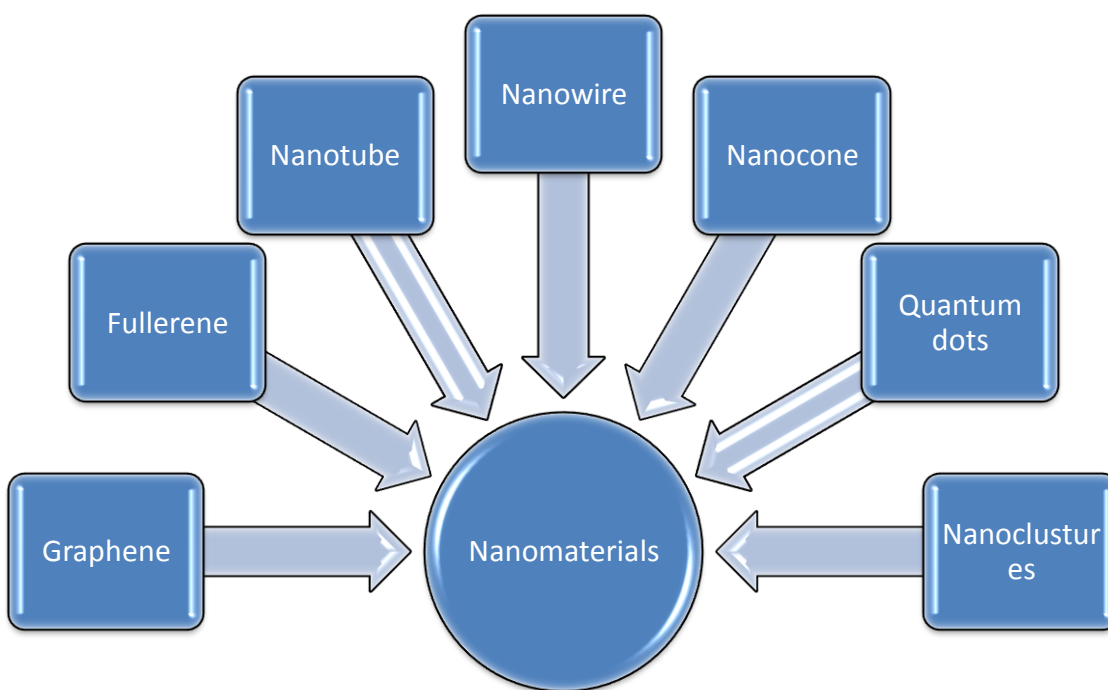


NANOMATERIALS

By:

Dr. R. K. Mohapatra, *M.Sc., M.Phil., M.B.A., Ph.D.*

Faculty (Chemistry), GCE Keonjhar



INTRODUCTION

The concept of nanotechnology was first given by renowned physicist Richard Feynman in 1959 and earned Nobel Prize. The term was also popularized by the invention of scanning tunneling microscope and fullerene. Nanotechnology

involves designing and producing objects at nanoscale size (~1 to 100 nm). One nanometer is one billionth (10^{-9}) of a metre. Nanomaterials are one of the main products of nanotechnology as nanoparticles, nanotubes, nanorods, etc. It is also explained as nanoparticles have a high surface to volume ratio. Nanoparticles can display properties significantly different from the bulk material because at this level quantum effects may be significant. Simply we can say the mechanical, electrical, optical, electronic, catalytic, magnetic, etc. properties of solids are significantly altered with great reduction in particle size. For example:

- ✚ Silver foil does not react with dilute HCl but silver nanoparticles rapidly react with dilute HCl.
- ✚ Gold and silver both are chemically inert but their nanoparticles show catalytic property.
- ✚ Gold nanoparticles are deep red but its bulk material (gold pieces) is gold-coloured.

CLASSIFICATION OF NANOMATERIALS

The classification of nanomaterials is based on the number of dimensions as shown in Fig. 1. According to Siegel, nanostructured materials are classified as: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanomaterials.

(i) Zero-dimensional nanomaterials: Here, all dimensions (x , y , z) are at nanoscale, i.e., no dimensions are greater than 100 nm. It includes nanospheres and nanoclusters.

(ii) One-dimensional nanomaterials: Here, two dimensions (x , y) are at nanoscale and the other is outside the nanoscale. This leads to needle shaped nanomaterials. It includes nanofibres, nanotubes, nanorods, and nanowires.

(iii) Two-dimensional nanomaterials: Here, one dimension (x) is at nanoscale and the other two are outside the nanoscale. The 2D nanomaterials exhibit plate-like shapes. It includes nanofilms, nanolayers and nanocoatings with nanometre thickness.

(iv) Three-dimensional nanomaterials: These are the nanomaterials that are not confined to the nanoscale in any dimension. These materials have three arbitrary dimensions above 100 nm. The bulk (3D) nanomaterials are composed of a multiple arrangement of nanosize crystals in different orientations. It includes dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multi-nanolayers (polycrystals) in which the 0D, 1D and 2D structural elements are in close contact with each other and form interfaces.

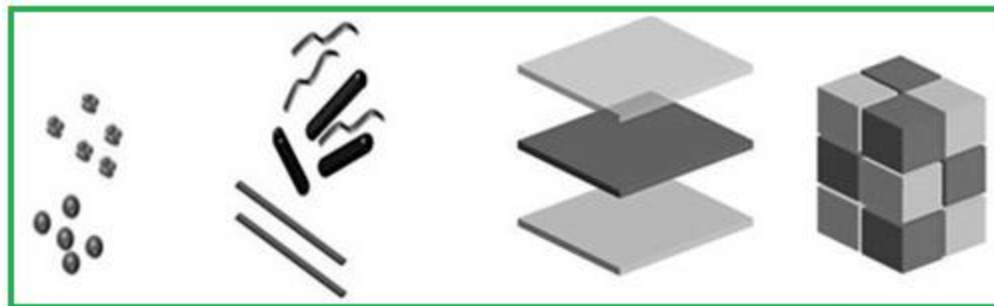


Fig. 1: Classification of nanomaterials.

For the better understanding, nanomaterials are again organized into four types as follows. Some types of nanomaterials are shown in Fig. 2.

(i) Carbon based materials

(ii) Metal based materials

(iii) Dendrimers

(iv) Composites

(i) Carbon based materials: These are composed of carbon, taking the form of hollow spheres, ellipsoids or tubes. The spherical and ellipsoidal forms are referred as fullerenes, while cylindrical forms are called nanotubes.

(ii) Metal based materials: These include quantum dots, nanogold, nanosilver and metal oxides like TiO_2 . A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, whose size is on the order of a few nanometers to a few hundred nanometers.

(iii) Dendrimers: Dendrimers are repetitively branched molecules. The name comes from the Greek word ‘dendron’ (tree). These nanomaterials are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can perform specific chemical functions. Dendrimers are used in molecular recognition, nanosensing, light harvesting, and opto-electrochemical devices. They may be useful for drug delivery.

(iv) Composites: Composites are combination of nanoparticles with other nanoparticles or with larger, bulk-type materials. Nanoparticles like nanosized clays are added to products (auto parts, packaging materials, etc.) to enhance mechanical, thermal, and flame-retardant properties.



Fig. 2 Some types of nanomaterials

GRAPHENE

Graphene was first isolated by A.K. Geim and K.S. Novoselov at the University of Manchester in 2004. They got Nobel Prize in 2010 for their pioneering work.

Graphene is a crystalline allotrope of carbon with two-dimensional, atomic scale,

hexagonal pattern. Here each carbon atom forms four bonds, three s bonds (sp^2 hybridized) with its three neighbours and one p bond oriented out of plane. It is the basic structural element of other allotropes like graphite, fullerene, nanotubes, nanocones, etc. hence called mother of all carbon nanomaterials (Fig. 3).

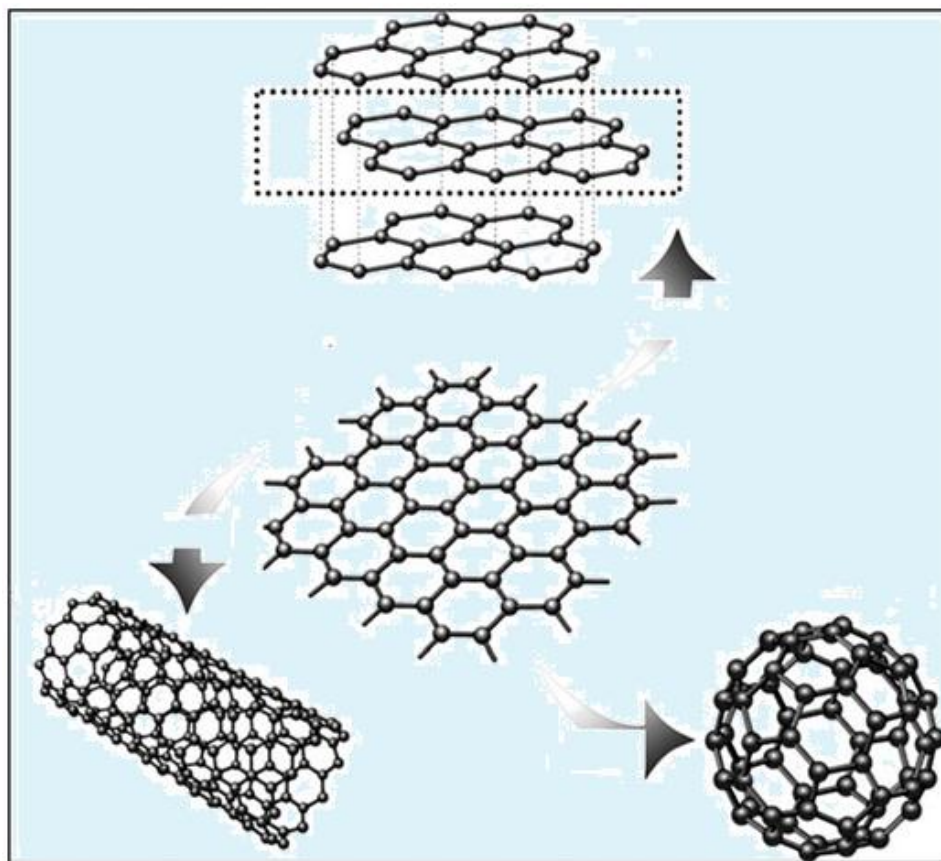


Fig. 3 Graphene and other carbon nanomaterials

Properties:

- ✚ It is nearly transparent.
- ✚ It is 200 times stronger than steel by weight due to its tightly packed carbon atoms.
- ✚ It conducts heat and electricity with great efficiency due to presence of p electrons.
- ✚ Nowadays, it is commonly used in semiconductors, batteries, electronics, composite industries, and many more.

FULLERENE

The first fullerene was discovered by Harold Kroto, Richard Smalley and Robert Curl in 1985 by using a laser to vaporise graphite rods in an atmosphere of helium gas. The fullerenes (allotropes of carbon) are graphene sheets rolled into tubes or spheres. It is a cage like molecule composed of 60 carbon atoms (C₆₀) joined together by single and double bonds to form a hollow sphere with 20 hexagonal and 12 pentagonal faces (a design that resembles a football). It was named as buckminsterfullerene or buckyball after the name of American architect Buckminster Fuller, the inventor of the geodesic dome. The structure of fullerene (C₆₀) is shown in Fig. 4.

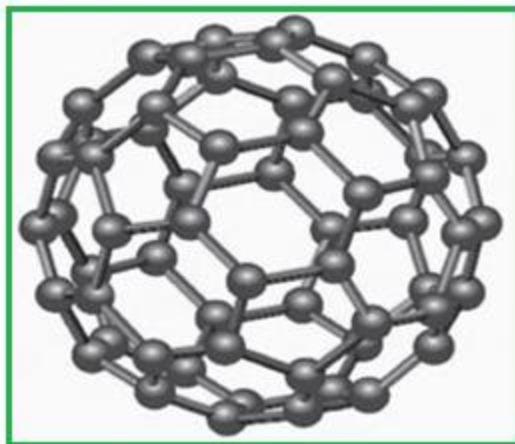


Fig. 4 Fullerene (C_{60})

Applications

The recent research has suggested that fullerene has many uses, including medical applications, superconductors, fiber-optics, etc. Some of the important applications are listed as follows:

- ✚ Fullerenes (C_{60}) and their derivatives have potential antiviral activity, and may be used for the treatment of HIV-infection.
- ✚ They have potential medicinal applications as they can bind specific antibiotics and target certain types of cancer cells such as melanoma.
- ✚ They are used as biological antioxidants.
- ✚ They are also used as potential photosensitizers in photodynamic therapy and catalysts for hydrogenation.

- ✚ Fullerenes incorporated with sulphides of tungsten and molybdenum exhibit excellent solid-lubricant properties.

NANOTUBES

The carbon nanotubes (elongated form of fullerenes) were identified in 1991 by Iijima Sumio of Japan. A carbon nanotube is a tube-shaped material, made up of carbon, having a diameter ranging from < 1 nm to 50 nm. Simply we can say, carbon nanotubes (CNTs) are cylinders of one or more layers of graphene (lattice). Carbon nanotubes show a unique combination of stiffness, strength, and tenacity compared to other fibre materials. Thermal and electrical conductivity are also very high as comparable to other conductive materials.

Carbon nanotubes may be categorized as follows:

- ✚ **Single-wall nanotubes (SWNT):** These may be zigzag, armchair and chiral depending on the manner in which the graphene sheets are rolled.
- ✚ **Multi-wall nanotubes (MWNT):** It consists of several single walled nanotubes with different diameters. A multi-wall nanotube is shown in Fig. 5.



Fig. 5: Multi-walled nanotube

Applications

Carbon nanotube technology can be used for a wide range of new and existing applications, which are as follows:

- ✚ Nanotubes can potentially replace indium tin oxide in solar cells to generate photocurrent.
- ✚ SWNTs are used in transistors and solar panels.
- ✚ MWNTs are used in lithium ion batteries to enhance cycle life.
- ✚ Parallel CNTs have been used to create loudspeakers.
- ✚ CNTs can serve as a multifunctional coating material.
- ✚ CNTs can be used to produce nanowires.

- ✚ CNTs are also used for applications in energy storage, automotive parts, boat hulls, water filters, thin-film electronics coatings, ultra-capacitors, biosensors for harmful gases, extra strong fibers, etc.

NANOWIRES

These are defined as the structures which have the diameters of the order of a nanometre and an unconstrained length. i.e., nanowires are much longer than their diameters. These are also called *quantum wires* because at this scale they have different quantum mechanical effects. There are different types of nanowires. For example: carbon nanowires, molecular nanowires, metallic nanowires, etc.

Applications

- ✚ They are useful in digital computing.
- ✚ These are used for the preparation of active electronic components like p-n junction, logic gates, etc.
- ✚ They have potential applications in high-density data storage.
- ✚ Silver chloride nanowires are used as photocatalysts to decompose organic molecules in polluted water.

NANOCONES

Carbon nanocones (Fig. 6) are conical structures made from carbon and have at least one-dimension of the order one micrometre or smaller. These are obtained from the wrapped graphene sheets. These are different from nanowires as nanocones have height and base diameter of the same order of magnitude. From electron microscopy, it is clear that the opening angle (apex) of the cones is not arbitrary, but has preferred values of approximately 20° , 40° , and 60° .

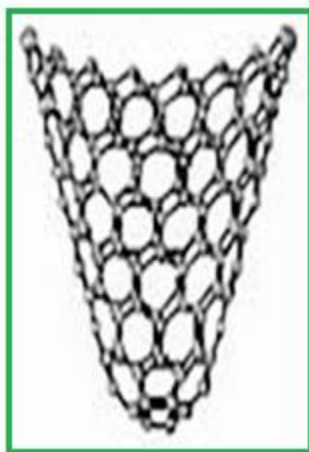


Fig. 6: Carbon nanocone

Applications

- ✚ They have interesting applications in nanolithography.
- ✚ These are used in chemical sensors, biosensors, spectroscopy, etc.

- ✚ They are used as electrode material in lithium ion batteries.

QUANTUM DOTS

Quantum dots (QDs) were first discovered by A. Ekimov in glass matrix and by L. Brus in colloidal solutions (Fig. 7). These are the semiconductor nanoparticles between 10 and 100 atoms in diameter. The properties of QDs can vary depending on its shape and size. These are not all uniform. In spite of having a variety of applications, QDs are a source of toxic compounds containing in their core. The QDs toxicity may be due to the leaching of toxic heavy metals from the colloid form. The toxicity may also be originated from intrinsic properties of the size and surface chemistry of quantum dots. Such materials might have potential risks to human health but still the use of these materials is growing quickly.

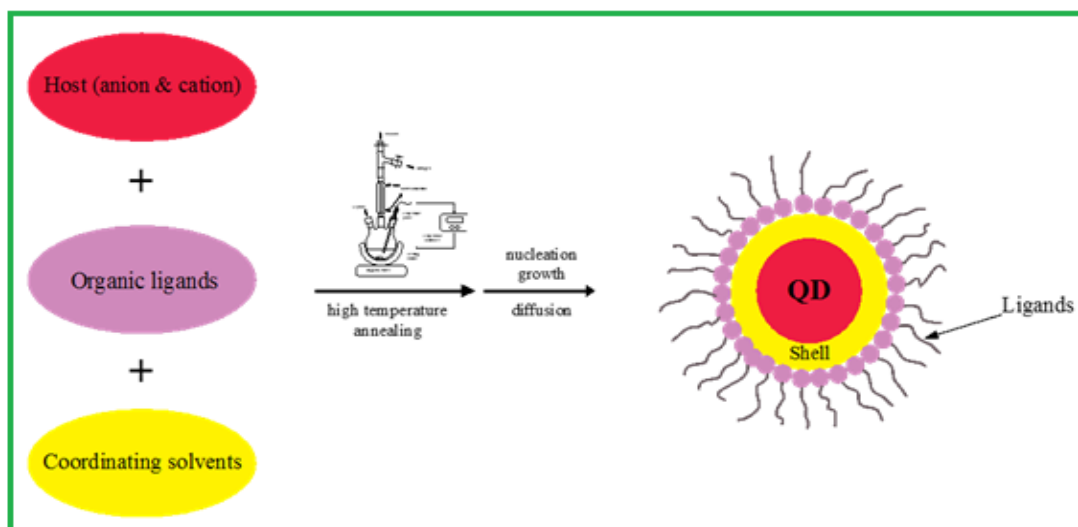


Fig. 7: Synthesis of Quantum dots (QDs)

Applications (Fig. 8)

- ✚ These are used in transistors, solar cells, diode lasers, LEDs, etc.
- ✚ These may increase the efficiency of silicon photovoltaic cells.
- ✚ These are also significant for optical applications like amplifiers, biological sensors, etc.
- ✚ These are used as photocatalysts.
- ✚ They have potential applications in spectroscopy and fluorescent biomedical imaging.

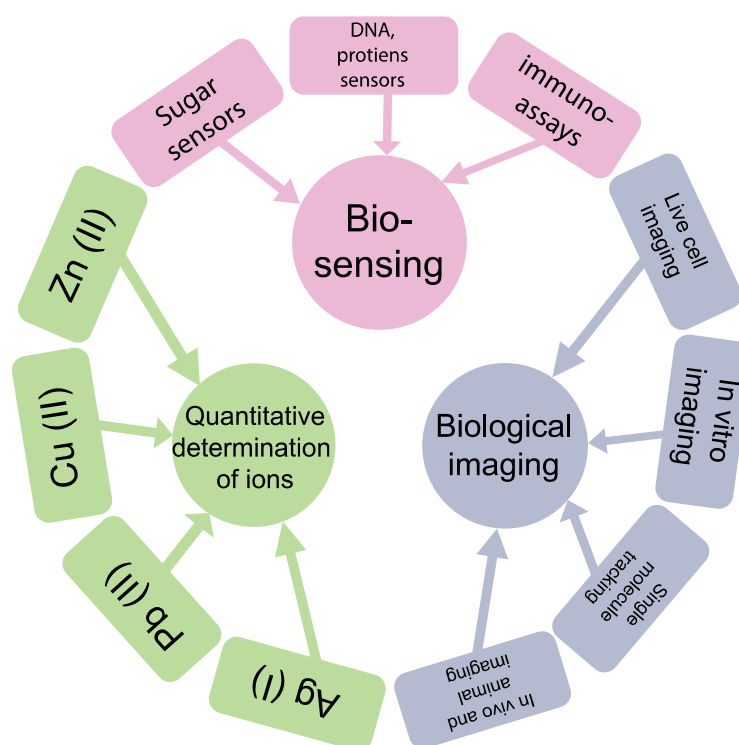


Fig. 8: Schematic representation of QDs' applications.

NANOCLUSTURE

It is the grouping of a number of nanoparticles (Fig. 9) in a narrow size distribution having at least one-dimension between 1 and 10 nm. Simply, they are fine aggregates of atoms or molecules. Nanoclusters contain a couple of hundred atoms but the larger aggregates may have more than 1000 atoms (called *nanoparticles*). The number of atoms in the clusters of critical size with higher stability is called *magic number*. The nanoclusters are bridge between bulk materials and atomic or molecular structures.



Fig. 9: Nanoclusture

Applications

A bulk material has constant physical properties but at the nanoscale, it has many properties.

- ✚ It is used in biotechnology and pharmacology.
- ✚ It has potential applications in microelectronics, telecommunications, sensors, transducers, electroluminescent displays, catalysis, etc.

References (for further reading....)

1. Engineering Chemistry with Laboratory Experiments, R. K. Mohapatra, PHI, Delhi, 2015.
2. Chemical Modification of Solid Surfaces by the Use of Additive, Chapter-2, R. K. Mohapatra and D. Das (edt.), Bentham Science, Singapore, 2020.

Thank you.