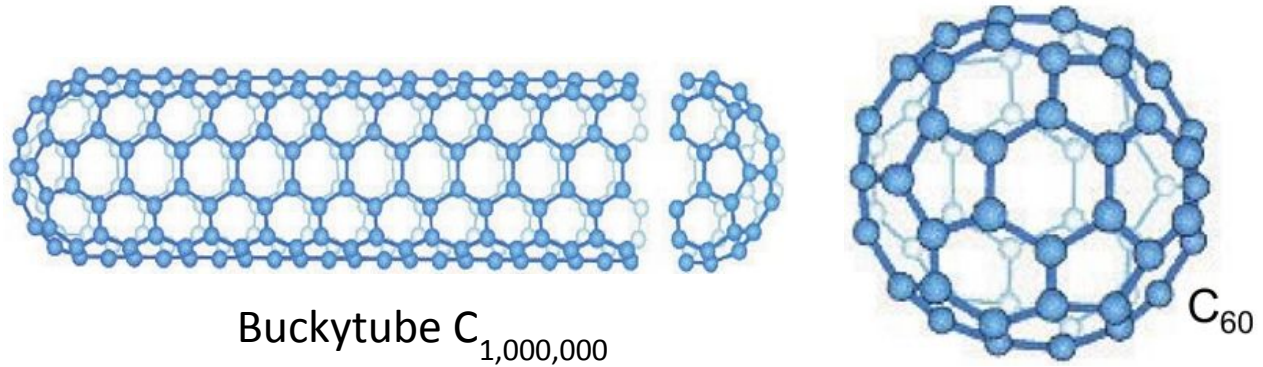
Graphene sheet

- Carbon
- Graphite (Ambient conditions) sp^2 hybridization: planar
 - Diamond (High temperature and pressure) sp^3 hybridization: cubic
 - Nanotube/Fullerene (certain growth conditions) $sp^2 + sp^3$ character: cylindrical

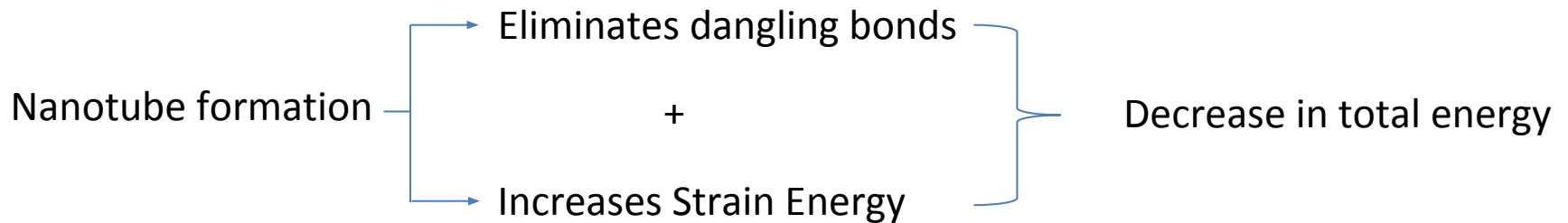
Carbon nanotube (CNT)



CNT

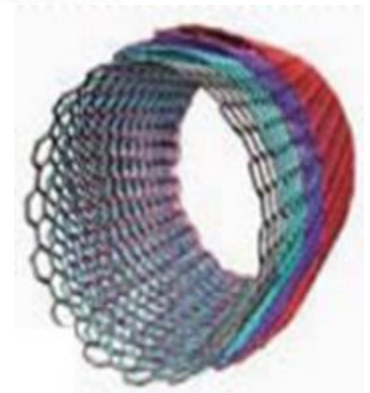
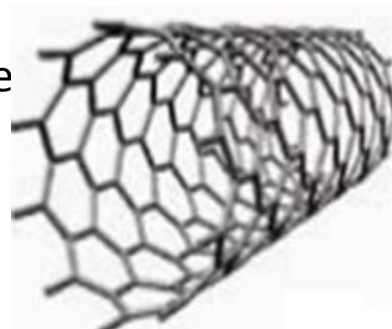
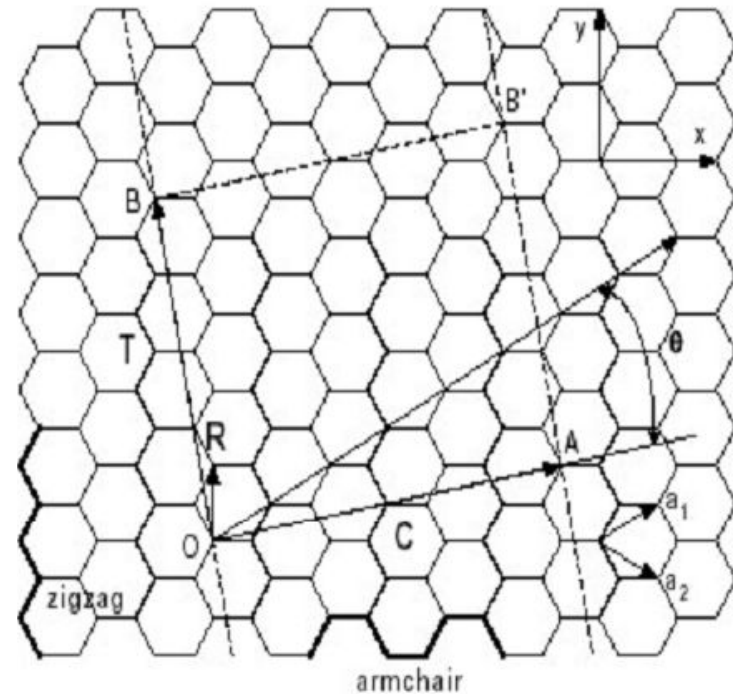


Finite size of graphene layer has dangling bonds. These dangling bonds correspond to high energy states.



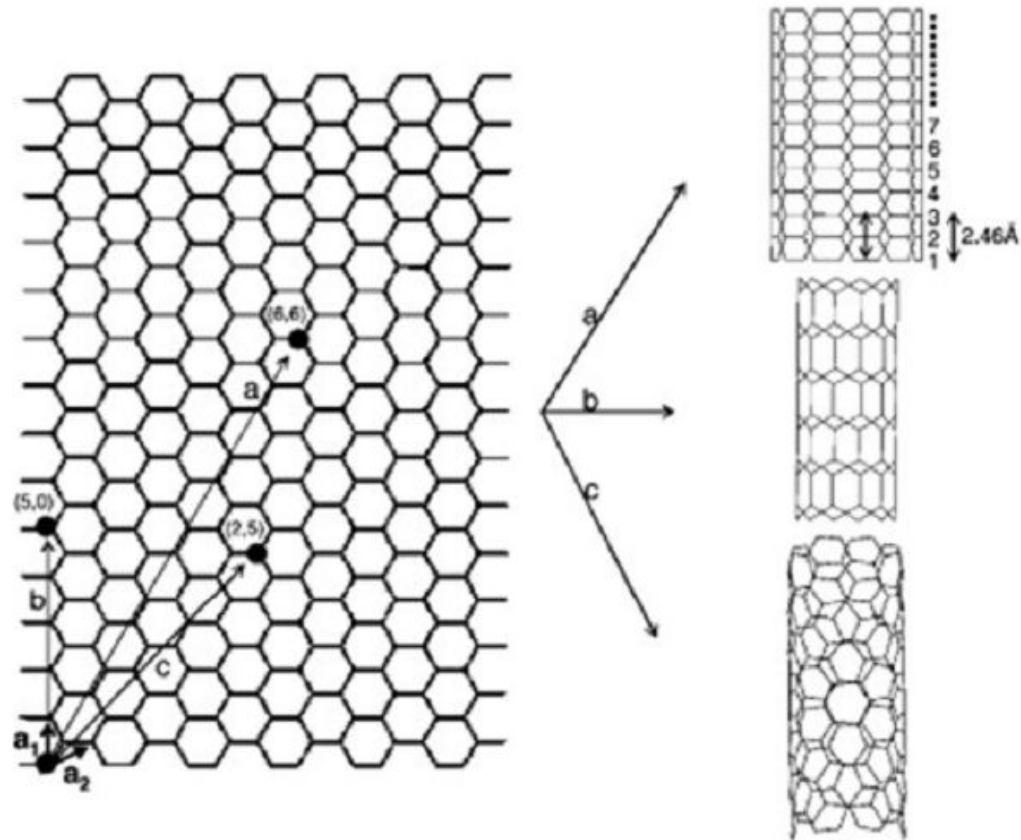
Carbon nanotube

- Carbon nanotubes are tubular forms of carbon that can be envisaged as graphene sheets rolled into cylindrical form.
- These nanotubes have diameters of few nanometers and their lengths are up to several micrometers.
- Each nanotube is made up of a hexagonal network of covalently bonded carbon atoms. CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.
- Carbon nanotubes are of two types: single-walled and multi-walled.
- A single-walled carbon nanotube (SWNT) consists of a single graphene cylinder whereas a multi-walled carbon nanotube (MWNT) comprise of several concentric graphene cylinders.
- A CNT is characterized by its chiral Vector: $\mathbf{C} = n\hat{a}_1 + m\hat{a}_2$; and ϑ is the chiral angle with respect to the zigzag axis.



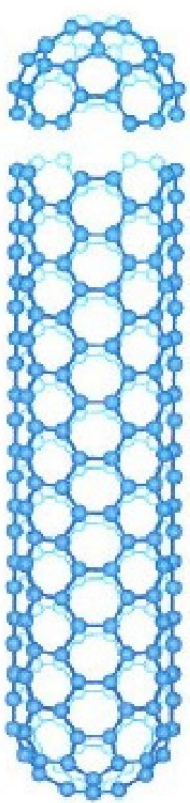
Carbon nanotube

- ✓ Depending on the way of rolling of graphene sheets, SWNT of different types, viz. armchair, zig-zag and chiral could be produced.
- ✓ They can be represented using the method given by Hamada.
- ✓ For example, to realize an (n, m) nanotube, one has to move n times \mathbf{a}_1 from the selected origin and then m times \mathbf{a}_2 .
- ✓ On rolling the graphite sheet about bravis vectors, these points coincide to form the (n, m) nanotube.
- ✓ Thus armchair, zig-zag and chiral nanotubes can be represented as (n, n) , $(n, 0)$ and (n, m) , respectively.

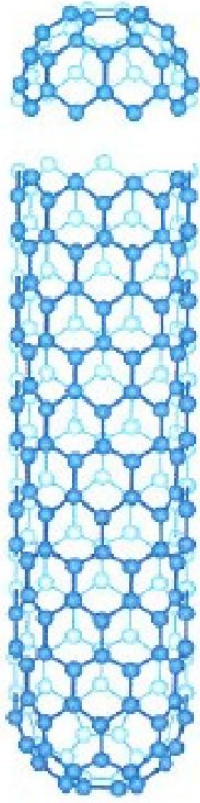


Rolling of a graphene layer to form single-walled carbon nanotubes of (a) armchair, (b) zig-zag and (c) chiral type.

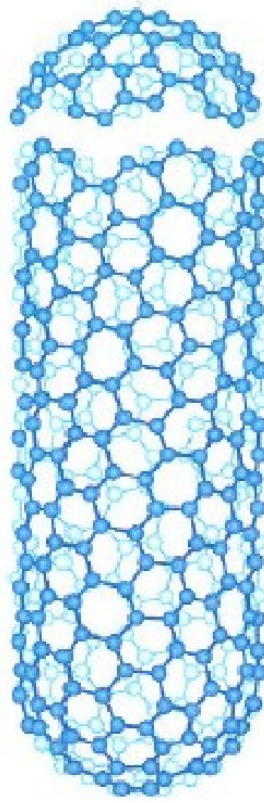
Carbon nanotube



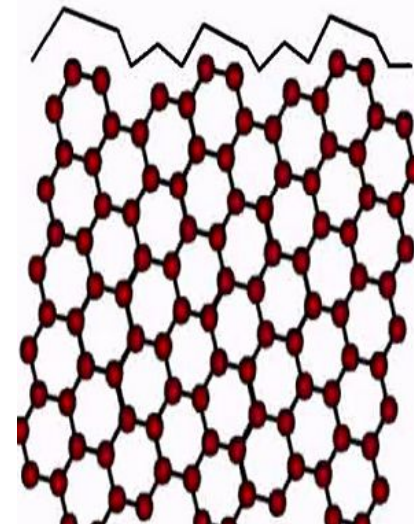
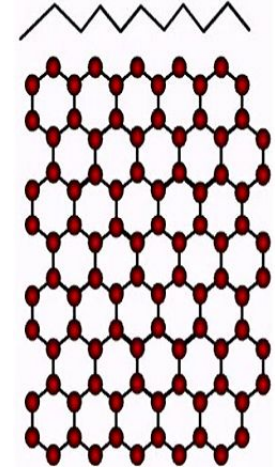
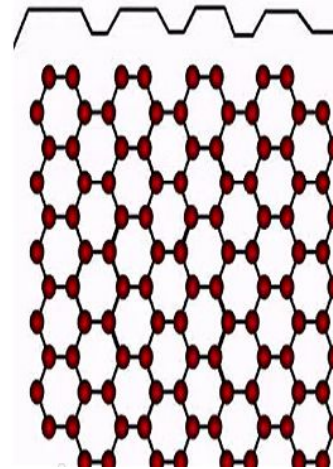
Armchair



Zig Zag



Chiral



Diameter of Carbon nanotube

CNT diameter

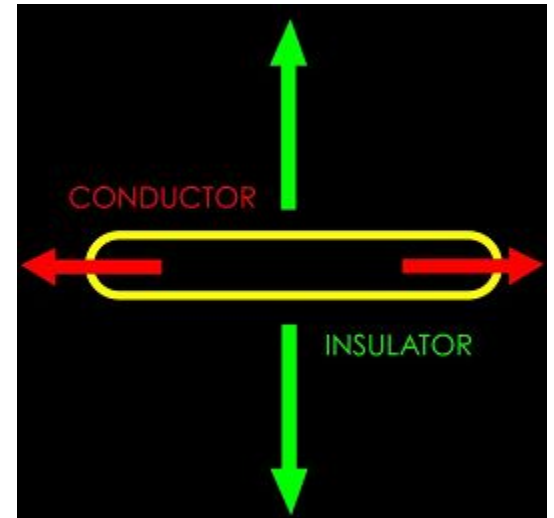
$$d = \frac{a_{cc}}{\pi} \sqrt{3(m^2 + mn + n^2)} \quad a_{cc}=0.142 \text{ nm C-C bond length}$$
$$= 0.0783 \sqrt{(m^2 + mn + n^2)} \text{ nm}$$

Chiral angle

$$\theta = \tan^{-1} \left(\frac{\sqrt{3}n}{2m + n} \right)$$

Properties of CNT

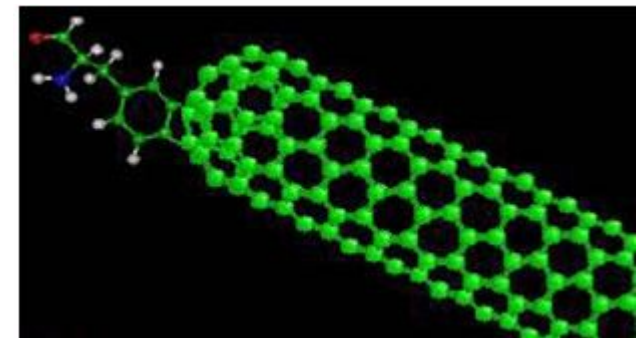
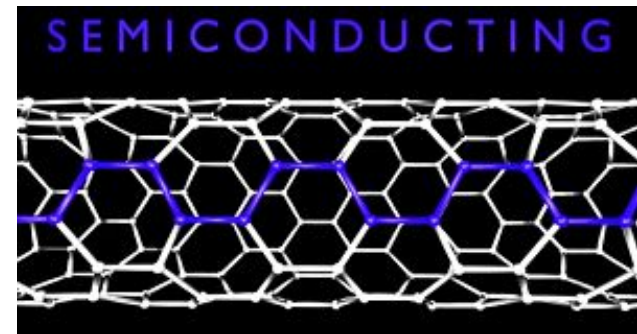
- remarkable electrical conductivity
- exceptional tensile strength,
 - ✓ Strong Like Steel
 - ✓ Light Like Aluminum
 - ✓ Elastic Like Plastic
- thermal conductivity



These properties are expected to be valuable in many areas of technology, such as electronics, optics, composite materials (replacing or complementing carbon fibers), nanotechnology, and other applications of materials science.

Electrical properties of CNT

- Electrical conductivity six orders of magnitude higher than Cu.
- Can be metallic or semiconducting depending on chirality.
 - ✓ Tuneable band gap
 - ✓ Electronic properties can be tailored through application of external magnetic field, mechanical deformation *etc.*
- Very high current carrying capacity
- Can be functionalized



Synthesis of CNTs

To produce nanotubes in sizable quantities, following techniques have been used:

1. Arc discharge
2. laser ablation
3. chemical vapor deposition

Mostly, these processes take place in a vacuum or with process gases.

The CVD growth method is popular, as it yields high quantity and has a degree of control over diameter, length and morphology. Using particulate catalysts, large quantities of nanotubes can be synthesized by these methods, but achieving the repeatability becomes a major problem with CVD growth.

CNT Application

- ❑ CNT technology in a number of their bicycle components – including flat and riser handlebars, cranks, forks, seatposts, stems and aero bars.
- ❑ carbon **nanoepony resin**: wind turbines, marine paints and a variety of sports gear such as skis, ice hockey sticks, baseball bats, hunting arrows, and surfboards.
- ❑ “**Gecko tape**” (also called “nano tape”, double-sided adhesive tape): It can be used to hang lightweight items such as pictures and decorative items on smooth walls without punching holes in the wall. No residue after removal and can stay sticky in extreme temperatures.

Under development

- ❑ Using carbon nanotubes for environmental monitoring due to their active surface area and their ability to absorb gases.
- ❑ The Boeing Company has patented the use of carbon nanotubes for structural health monitoring of composites used in aircraft structures. This technology will greatly reduce the risk of an in-flight failure caused by structural degradation of aircraft.
- ❑ IBM expected carbon nanotube transistors to be used on Integrated Circuits.
- ❑ Many more..

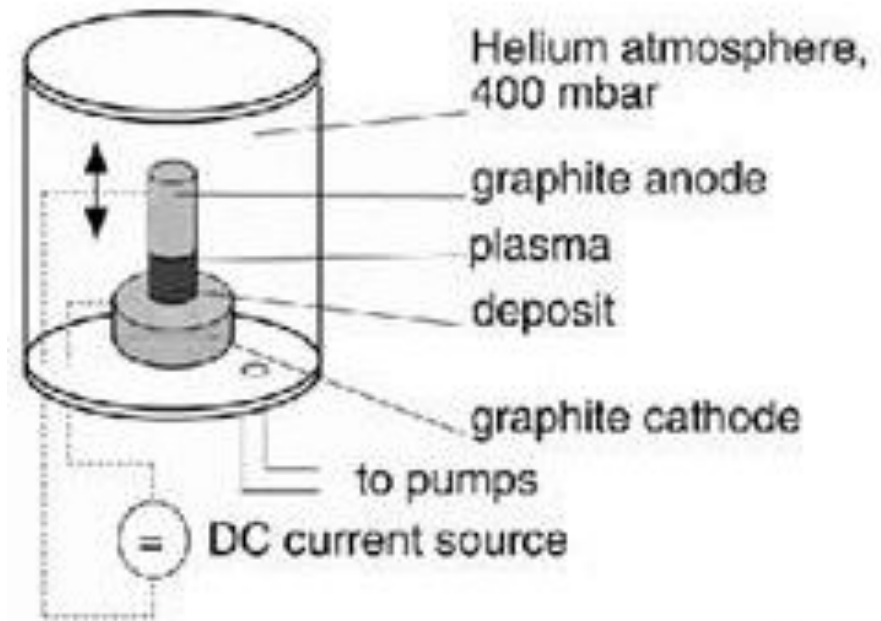
Nanotubes Growth Methods: Arc Discharge

The arc discharge technique generally involves the use of two high-purity graphite electrodes as the anode and the cathode.

The electrodes were vaporized by the passage of a DC current (~ 100 A) through the two high-purity graphite separated ($\sim 1\text{--}2$ mm) in 400 mbar of Helium atmosphere.

After arc discharging for a period of time, a carbon rod is built up at the cathode. This method can mostly produce MWNTs but can also produce SWNT with the addition of metal catalyst such as Fe, Co, Ni, Y or Mo, on either the anode or the cathode.

The quantity and quality such as lengths, diameters, purity and etc. of the nanotubes obtained depend on various parameters such as the metal concentration, inert gas pressure, type of gas, plasma arc, temperature, the current and system geometry.



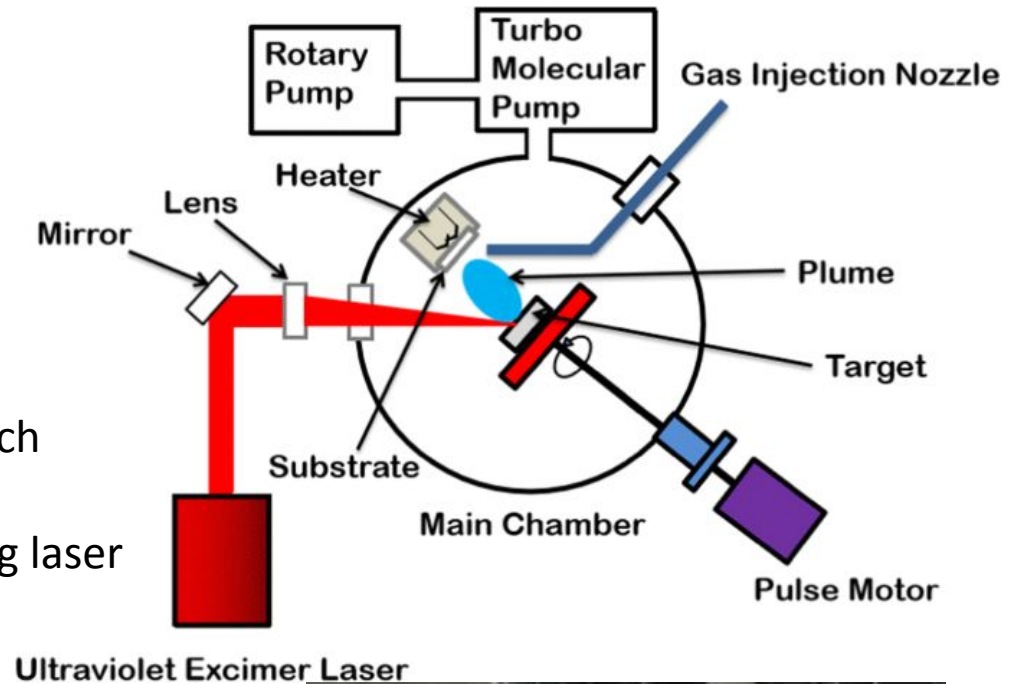
Nanotubes Growth Methods:Pulsed Laser Deposition

Advantages

- Flexible, easy to implement
- Growth in any environment
- Exact transfer of complicated materials ($\text{YBa}_2\text{Cu}_3\text{O}_7$)
- Variable growth rate
- Epitaxy at low temperature
- Atoms arrive in bunches, allowing for much more controlled deposition
- Greater control of growth (*e.g.*, by varying laser parameters)

Disadvantages

- Particulates
- Loss of volatile elements
- Small area deposition, Uneven coverage
- High defect or particulate concentration
- Mechanisms and dependence on parameters not well understood



Nanotubes Growth Methods: CVD

Hydrocarbon + Fe/Co/Ni catalyst $\xrightarrow{550-750^{\circ}\text{C}}$ CNT

Steps:

- Dissociation of hydrocarbon.
- Dissolution and saturation of C atoms in metal nanoparticle.
- Precipitation of Carbon.

