UNIT VI
Engineering Materials

CHAPTER-19
Nanomaterials and Their Applications

“We are placing bets on things we can do uniquely well.

First, new ways to power the world.

Second, molecular medicine.

And third, ***nanotechnology****.”*

- Jeff Immelt, CEO, General Electric

What is Nanotech?

Nano Technology – Art and science of manipulating atoms and molecules to create new systems, materials, and devices.

Nanomeasurement – Size

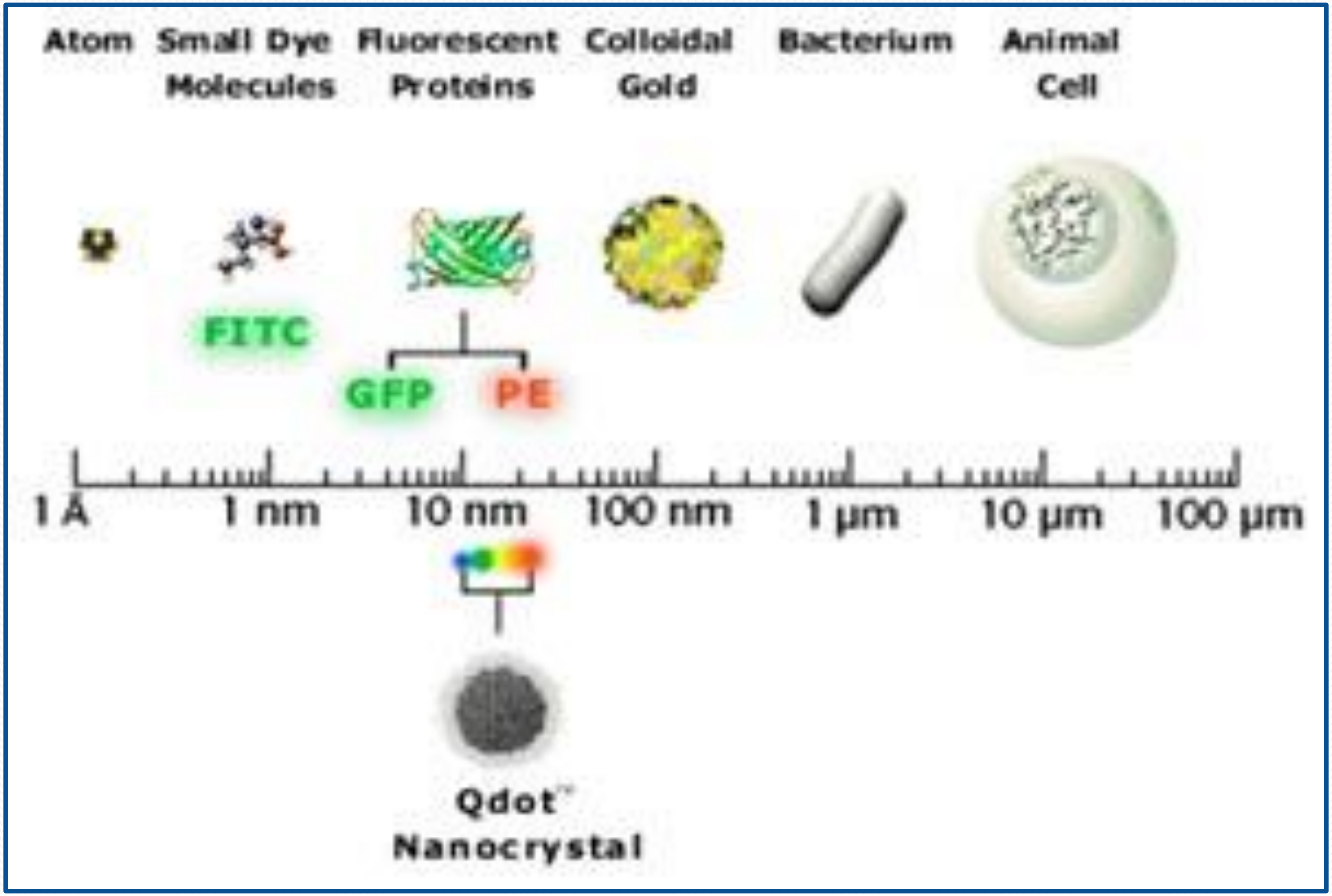
Nanomanipulation – Building from the bottom up.

Size Matters

- How Big is a Nano?
  - Nano = 1 billionth;100,000 x's smaller than the diameter of a human hair.

- Examples of Nanoscale
  - A cubic micron of water contains about 90 billion atoms. A micron is one thousandth of a millimeter, and a thousand times larger than a nanometer.
  - Another way to visualize a nanometer:
    1 inch = 25,400,000 nanometers

Size Matters in context to Nano Size



SIGNIFICANCE OF THE NANOSCALE

- The science dealing with the materials of the nanoworld is an extension of the existing science into the nanoscale or a recasting of existing sciences using a newer, more modern terms.

- Nanoscience is based on the fact that the properties of materials change with the function of physical dimensions of the materials.

- The properties of the materials are different at nanolevel due to two main reasons: increased surface area and quantum mechanical effect.

Surface Area

- For a sphere of radius *r, the surface area* and its volume can be given as

$$\text{Surface area} = 4\pi r^2$$

and its volume can be given as

$$\text{Volume} = \frac{4}{3}\pi r^3$$

Now, the surface to volume ratio $= \frac{3}{r}$

- Thus, we find that when the given volume is divided into smaller parts, surface area increases.

Quantum Confinement Effect

- At reduced dimensions, they are said to be either a quantum well, a quantum dot, or a quantum wire.

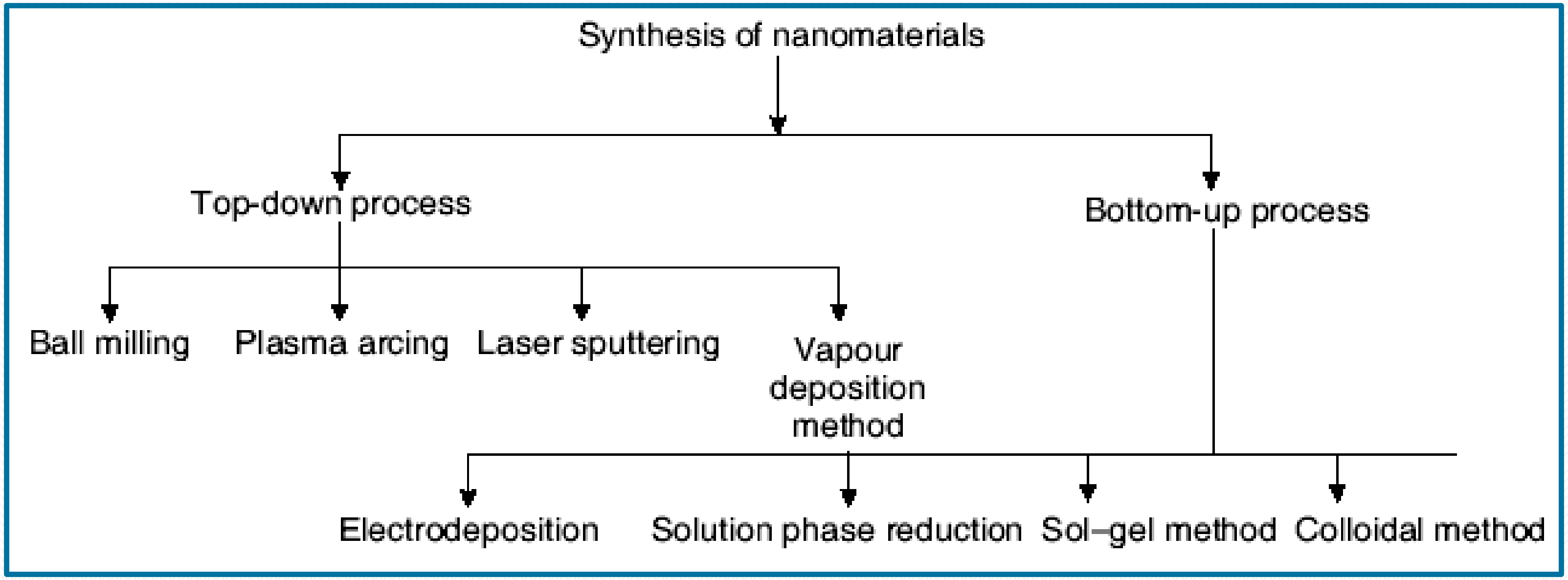
- The physics at these dimensions is entirely different. Actually, when the size of the grains is reduced to nanolevel, then overlapping of wavefunction and quantum confinements occurs.

- If *d is the diameter of the grain size, then the energy* goes up by factor $1/d^2$
- When the dimensions of a potential well or a box concerned with a particle are reduced to the order of de Broglie wavelength of electron (within few tens of nanometres), then energy levels of electrons change.

- This effect is called *quantum confinement. This can affect the optical*, electrical, and magnetic behaviour of materials at nanolevels.

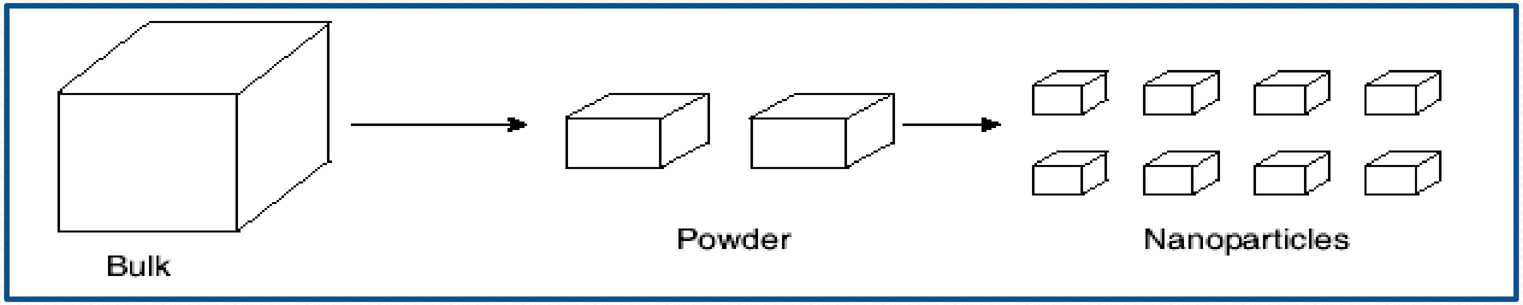
FABRICATION OF NANOMATERIALS

- Nanomaterials can be fabricated in two ways, namely, top-down and bottom-up .
- In top-down approach, nanomaterials are constructed by removing existing material from larger entities.
- In bottom-up approach, materials and devices are built atom by atom or molecule by molecule.



Top-Down Process

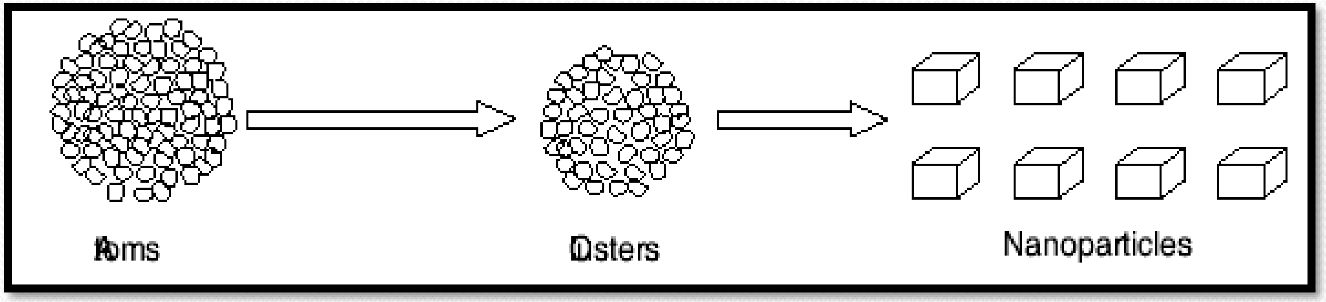
- Under this process of fabrication, bulk materials are broken into nano-sized particles.
- In this approach, there is no control over the size and the morphology of particles.



- Some common methods of top-down method are as follows.
  (i) Ball milling method
  (ii) Plasma arcing
  (iii) Laser sputtering
  (iv) Vapour deposition method

Bottom-Up Process

- Bottom-up approach refers to the building up of a material from the bottom, i.e., atom by atom, molecule by molecule, or cluster by cluster.
- Colloidal dispersion is a good example of bottom-up approach in the synthesis of nanoparticles.
- There are different methods used for the synthesis are:
  - (i) Sol–gel method
  - (ii) Colloidal method
  - (iii) Electrodeposition
  - (iv) Solution phase reductions
- The most important feature of this process is that the size and morphology of fabricated nanoparticles are well controlled.



Sol–Gel Method

Four steps are used in sol–gel method

Preparation of sol: The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides.

Preparation of gel: a typical sol–gel process, the precursor is subjected to a series of hydrolysis and polymerisation reaction to form a colloidal suspension known as gel.

Drying and purification: In this step, heat treatment is given to the gel emulsion to dry it up to the level necessary for further processing.

Product formation*:* different techniques, we can fabricate the particles or films of desired shape and size.

Flowchart of sol–gel method to produce nanomaterials

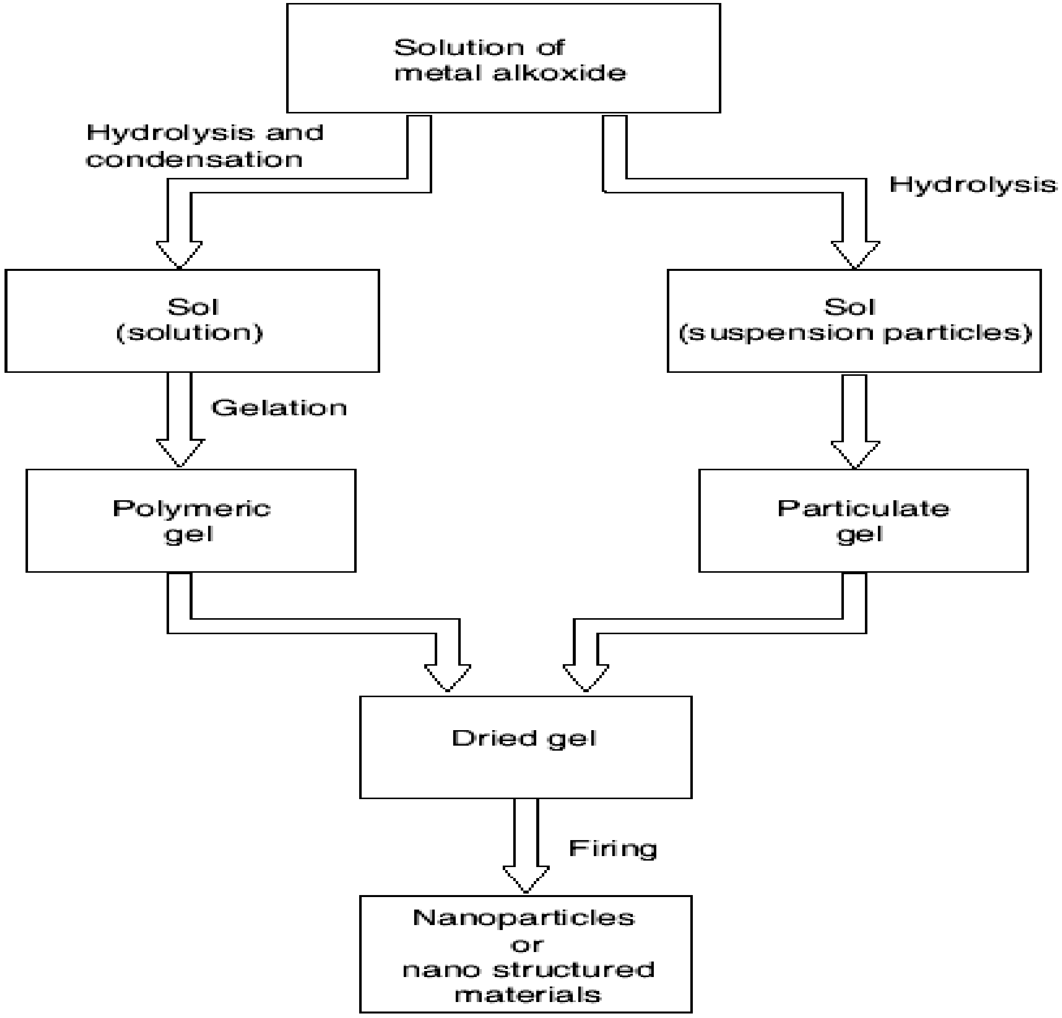
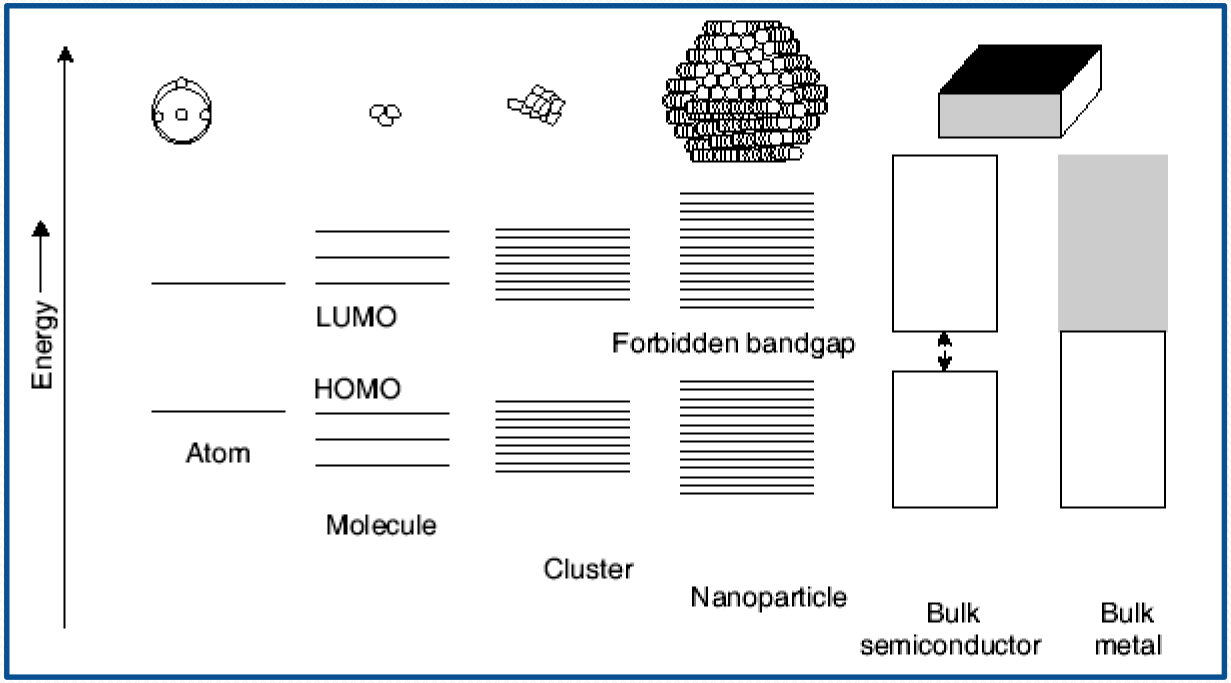


Fig. 19.5 Flowchart of sol–gel method to produce nanomaterials

QUANTUM SIZE EFFECT IN METAL OR SEMICONDUCTOR NANOPARTICLES

- Quantum effects dominate at nanolevel, which affects the optical, electrical, and the magnetic behaviour of the materials.

- Size quantisation effect and electronic state transition from bulk to atomic level are shown in Fig. 19.6.



DIFFERENT TYPES OF NANOSTRUCTURES: (CONFINEMENT DIMENSIONS 0-D, 1-D, 2-D, AND 3-D)

- A bulk conductor has all its three dimensions more than 100 nm.
- If one dimension is reduced to the nanorange while the other two dimensions remain large, then we get a structure known as *quantum well.*
- *If two dimensions are reduced and one remains large, the resulting structure is referred to as the quantum wire.*
- *The extreme case of this process of size reduction in which all three dimensions reach at the* nanorange is called *quantum dot.*

Nanostructures of different dimensions

- 0-D (Delocalisation dimensions)

  All dimensions (*x, y,z) at nanometric scale; the other* dimension is large.

Example: Nanoparticles

- 1-D (Delocalisation dimensions)

  Two dimensions (*x, y) at nanometric scale; the other* dimension is large.

Example: Nanorods, nanotubes

- 2-D(Delocalisation dimensions)

  One dimension (*t measured along z-axis) at nanometric scale;*

  two other dimensions (*Lx, Ly) are large.*

Example: Thin nanofilms

- 3-D (Delocalisation dimensions)

  All of the three dimensions (*Lx, Ly, Lz) are not at nanometric scale.*

Example: Nanocrystalline and nanocomposite materials.

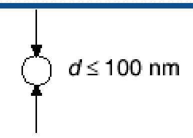


Fig. 19.7 (a) Quantum dot

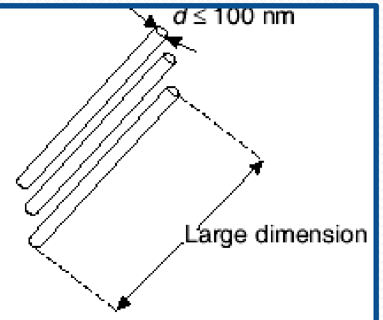


Fig. 19.7 (b) Quantum wire

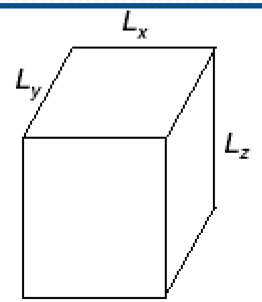


Fig. 19.7 (d) Bulk material

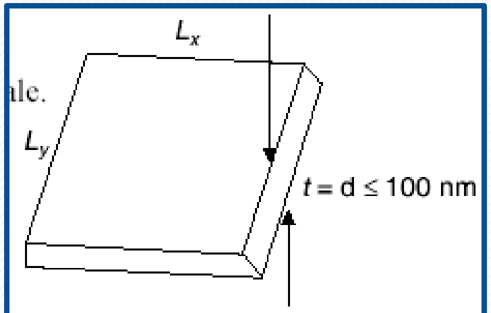


Fig. 19.7 (c) Quantum well

UNUSUAL PROPERTIES OF NANOMATERIALS

Some important properties of nanomaterials are as follows

(i) They are very hard

(ii) They are exceptionally strong

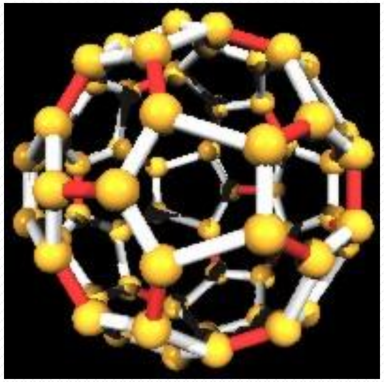
(iii) They are ductile at high temperatures

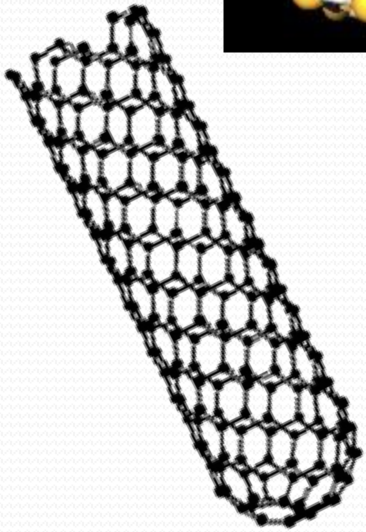
(iv) They are chemically very active

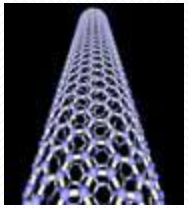
(v) They are wear and erosion resistant

Key Terms You Need to Know

- BuckyBalls
- Carbon Nanotubes
- MEMS
- Quantum Dots
- Molecular Self Repair/Assembly
- MRAM/Spintronics
- Lithography







CATEGORIES OF NANOMATERIALS

1. Fullerenes

- *The fullerenes are a class of allotrops of carbon, which are basically graphene sheets* rolled into tubes or spheres.

- Graphene is a one atom thick layer of graphite. Buckminsterfullerene *C_{60}, also known as buckyball, is the smallest member of the fullerene family.*

- *Carbon nanotubes* (CNT) are also members of this family.

- Fullerenes are produced by sending a large current between two nearby graphite electrodes in an inert atmosphere.

- This results in carbon plasma arc between electrodes, which on cooling gives fullerenes.

2. Nanoparticles:

- *Nanoparticles are defined as particles of approximately 100 nm diameter which* exhibit new or enhanced physical, chemical, and other properties compared with larger particles of the same material.

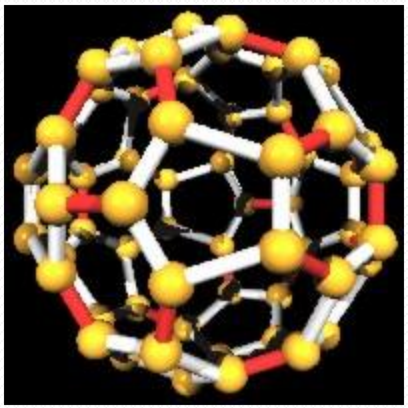
- Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in metals, and super paramagnetism in magnetic materials.

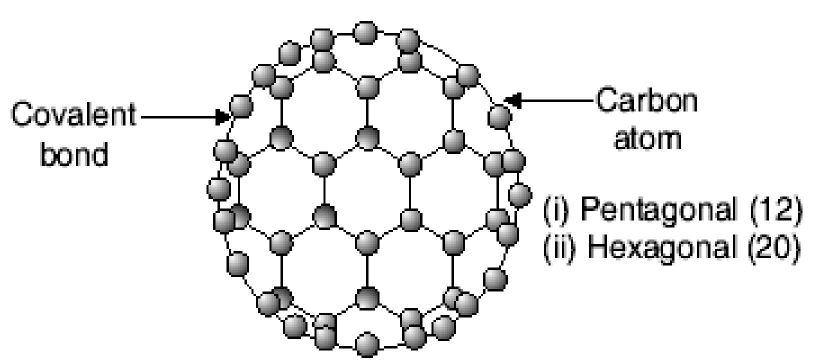
- Nano-semiconductor particles are called *quantum dots*. *These dots find applications in composites*, solar cells, and fluorescent biological labels.

Fullerene or Buckyball

- Pure carbon can have either of the two forms: graphite or diamond. Both of them greatly differ in their chemical and physical properties.
- The third form of carbon was discovered in 1985. This form is a hollow cluster of 60 carbon atoms linked like a football.
- The arrangement of carbon atoms is just like in graphite, but they are arranged in a nanometre-sized sphere.
- It was named Buckminsterfullerene or buckyball after the name of the architect R. Buckminsterfuller who designed dome-like structures. Buckyball is the rounded and the most symmetrical large molecule known in the world.
- It has carbon atoms at 60 chemically equivalent vertices, which are connected by 32 faces, 12 of which are pentagons and 20 are hexagons.

BuckyBalls – C60





- Roundest and most symmetrical molecule known to man
- Compressed – becomes stronger than diamond
- Third major form of pure carbon
- Heat resistance and electrical conductivity

Properties of Buckyballs

- Buckyballs can be used in many applications because of their unusual hollow structure.

- Buckyballs are extremely stable and can bear very high temperature and pressure.

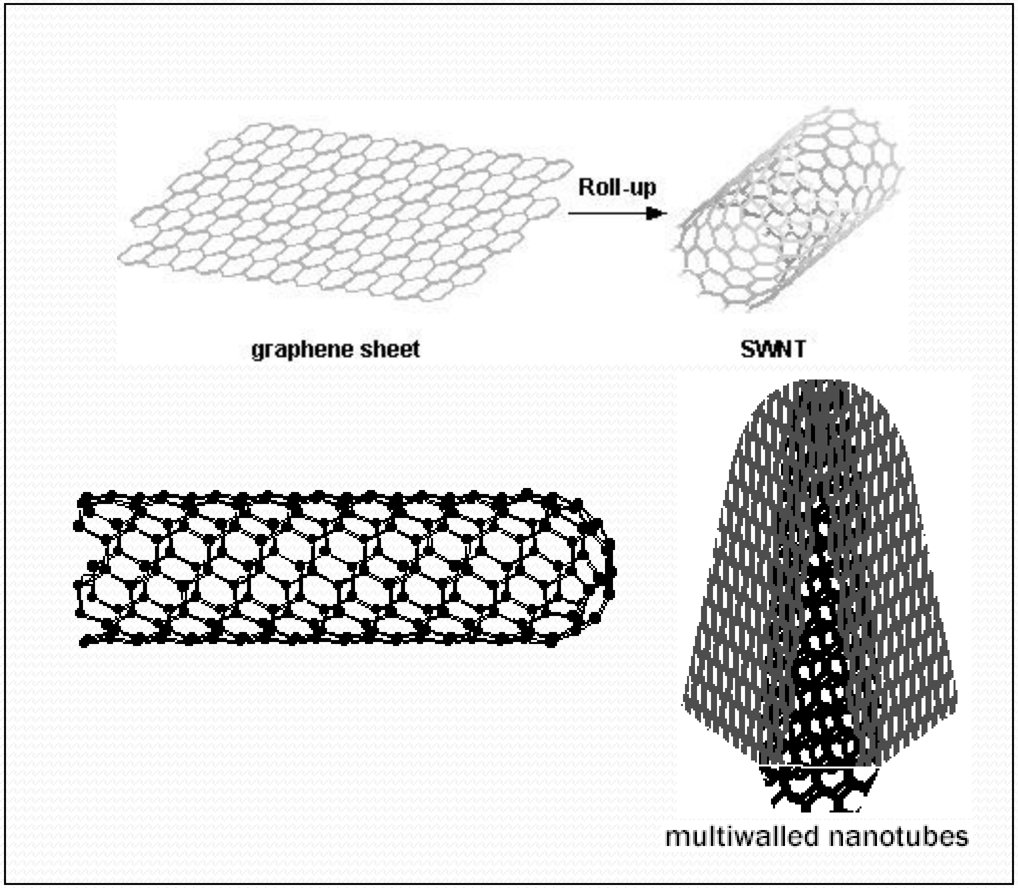
- Even after reaction with other atoms and molecules, their stable spherical structure remains intact.

- Addition of other molecules outside and a buckyball trapping smaller molecules inside a buckyball creates a new molecule.

Uses of Buckyballs

- A buckyball becomes a superconductor when doped with a little amount of potassium or cesium.
- This is the best superconductor known to us.
- A buckyball can be a better storage of hydrogen because when the C_{60} *molecule absorbs one molecule* of hydrogen, its structure does not disrupt. Hence, buckyballs may replace metal hydrides for the storage of hydrogen fuel.
- Buckyballs can deliver drugs directly to the infected regions of the body.
- They also have the ability to act as antioxidants, thereby, counteracting free radicals in the human body.
- Anti-ageing and anti-wrinkle creams are also being manufactured by using buckyballs.
- Strong polymers are also developed using buckyballs.
- Buckyballs are also used as cutting tools.

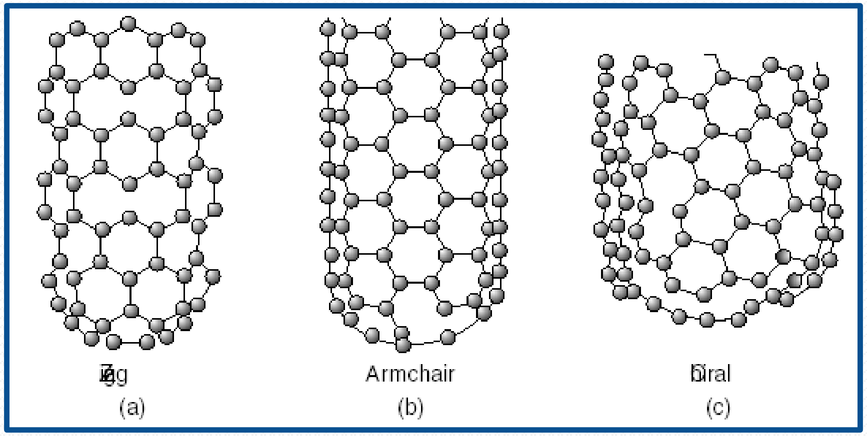
Carbon Nanotubes



- 4 nm width (smaller diameter than DNA)
- 100x's stronger than steel 1/6 weight
- Thermal/electrically conductive
- Metallic and Semi-Conductive

Carbon Nanotubes…….

- The structure of a nanotube influences its properties including electrical and thermal conductivity, density, and lattice structure.
- Both diameter and type of nanotube are important.
- The wider the diameter, the more it behaves like graphite.
- The narrower the diameter of the nanotube, the more its intrinsic properties depend upon its specific type.



APPLICATIONS OF NANOMATERIALS

- In dispersed state, nanoparticles are used as files, paints, magnetic recording media, ferrofluids, drugs, phosphors, rocket propellant, and fuel additives.

- In consolidated state, nanoparticles are used as catalysts, electrodes of solar cells and fuel cells, sensors, adsorbents, synthetic bone, self-cleaning glass, and so on.

- In an ordered assembly form, they are used as quantum electronic devices, photonic crystals, DNA chips, biosensors, etc.

- In very dense phases, they are used in the synthesis of flexible ceramics and insulators.

Applied Nanotechnology –

Examples of Current Research and Applications

Materials Science	Powders, Coatings, Carbon Nano-Materials, C-NanoFabrics
Energy	Solar Power and PhotoVoltaics, Hydrogen Fuel Cells, LED White Light
Medicine/Biotech	Genomics, Proteomics, Lab on a Chip, C-Nanotubes,BuckyBalls
Electronics	MRAM, NRAM, Q-Dots, Q-Bits
Devices	Lithography, Dip Pen Lithography, AFM, MEMS

Disruptive Apps - Materials

- Fiber that is stronger than spider web
- Metal 100 x's stronger than steel, 1/6 weight
- Catalysts that respond more quickly and to more agents
- Plastics that conduct electricity
- Coatings that are nearly frictionless –(Shipping Industry)
- Materials that change color and transparency on demand.
- Materials that are self repairing, self cleaning, and never need repainting.
- Nanoscale powders that are five times as light as plastic but provide the same radiation protection as metal.

Disruptive Apps - Energy

- Fuel cell technology becomes cost effective within 3 years.
- Batteries that store more energy and are much more efficient
- Plastics and paints that will store solar power and convert to energy for $1 per watt.

Disruptive Apps - Computing

- Silicon is hitting its size limit, Moore's law reaches maximum in 2007
- SuperChips –Combination of Silicon and Galium Arsenide create wireless chips
- Plastic semiconductors manufactured by regular printing devices – cheaply produced.
- Electronic Paper

Disruptive Apps – Bio Medicine

- Cosmetics that can penetrate the skin
- Cures for Aids, Cancers, Alzheimer's, Diabetes
- Ability to view cells In *vivo* - Fast Drug Creation
- Nanomaterials that can see inside vessels for plaque buildup
- Technology that can re-grow bone and organs
- NanoSensors for disease detection – 10x's faster and 100,000 x's more accurate
- Nanofilters will help create impurity free drugs.