

**1.1 Nanoparticles**

Novel approaches to solving the difficulties associated with proper aeration always excite **Nanotechnology** is a general term that refers to a relatively new frontier of scientific endeavor. Nanotechnology is the technology of materials dealing with nano dimension materials usually in the range of 0.1 to 1000 nm. A nanometer is one-billionth of a meter. The property of matter depends on its size and many of the chemical and physical characteristics change significantly when matter is reduced in size. Fundamentally, nanoparticle study arises because the physical as well as chemical properties are very different when dimensions are reduced to the nanometer range. It is one of the most important growth areas in the 21<sup>st</sup> century [Shong *et al.* (2010)]. Nanotechnology is a multidisciplinary and interdisciplinary science dealing with various aspects of research and technology at nano-level [Rai *et al.* (2011)].

The concept of nanotechnology was given by physicist Professor **Richard Feynman** in his history talk entitled “There’s plenty of room at the bottom” at the American Institute of Technology in 1959 [Huang *et al.* (2007)].

The prefix nano comes from the Greek word for dwarf (extremely small) and hence nano science deals with the study of atoms, molecules and nanoscale particles in a word that is measured in nanometer ( $=10^9$  m) [Rai *et al.* (2011), Rai *et al.* (2008)]. Nanoscience, the science under pinning nanotechnology is a multidisciplinary subject covering atomic, molecular & solid state physics, as well as much of chemistry. Nanostructures are known to exhibit novel and improved material properties. Nanomaterial is a field that takes a directly & sometimes indirectly through subjects like solid state physics or chemistry that use it to explain the properties and phenomena of different materials. Nanoparticles form building

blocks of nanotechnology and exhibits different shapes like spherical, triangular, rods etc. [Kulkarni (2009), Rai *et al.* (2009)].

The interesting and sometimes unexpected properties of nanoparticles are due to the large surface area of the material. At this size scale, everything, regardless of what it is, has new exotic properties and these make “Nano” so fascinating. Nano size regime, makes it very reactive to the species approaching from surface leading to appropriate catalytic & sensor applications. Also since the biological system contain materials in the size regime (Proteins are 1-20 nm in size, the diameter of DNA is approximately 2.5 nm), it is possible to fabricate artificial nanomaterials for cell (10-20 nm) diagnostics. Owing to enhanced surface interaction among nanoparticles quantum confinement effects give rise to size tunable electronic & optical properties [Rao *et al.* (2000), Mohamed *et al.* (2000)]. In general, nanomaterials exhibits significant in physical, electronic & optical properties over their bulk counterparts Reviews [Rao *et al.* (2000), Link *et al.* (2003), Mohamed *et al.* (2000), Burda *et al.* (2005)] pertaining to all these aspects are available in the literature. Decreasing the crystal volume by nanotechnology markedly increases the exposed surface area of the crystal which increases the available surface for chemical reactions to take place of a short time period. Examples of changed properties resulting from nano-sized metals include increased superconductivity and increased optical and electrical properties. Nano-sizing can also lead to a more economical utilization of expensive materials-meaning that can use less material because the reactions are more efficient. Change of physical properties are caused by their large surface area, large surface energy, spatial confinement and reduced imperfections.

Mihail (Mike) Roco of the U.S. National Nanotechnology Initiative has described four generations of nanotechnology development. The current era, as Roco depicts it, is that of passive nanostructures, materials designed to perform one task. The second phase, which

we are just entering, introduces active nanostructures for multitasking; for example, actuators, drug delivery devices, and sensors. The third generation is expected to begin emerging around 2010 and feature nanosystems with thousands of interacting components. A few years after that, the first integrated nanosystems, functioning (according to Roco) much like a mammalian cell with hierarchical systems within systems, are expected to be developed.

Bioactive nano particle describes the beneficial or adverse effect of a nano material on living matter. A material is considered bioactive if it has interaction with or effect on any cell tissue in the human body, pharmacological activity is usually taken to describe beneficial effects. [Kulkarni (2009)].

A *colloid* is a substance microscopically dispersed evenly throughout another substance. It consists of two phases: a dispersed phase and a continuous phase in which the colloid is dispersed. A colloid system may be solid, liquid or gas.

*Precious metals* includes 6 platinum group element (PGE), silver (Ag) and gold (Au). PGE includes ruthenium (Ru), Osmium (Os), rhodium (Rh), iridium (Ir), palladium (Pd) and platinum (Pt). Ru & Os, Rh & Ir, Pd & Pt and Ag & Au respectively come under 8, 9, 10 & 11 group of the transition metal [Reddi *et al.* (2000), Qu (1996)].

## **1.2 Properties of Nanoparticles**

It is well established that all the materials – may be metals, semiconductors or insulators – have size dependent physico-chemical properties below a certain critical size. However, for most of the materials this critical size is below ~1000 nm.

It includes mechanical, structural, thermal, optical, electrical and magnetic properties of nanomaterials. It is having various applications based on their unique properties.

### 1.2.1 Mechanical Nature

Mechanical properties of materials depends upon the composition and bonds between the atoms viz. covalent, ionic, metallic etc. As a result purest materials may be inherently weak or strong or brittle. Presence of impurities affects all these properties. Most of the materials have various impurities like C, O N, P, S etc. present in them as well as point defects, grain boundaries, dislocations etc., which are responsible for the deviations of the properties expected from high purity and ordered materials. When the size of materials is reduced to nanoscale, materials tend to be single crystals. It should be, however, noted that measurements on single nanoparticles, nanorods, nanotubes, nanocrystalline solids, granular thin films, homogeneous thin film, multilayer etc. would inherently be difficult, though not impossible.

Materials resistance to deformation or to produce indentation or abrasion is called **hardness**. There are different scales to measure hardness viz. Brinell hardness test, Rockwell hardness test, Knoop's hardness test, Vicker's hardness test and Mohs hardness test. Out of these, **Mohs hardness test** is one of the oldest and give a scale from 1 to 10. One is for the softest material viz. talc and ten is for hardest materials viz diamond.

Hardness series of some standard materials

**Talc < Gypsum < Calcite < Fluorite < Apatite**

**< Orthoclase < Quartz < Topaz < Corundum < Diamond**

Ceramic materials are often compacted and sintered using powder materials. This also increases the hardness of materials. It has been shown that in case of TiO<sub>2</sub> nanoparticles (~12 nm size) produced in powdered form, much less temperature was required to densify and achieve the hardness comparable to usual polycrystalline material.

In fact, density of nanocrystalline pellet is often low due to some pores left when powders are compressed to form pellets. Nanocrystalline pellets densities approach those of bulk polycrystalline materials as the sintering at high temperature progresses.

In nanometer size range the hardness increases with decrease of particle size linearly. Similar results are found in case of palladium nanoparticles and microparticles.

Nanoparticles were widely used in the preparation of common products like cosmetics, soaps, toothpaste, shampoos, and medicines. Typically, nanoparticles possess a wavelength below the critical wavelength of light. This renders them transparent, a property that makes them very useful for applications in cosmetics, coatings, and packaging [Thakkar *et al.* (2010)].

### **1.2.2 Chemical Nature of Nanoparticles**

On the basis of Chemical nature, nanoparticles can be broadly grouped into three, namely:

- a) **Organic nanoparticles** which includes carbon nanoparticles (fullerenes).
- b) **Inorganic nanoparticles** which includes magnetic nanoparticles, noble metal nanoparticles (like gold and silver). There is a growing interest in inorganic nanoparticles as they provide superior material properties with functional versatility. It has been widely used for cellular delivery due to their versatile features like wide availability, rich functionality, good compatibility and capability of targeted drug delivery and controlled release of drugs.
- c) **Semiconductor nanoparticles** includes titanium oxide and zinc oxide [Xua *et al.* (2006)].

### **1.2.3 Structure and Bonding of Nanoparticles**

Matter is composed of atoms and molecules. Gas, liquid and solid was different states of matter. Solid particles like wires, thin films etc. having at least one of the dimensions less than the 100 nm. It is also required to know the stability of these materials under different

conditions like temperature, pressure etc. Three different forms of solids known as single crystal, polycrystalline and amorphous. In a 'single crystal' there is almost infinitely long arrangement of atoms or molecules with certain symmetry characteristics of the material. An infinite distance means a length many a times larger than the distance between two atoms.

In polycrystalline solid, there are some 'grain boundaries'. Size of the grain can depend upon the processing and typically can be few micrometers in length. Each grain itself is single crystals are different or random. Each grain also has a kind of 'grain wall' in which in which atoms may be more or less randomly distributed. The thickness of each wall is often very crucial in determining the various properties of materials like electrical, mechanical etc.

If each grain in the material becomes too small, comparable to the distance between atoms or molecules, then it is known as an '**amorphous**' solid. In amorphous solids, the grain boundaries disappear. Although the distance and even the arrangement between nearest atoms may look similar for most of the atoms, they lack a long range order as in a poly or a single crystal. The situation is similar to a liquid where a snapshot of atoms if taken would be similar to amorphous solid.

#### **1.2.4 Arrangement of Atoms in Nanoparticles**

**Lattice:** It is an arrangement of points repeated in one, two & three directions making it a one, two or three dimensional lattice.

**Crystal:** When an atom or a group of atoms are attached to each lattice points, it forms a crystal.

**Unit Cell:** A unit cell when translated in any direction, can fill the complete space without leaving any space in between or without overlapping. Unit cell is a conventional cell and

can be of any volume, size or shape. However it is often taken in such a way that it has atoms at some corners or centre.

### 1.2.5 Cathodophilic and Anodophilic

Cathodophilics can be defined by the following terms. (Towards) Cathode/ Acid (Electron pair acceptor)/ Reduction (Removal of Oxygen & Proton)/ Electrophile (Electron loving)/ Positive charge/ Addition of electron/ Acidophilic/ Cation.



Anodophilics can be defined by the following terms. (Towards) Anode/ Base (Electron pair donor)/ Oxidation (Addition of Oxygen & Proton)/Nucleophile (Nucleus loving)/ Negative charge/ Removal of electron/ Basophilic/ Anion.

Potential of the cathode electrode is **Reduction Potential**. Greater the reduction potential, stronger the **Oxidizing Agent**.

Trends of oxidizing agent

**Lead (Pb) < Silver (Ag) < Gold (Au)**

### 1.2.6 Nanoparticle aggregation or agglomeration?

It is very important to mention the clear difference of nanoparticles aggregation and agglomeration since this effects their optical, catalytic and electronic properties significantly. The biological effects of these two classes of nanoparticles will be different. Owing to the high surface energies in the nano-size regime, there is strong tendency of the nanoparticles to agglomerate both in liquid as well as in solid state. Nanoparticles in the dry state can be in two forms:

- i. Aggregated (hard bonds between primary particles during sintering)
- ii. Agglomerated (held by weaker Van Der Waals forces).

The dispersion of nanoparticles in dilute polar solvents, leads to increase in thickness of the electrical double layer. Depending on the inter-particle repulsion induced, the agglomerates may therefore separate into single nanoparticles or smaller sized aggregates. Thus, typical nanoparticles agglomerates in liquid suspensions may break up by overcoming the weaker attractive forces whereas the aggregated nanoparticles cannot be separated. The size of the nanoparticles aggregates can be better termed as the hydrodynamic size. The hydrodynamic diameter is the diameter of the sphere that has the same diffusion coefficient as the particles/aggregates [Jiyang *et al.* (2009)].

### 1.3 Some Special Nanomaterials

**A. Carbon Nanotubes (CNT):-** Carbon nanotubes can be considered as cylinders made of graphite sheets, mostly closed at the ends, with carbon atoms spread at the apexes of the hexagons, just like on a graphite sheet. Many concentric cylinders may be formed as a nanotube. Such concentric nanotubes are termed as Multi Wall Carbon Nanotubes (MWCNT). The distance between their walls is ~0.334 nm.

Table 1.1: Carbon polymorphs & their properties

<b>Polymorph</b>	<b>Diamond</b>	<b>Graphite</b>	<b>Nanotube</b>	<b>Fullerene</b>
<b>Dimension</b>	3D	2D	1D	0D
<b>Bonding type</b>	$sp^3$	$sp^2$	$sp^2$	$sp^2$
<b>Conductor type</b>	insulator	metal	semiconductor to metal	semiconductor

**B. Porous Silicon:-** Silicon is the most widely used semiconductor material by electronics industry. It is abundant in nature and techniques to purify grow single crystals economically and on large scale are well developed. The methods of doping, polishing etc. also have been



perfected. Oxide of silicon is stable and metal silicon-silicon contacts can be made and understood to good extent. Thus microelectronics industry is well established to use silicon is used to make various components and systems like diode, transistors, Field Effect Transistors (FETs), Metal Oxide Semiconductor FET (MOSFETs), Integrated Circuits (ICs), Very Large Scale Integrated Circuits (VLSIs), Mechano-Electrical Machines (MEMs) etc. However there is a basic drawback with silicon viz unlike some other semiconductors like ZnS, CdS, GaAs, InAs, InP etc. light emission capability of silicon is extremely poor. Therefore it is not possible to make Light Emitting Diode (LED) or lasers using silicon wafers that are usually used in electronics. It was thus considered for a long time that silicon cannot be an optoelectronics material.

**C. Aerogels:-** Aerogels constitute another class of highly porous materials. They are synthesized by **sol-gel method** and dried by specialized procedures to retain their porous structure. Mixtures of reactant forming colloidal particles, which are dispersed in liquid, are known as 'sol'. These colloidal particles aggregate to form a continuous three dimensional network, which total volume of the solution. The viscous semi fluidic solid hence formed is known as 'gel'. Formation of gel from solution is dependent on various parameters such as reactant concentration, temperature, pH values etc. In such gels, liquid is filled in the pores (empty space between the networks of solid particles). In simple evaporation, liquid and vapour coexist within the pore and surface tension of liquid at liquid vapour interface causes collapse of the network.

**D. Zeolites:-** Zeolites has pores usually smaller ( $<2\text{nm}$ ) than aerogels or porous silicon. The zeolites have not only the pores of uniform size but are periodically arranged to have long range order. The material is crystalline. Some zeolites occur naturally. However due to their technological importance as catalyst and as highly sorbent material they are also synthesized on large scale.

## 1.4 Gold Nanoparticles

**Gold** is one of the rarest metal on earth and its importance has acknowledged since old times. Gold is not only used in jewelry industry but also in a diverse range of industrial applications including the fields of biology, medicine, environment and technology.

Gold is a dense, soft, shiny, malleable (sheet) and ductile (wire) transition metal. It is a chemical element with symbol Au (Aurium in latin, meaning 'glow of sunrise') & atomic number 79; Electron configuration:  $[\text{Xe}] 4f^{14}5d^{10}6s^1$ ; Atomic mass:  $196.96657 \pm 0.00004$  u. In the modern table, it is having position of 11<sup>th</sup> group & 6<sup>th</sup> period. Its oxidation state varies from +5 to -2. But the typical ones are +1 (AuCl) & +3 (Au<sub>2</sub>Cl<sub>6</sub>). Gold (III) chloride (Au<sub>2</sub>Cl<sub>6</sub>) traditionally called auric chloride is very hygroscopic & highly soluble in water. Auric chloride is Red crystals (anhydrous); golden, yellow crystals (monohydrate) [Wiberg *et al.* (2001)]. Chloroauric acid (HAuCl<sub>4</sub>) is formed when dissolved in aqua regia (1HNO<sub>3</sub>:3HCl). AuCl<sub>3</sub> exists as a chloride-bridged dimer both as a solid and as a vapour, at least at low temperatures [Clark *et al.* (1958)]. In gold (III) chloride, each gold center is square planar, which is typical of a metal complex with a d<sup>8</sup> electron count. The bonding in AuCl<sub>3</sub> is considered somewhat covalent. Gold has a bright yellow color and luster traditionally considered attractive, which it maintains without oxidizing in air or water.

**Colloidal gold** is a suspension of sub-micrometer-sized particles of gold in a fluid usually water. The liquid is usually either an intense red color (for  $\leq 100$  nm), or a dirty yellowish or blue/purple color (for larger particles) [Wessling B.(1996)]. Due to the unique optical, electronic, and molecular-recognition properties of gold nanoparticles (AuNPs), they are the subject of substantial research, with applications in a wide variety of areas,

including electron microscopy, electronics, nanotechnology, [Rao *et al.* (2000)] and materials science.

Gold salts are ionic chemical compounds of gold. The term has evolved into a synonym for the gold compounds used in medicine. The application of gold compounds to medicine is called "chrysotherapy" and "aurotherapy" [Shaw (1999)].

Gold chloride salt occurs mainly in four forms viz. Gold (I) chloride (gold monochloride) AuCl; Gold (I, III) chloride (gold dichloride, tetragold octachloride) Au<sub>4</sub>Cl<sub>8</sub>; Gold (III) chloride (gold trichloride, digold hexachloride) Au<sub>2</sub>Cl<sub>6</sub> and Chloroauric acid, HAuCl<sub>4</sub>.

#### **Chloroauric acid, HAuCl<sub>4</sub>**

Of which Gold chloride in the form of Chloroauric acid, HAuCl<sub>4</sub> can only be used to make gold nanoparticles. Chloroauric acid is an inorganic compound. Both the trihydrate and tetrahydrate are known. It is an orange-yellow solid, a common precursor to other gold compounds and an intermediate in the purification of gold metal. Both the trihydrate and tetrahydrate are available commercially.

Generally, **gold nanoparticles** are produced in a liquid ("liquid chemical methods") by reduction of chloroauric acid (HAuCl<sub>4</sub>), although more advanced and precise methods do exist. After dissolving HAuCl<sub>4</sub>, the solution is rapidly stirred while a reducing agent is added. This causes Au<sup>3+</sup> ions to be reduced to neutral gold atoms. As more and more of these gold atoms form, the solution becomes supersaturated, and gold gradually starts to precipitate in the form of sub-nanometer particles. The rest of the gold atoms that form stick to the existing particles, and, if the solution is stirred vigorously enough, the particles will be fairly uniform in size.

To prevent the particles from aggregating, some sort of stabilizing agent that sticks to the nanoparticle surface is usually added. They can be functionalized with various organic ligands to create organic-inorganic hybrids with advanced functionality. It can also be synthesised by laser ablation.

### **1.5 Silver Nanoparticles**

Silver is an extremely soft, ductile and malleable transition metal, though it is slightly less malleable than gold. Silver is similar in its physical and chemical properties to its two vertical neighbours in group 11 & period 5 of the periodic table, copper and gold. Its 47 electrons are arranged in the configuration  $[\text{Kr}]4d^{10}5s^1$ , similarly to copper ( $[\text{Ar}]3d^{10}4s^1$ ) and gold ( $[\text{Xe}]4f^{14}5d^{10}6s^1$ ); group 11 is one of the few groups in the d-block which has a completely consistent set of electron configurations. This distinctive electron configuration, with a single electron in the highest occupied s subshell over a filled d subshell, accounts for many of the singular properties of metallic silver.

Silver crystallizes in a face-centered cubic lattice with bulk coordination number 12, where only the single 5s electron is delocalized, similarly to copper and gold. Its oxidation state varies from +3 to -2. Unlike metals with incomplete d-shells, metallic bonds in silver are lacking a covalent character and are relatively weak. This observation explains the low hardness and high ductility of single crystals of silver. Silver has a brilliant white metallic luster that can take a high polish, and which is so characteristic that the name of the metal itself has become a colour name.

Silver nanoparticle is obtained by reduction of Silver nitrate ( $\text{AgNO}_3$ ). Silver nanoparticles are utilized in the area of electronics, silica-coated Ag nano wires and electronic circuits [Kvistek *et al.* (2005)]. Silver nanoparticles find use in many fields, and the major applications include their use as catalysts, as optical sensors of zeptomole ( $10^{-21}$ )

concentration, in textile engineering, in electronics, in optics, and most importantly in the medical field as a bactericidal and as a therapeutic agent. Silver ions are used in the formulation of dental resin composites; in coatings of medical devices; as a bactericidal coating in water filters; as an antimicrobial agent in air sanitizer sprays, pillows, respirators, socks, wet wipes, detergents, soaps, shampoos, toothpastes, washing machines, and many other consumer products; as bone cement; and in many wound dressings to name a few. Though there are various benefits of silver nanoparticles, there is also the problem of nano toxicity of silver. There are various literatures that suggest that the nanoparticles can cause various environmental and health problems; though there is a need for more studies to be conducted to conclude that there is a real problem with silver nanoparticles.

**Silver** has **white colour** and luster traditionally considered attractive, which it maintains without oxidizing in air or water. **Silver Nanoparticles** is a suspension of sub-micrometer-sized particles of silver in a fluid usually water. The liquid is usually **intense brown color** (for  $\leq 100$  nm).

### **1.6 Bimetallic Nanoparticles**

Bimetallic Nanoparticles (BNPs) involving Au–Pd, Au–Ag, and Au–Pt have been produced in a single step by a sol–gel process and stabilized in liquid and solid matrix.

BNPs have four types of integration patterns:

- i. core–shell NPs,
- ii. subcluster NPs,
- iii. alloy NPs,
- iv. multishell NPs [Turkevich et al. (1951)].

Alloying of metals is a method of developing novel materials that have technological usefulness than their starting substances. Alloy NPs show various structural and physical properties than bulk samples [Couchman *et al.* (1977), Ceylan *et al.* (2006)].

Biosynthesis of bimetallic nanoparticles by algae, fungi and higher plants as reducing agents have been gaining immense attention as a viable alternative for the hazardous physiochemical techniques.

Ongoing extensive studies on non-supported BNP dispersions, stabilized by polymers or ligands, were started only 13 years ago. Studies on BNPs received huge attention from both scientific and technological communities, because most of the NPs catalytic activity depends on their structural aspects [Toshima *et al.* (1998)]. In bulk metals, atoms are arranged in diverse geometries, each metal having its own atomic position. The follow-on crystal structure is typically simple and depends on the identity of the metal and other factors such as temperature. BNPs can exist in another type of structure, in which the distribution of each metal element is not the same as that found in the bulk [Thulasiramaraju *et al.* (2014)].

Layered core-shell Silver-gold BNPs were arranged by coating Au layers over Ag seeds using a seed-growth technique. The arrangement of  $\text{Ag}_{100-x}\text{Au}_x$  particles can vary from  $x = 0$  to 30 [Cui *et al.* (2006)]. Nano-sized materials serve as an ideal candidate for diverse applications due to their extraordinarily small size and correspondingly large surface-to-volume ratio. Additionally, their properties may be modified by changing their size, shape, and composition using synthetic methods [Hyning *et al.* (1998), Adair *et al.* (2000), Jana *et al.* (2001), Velikov *et al.* (2003), D'Souza *et al.* (2004)].

### **Structure of Bimetallic Nanoparticles**

In the late 1980s, it was found that heterogeneous, composite or sandwich colloidal particles have better efficiency than their corresponding single particles. Generally, bimetallic nanoparticles can be categorized into two main groups: core-shell and alloys structures.

Depending on the synthetic approach used in the preparation of BNPs, the distribution of each metal within a particle and their organization will vary to adopt either core–shell, random alloy, alloy with an inter-metallic compound type or cluster-in-cluster, sub clusters, etc., as shown in Fig. 1.1 It was found that for nanoparticles composed of a few metals, such as bimetallic and tri metallic nanoparticles, the alloying or phase segregation process is strongly dependent on the particle size [Wanjala *et al.* (2011), Wanjala *et al.* (2010)].

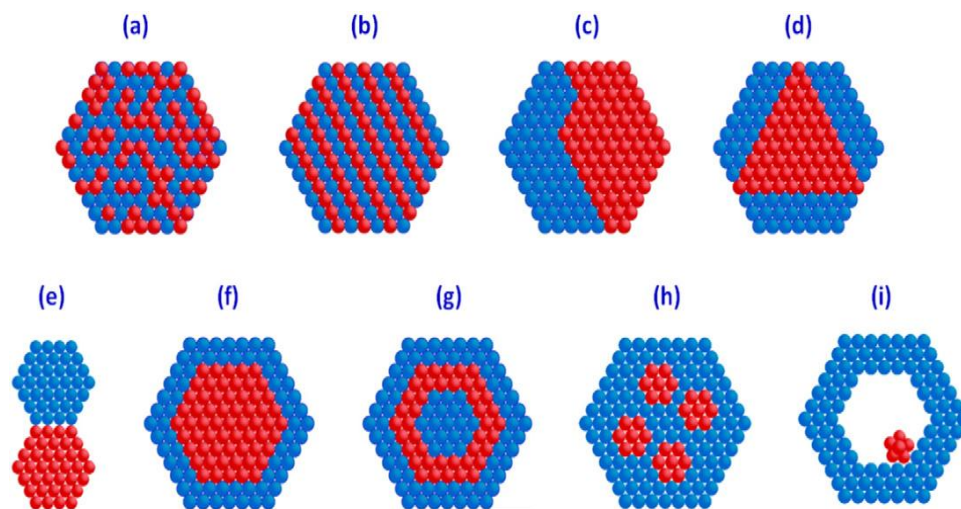


Figure 1.1 Nine structures of bimetallic nanoparticles

(a) mixed alloys; (b) random alloys; (c) sub clusters with two interfaces (d) sub clusters with three interfaces; (e) subclusters with small number of A–B bonds; (f) core–shell nanoparticles; (g) multi shell core–shell nanoparticles; (h) multiple small core material coated by single shell material, (i) movable core within hollow shell material based on Ref. [Ghosh *et al.* (2011), Ferrando (2008)].

Mixed A–B nanoalloys may be either ordered (Fig. 1.1a) or random (i.e., a solid solution, Fig. 1.1b). Random mixed nano alloys are often termed “alloyed” nanoparticles in the

literature, but also the terms “mixed” or “intermixed” are used. The intermixed pattern is common to many systems. In bulk metals, two kinds of metal elements often provide an alloy structure. If the atomic sizes of two elements are similar to each other, then it will be a random alloy. When the atom sizes are quite different from each other and the mole ratio of the two elements is simple and adequate to the structure, then they form an inter metallic compound. In the case of bimetallic nanoparticles, these kinds of alloy structures seem to be more easily produced than in the case of bulk metals. In fact, it was found that bimetallic nanoparticles between noble metals and light transition metals have such alloy structures [Major *et al.* (2009)]. Subcluster segregated nanoalloy consist of A and B subclusters, which may share a mixed interface (Figs. 1.1c & 1.1d) or may only have a small number of A–B bonds (Fig. 1.1e). According to definition given by Ferrando *et al.* [Ferrando *et al.* (2008)] clusters or nanoparticles of metals are aggregates of between a few and many millions of atoms, since alloys or nano alloys are homogenous mixture of elements. In the bimetallic nanoparticles with cluster-in-cluster structures, one element forms nano clusters and the other element surrounds the nano clusters and acts as a binder. The cluster-in-cluster structure may be considered as a modification of the core–shell structure.

Core–shell nanostructures consist of a shell made of one type of metal atoms surrounding a core made of other metal atoms. Different categories of core–shell structures are shown in Fig. 1.1 f–i. Concentric core–shell nanoparticles are the most common (Fig. 1.1 f) where a core metal A is completely coated by a shell of a different material (metal B). Multiple nanoparticles may present onion-like alternating –A–B–A– shell structures (Fig. 1.1 g) or multiple core core/shell particles formed when a single shell materials is coated onto many small core particles together (Fig. 1.1 h). It was demonstrated by dynamic simulation that onion like structures, such as A–B–A could be favored for Cu–Ag, Ni–Ag and Pd–Ag clusters, while A–B–A–B arrangements could be formed in case of Co–Rh and Pd–Pt



clusters, respectively [Baletto *et al.* (2003)]. Three shell Pd–Au nanoparticles – made of an intermixed core, an Au-rich intermediate shell, and a Pd-rich outer shell – were obtained by successive reduction of corresponding metallic precursors by Ferrer *et al.* [Ferrer *et al.* (2007)].

It's also possible to synthesize a movable core particle within a uniformed hollow shell particle (Fig. 1.1 i) after a bilayer coating of the core material and just removing the first layer by using a suitable technique, e.g. dissolution [Gao *et al.* (2007)] or thermal treatment [Zhang *et al.* (2011)] to remove interior shell. Movable core–shell structure could be also obtained by slow and fully controlled dissolution of melamine formaldehyde (MF) core encapsulated in silica shell, resistant for reaction conditions [Choi *et al.* (2008)]. According to the available literature, movable core made of noble metal (Ag, Au, Pt) are usually encapsulated in polymer [Heshmatpour *et al.* (2012), Sun *et al.* (2012)] or silica shell [Choi *et al.* (2008), Min *et al.* (2008)].

Ferrando *et al.* [Ferrando *et al.* (2008)] distinguished six factors influencing the degree of segregation/mixing and atomic ordering in  $A_mB_n$  nanoalloys:

- (1) Relative strengths of A–A, B–B and A–B bond. Generally alloying/mixing of metals is favored if A–B bonds are stronger than homonuclear bonds (A–A and B–B). Contrary, segregation of metals is observed for the species forming stronger homonuclear bond tending to be at the center (core) of the cluster;
- (2) Surface energies of bulk elements A and B. The metal with lower surface energy has a susceptibility to migrate to the surface;
- (3) Relative atomic sizes. Atoms with smaller size have a tendency to occupy the more sterically packed core;
- (4) Charge transfer. Mixing of metals are favored by electron transfer from less to more electronegative elements;

(5) Strength to bindings to surface ligands (surfactants). In case of supported or passivated clusters, the metal that couples most strongly to the support or ligands could be hold out towards the surface;

(6) Specific electronic/magnetic effects. Established sizes, constitutions, and/or segregation arrangements could be fixed by electronic shell structure or electron spin interactions.

Silver and gold have the lowest surface energy, thus in mixtures with other metals (such as Pt, Pd, Ru and Rh) they tend to migrate to the surface of bimetallic nanoparticle. On the other hand, the strengths of Au–Au bonding ( $D_0 = 215$  and  $218$  kJ/mol at  $0$  K and  $289$  K, respectively) is higher than Au–Pd and Au–Ag favoring to form an Au rich core of bimetallic particle, while is lower than Au–Rh and Au–Ni tending to mix with those metals. Strengths of silver homonuclear bonding ( $D_0 = 159$  and  $163$  kJ/mol at  $0$  K and  $289$  K, respectively) is lower than silver bonding with gold

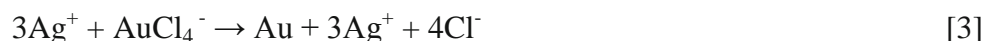
(Ag–Au) and copper (Ag–Cu) favoring alloys formation. According to the available data, the strength of homo nuclear bond is found to change in the following order: Rh–Rh  $\approx$  Ni–Ni  $\approx$  Au–Au  $\approx$  Pt–Pt  $\approx$  Cu–Cu  $\approx$  Ag–Ag  $\approx$  Pd–Pd.

The structure of bimetallic nanoparticles obtained by simultaneous reduction of ions of both metals (induced by chemical reducing agent, UV or gamma irradiation) could be initially predicted based on difference between metal reduction potentials.

Moreover, it is well know that various pairs of metals are susceptible to segregation, if their standard potentials are different. Generally it could be assumed that large difference in the reduction potentials usually results in a core–shell structure while a small difference in the reduction potential leads to an alloy one [Tojo *et al.* (2014)].

### 1.7 Bimetallic (Gold-Silver) Nanoparticles

Bimetallic (Gold-Silver) Nanoparticles having various structures and varying Gold/Silver ratios are one of the most widely studied bimetallic systems. These materials show interesting optical properties that are dependent not only on the composition but also on the geometrical structure, specially a random alloy or has a core/shell structure. Au and Ag nanoparticles have a broad absorption band in the visible region in the electromagnetic spectrum. Features that arise from the collective oscillation of free conduction electrons persuaded by an interacting magnetic field [Asakura *et al.* (1992)]. Au and Ag nanoparticles are excellent nanomaterials providing a powerful platform in the biomedical applications of biomolecular recognition, biosensing, drug delivery, and molecular imaging [Sperling *et al.* (2008)]. When compared to monometallic nanoparticles, bimetallic nanoparticles having good catalytic properties due to the synergetic effects between two metals.



### 1.8 Selection of Gold/Silver Nanoparticles

Gold/Silver nanoparticles having electronic, magnetic, optical, physical and chemical properties that are completely different from both the bulk and the individual atoms or molecules. Applications of Gold/Silver nanoparticles are based on their unique properties, and this uniqueness can be interpreted in terms of the high relativistic contraction of its 6s/5s orbitals resulting in a very small atomic radius.

## 1.9 Microorganism

A microbe or microorganism is a member of a large, extremely diverse, group of organisms that are lumped together on the basis of one property – the fact that, normally, they are so small that they cannot be seen without the use of a microscope. The word microbe is therefore used to describe Virus (0.01-0.25  $\mu\text{m}$ ), Bacteria (0.1-750  $\mu\text{m}$ ), Fungi (2  $\mu\text{m}$  to 1 m) and Protista (2-1000  $\mu\text{m}$ ). Viruses are acellular. Bacteria are prokaryotes. Fungi and Protista are eukaryotes. Prokaryotic cells lack a distinct nuclear membrane, and they do not have complex internal organelles such as mitochondria or chloroplasts which are associated with energy generation in eukaryotes. Members of the protista are heterotrophic or photosynthetic, unicellular eukaryotes. There are three major groups within the protista, the Euglenozoa (containing the euglenids), the Alveolata (containing the ciliates & dinoflagellates) and the Stramenopila (containing the diatoms, amoebae and slim moulds). Until fairly recently, the photosynthetic and non-photosynthetic protistan genera were divided into two phylogenetic form groups, the algae and protozoa based on the presence or absence of chloroplasts. Bacteriophage, normally called phage, is viruses that infect prokaryotes [Nicklin *et al.* (2003)].

Biosynthesis of nanoparticles has been demonstrated by the use of biological agents such as bacteria, fungi, yeasts, actinomycetes and plants. The biological synthesis of nanoparticles from fungi is considered to be a significant branch due to the fungi's tolerance and metal bioaccumulation capability. The fungi are capable of biogenic inorganic nanoparticles (gold, silver & bimetallic) formation and their biomass is easier to handle, hence they are favoured over bacteria and other microorganisms. Filamentous fungi species are of particular interest because they are able to produce highly stable NPs, which prevent molecular aggregation even after prolonged storage, and therefore have improved longevity [Mukherjee *et al.* (2001)].

While exploring the secrets of nature for the synthesis of nanoparticles by microbes, which are regarded as potent eco-friendly green nano factories, scientists have discovered magnetite particle by magneto tactic bacteria, siliceous materials by diatoms, and gypsum & calcium layers by S-layer bacteria [Lovely *et al.* (1987), Milligan *et al.* (2002), Pum *et al.* (1999)].

### **1.9.1 Bacteria**

Bacteria (common noun bacteria, singular bacterium) are a type of biological cell. They constitute a large domain of prokaryotic microorganisms. Typically a few micrometers in length, bacteria have a number of shapes, ranging from spheres to rods and spirals. Bacteria were among the first life forms to appear on Earth, and are present in most of its habitats. Bacteria inhabit soil, water, acidic hot springs, radioactive waste, and the deep portions of Earth's crust. Bacteria also live in symbiotic and parasitic relationships with plants and animals. Most bacteria have not been characterised, and only about half of the bacterial phyla have species that can be grown in the laboratory. The study of bacteria is known as bacteriology, a branch of microbiology.

### **1.9.2 Fungus**

Fungi is the plural of the word FUNGUS which is derived from the latin word FUNGOUR which means to flourish. The word was primarily used with reference to MUSHROOMS which develops overnight. In usage the meaning of the word has been expanded to include thallus like achlorophillous plants (lacking chlorophyll) such as the molds and other similar organisms related to mushrooms. About 51,000 genera and more than 50,000 species of fungi are known today. Familiar examples of the fungi are the yeasts, **molds**, toad stools mushrooms, polypores, puffballs, rusts and smuts.

The branch of botany that deals with fungi is called mycology. Etymologically mycology is the study of mushrooms. The scientist who is concerned with fungi is called mycologist. P.

A. Micheli has the honour of being referred to as **Father of Mycology**. Sir E. J. Butler is aptly referred to as **Father of Indian Mycology**.

Fungi are heterotrophic, eukaryotic organism with a filamentous, tubular structure, a single branch of which is called **hypha**. A network of hyphae is called a **mycelium**. Hyphae are bound by firm, chitin containing walls and contain most eukaryotic organelles. Not all fungi are multicellular; some are single-celled and are termed yeasts.

There are four phyla within the fungi, divided from each other on the basis of differences in their mechanisms of sexual reproduction. The four phyla are the Oomycota/Chytridiomycota (Oospore), Zygomycota (Zygosporangium), Ascomycota (Ascospore) and Basidiomycota (Basidiospore). A fifth group exists which contains fungi where sexual reproduction is not known but where asexual reproduction is seen. These fungi are placed in the phylum Deuteromycota (Conidiospore).

Fungi require Carbon, Nitrogen, Phosphorus, Iron, Vitamins, Sterols and Growth factors as nutrition. It requires organic carbon compounds to satisfy their carbon and energy requirements. They obtain this carbon by saprotrophy, symbiosis or parasitism. The **carbon** must be available in a soluble form in order to cross the rigid cell wall, or must be broken down by enzymes secreted by the fungal cells. They normally utilize glycolysis and aerobic metabolism of carbohydrates. Some of can use fermentive pathways under reduced oxygen levels. A few fungi are truly anaerobic. They cannot fix gaseous **nitrogen** but can utilize nitrate, ammonia and some amino acids as nitrogen sources. Most macro- and micro-nutrients that they require are present in access in their environments. Phosphorus and iron may be in short supply and they have specific mechanisms to obtain their nutrients. Some fungi may require external supplies of some vitamins, sterols and growth factors.

Fungi require water for nutrient uptake and therefore restricted to their activity further acidify it. Most fungi are mesophilic, growing between 5° - 40° C, but some can tolerate high or low temperatures [J. Nicklin et. al. (2003)].

## **Molds**

A **mold** (US) or **mould** (UK / NZ / AU / ZA / IN / CA / IE) is a fungus that grows in the form of multicellular filaments called *hyphae*. Molds are considered to be microbes and do not form a specific taxonomic or phylogenetic grouping, but can be found in the divisions Zygomycota and Ascomycota. In the past, most molds were classified within the Deuteromycota.

The colloquial term mold (or Mould) is applied to a large and taxonomically diverse number of fungal species where their growth results in a moldy appearance of objects, especially food. The objects become discolored by a layer of fungal growth.

Although molds and fungus are related – the former is actually a subset of the latter – the term cannot be used interchangeably. Each has its own distinct characteristics, features and functions.

Molds are considered to be microbes and do not form a specific taxonomic or phylogenetic grouping, but can be found in the divisions Zygomycota, Ascomycota & Deuteromycota. In the past, most molds are classified within the Deuteromycota.

Mold is one type of fungus. It can measure from 2-10 microns in diameter, making it virtually invisible to the naked eye. When multiple mold spores grow close together they become visible as they spread rapidly across a surface.

Mold growth begins when a single spore of fungus lands on an organic surface. This includes all biodegradable materials, ranging from paper to leather. As the mold absorbs moisture in the air, it swells in size to form a thin thread known as hyphae. The hyphae quickly spread and extend across the surface, assuming conditions are sufficient for

growth. Molds grow best in dark, damp conditions. A mold is a fungus that grows in the form of multicellular filaments called hyphae. In contrast, fungi that can adopt a single-celled growth habit are called yeasts.

Molds are a large and taxonomically diverse number of fungal species in which the growth hyphae results in discoloration and fuggy appearance, especially on food. The dusty texture of many molds is caused by profuse production of asexual spores (conidia) formed by differentiation at the end of hyphae. The mode of formation and shape of these spores is traditionally used to classify molds. Many of these spores are coloured, making the fungus much more obvious to the human eye at this stage in its lifecycle.

Slim mold or slim mould is an informal name given to several kind of unrelated eukaryotic organisms that can live freely as single cells, but can aggregate together to form multicellular reproductive structures. Slim moulds were formerly classified as fungi but no longer considered part of that kingdom. Although not related to one another, they are still sometimes grouped for convenience within the paraphyletic group referred to as kingdom Protista.

The oomycetes are also often referred to as water molds (or water moulds), although the water-preferring nature which led to that name is not true of most species, which are terrestrial pathogens. Oomycota or oomycetes form a distinct phylogenetic lineage of fungus-like eukaryotic microorganisms. They are filamentous, microscopic, absorptive organisms that reproduce both sexually and asexually. Oomycetes occupy both saprophytic and pathogenic lifestyles.

### **Yeast**

**Yeast** are single-celled microorganisms that are classified, along with molds and mushrooms, as members of the Kingdom Fungi. **Yeasts** are evolutionally diverse and are



therefore classified into two separate phyla, Ascomycota or sac fungi and Basidiomycota or higher fungi, that together form the subkingdom Dikarya.

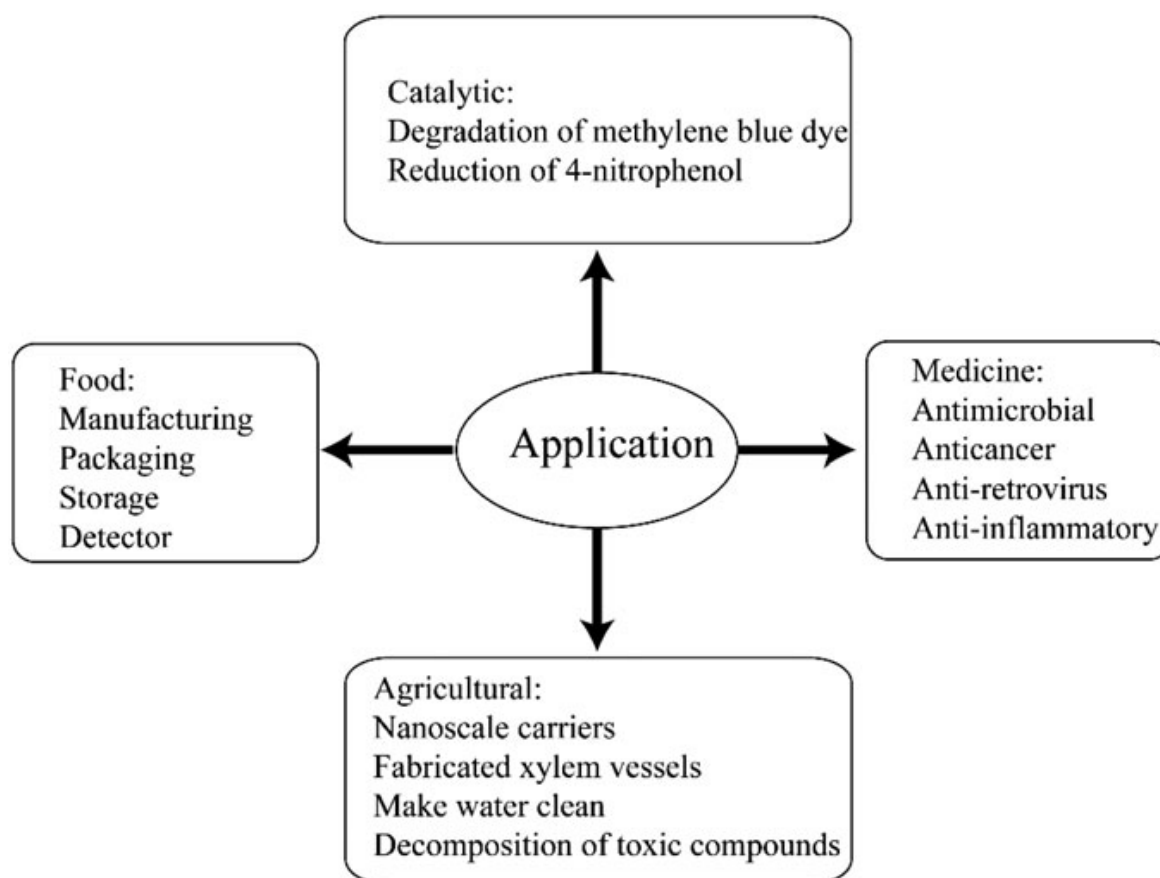
The first yeast originated hundreds of millions of years ago, and 1,500 species are currently identified. They are estimated to constitute 1% of all described fungal species. Yeasts are unicellular organisms which evolved from multicellular ancestors, with some species having the ability to develop multicellular characteristics by forming strings of connected budding cells known as pseudohyphae or false hyphae. Yeast sizes vary greatly, depending on species and environment, typically measuring 3–4  $\mu\text{m}$  in diameter, although some yeasts can grow to 40  $\mu\text{m}$  in size. Most yeasts reproduce asexually by mitosis, and many do so by the asymmetric division process known as budding.

Yeasts, with their single-celled growth habit, can be contrasted with molds, which grow hyphae. Fungal species that can take both forms (depending on temperature or other conditions) are called dimorphic fungi ("dimorphic" means "having two forms").

### **1.10 Selection of Mold**

Molds have several beneficial characteristics that are advantageous over other microorganisms. Molds (2.0-10.0  $\mu\text{m}$ ) are eukaryotic; multicellular, with many distinctive structural features; They grow in the form of multicellular filaments called hyphae. The mold's have high tolerance and metal bioaccumulation capability. The Molds are capable for the formation of stable, biogenic inorganic Nanoparticles (Gold, Silver & Bimetallic) formation. Mold biomass is easier to handle, hence they are favoured over bacteria and other microorganisms. They prevent molecular aggregation even after prolonged storage, and therefore have improved longevity.

## 1.11 Applications of Nanoparticles



Metal and metal oxides have been widely studied for their antimicrobial activities. Metal oxide nanoparticles, well known for the highly potent antibacterial effect, includes silver (Ag), Iron oxide ( $\text{Fe}_3\text{O}_4$ ), Titanium oxide (TiO), Copper oxide (CuO) and Zinc oxide (ZnO). Microbial assays have verified that surface modified using Au nanoparticles demonstrate anti-adherent properties and significantly reduce both Gram-negative and Gram-positive bacterial colonization [Loomba *et al.* (2013)].

It includes Fluorescent biological labels, Drug & gene delivery, Bio detection of pathogens, Detection of proteins, Probing of DNA structure, Tissue engineering, Tumor detection via heating (hyperthermia), Separation and purification of biological molecules and cells, MRI contrast enhancement and Phagokinetic studies. Other interesting applications of nanoparticles includes Catalytic breakdown of volatile organic compounds, Nanoparticle

aided organic transistors (NOMFET), High energy battery packs, Gas impermeable coatings, UV protection coatings, Fillers in composite materials and Low cost solar-cells [Salata (2004)].

Interactions between metals and microbes have been exploited for various biological applications in the fields of bioremediation, biomineralization, bioleaching and biocorrosion and the microbial synthesis of nanoparticles have been emerged as a promising field of research as nanobiotechnology in connecting biotechnology and nanotechnology [Klaus-Joerger *et al.* (2001)].

### **1.12 Significance (Properties) of Nanoparticles**

#### **Drug and gene delivery**

Drugs can be encapsulated in nanocapsules and targeted towards desired parts of body. Drug can then be fast or slow delivered, as desired, by opening the capsule using some external stimulus like magnetic field or infrared light or under some physiological conditions. Nanoparticles can be used in the construction of miniature devices, which can be helpful in drug delivery [Mukherjee *et al.* (2008)].

#### **Sensors**

Nanomaterials based sensors would be smart sensors i.e. They will be able to detect and rectify the problem. Sensors will be useful in water purification systems, detection of toxic ions, metal ions, pesticides etc. and their remediation on large scale. Detection of Viruses is generally performed by either antigens (immunoassays) or genome sequences (polymerase chain reaction-based methods).

#### **Fuel Cells**

Numerous gadgets like laptops, cellular phones, cordless phones, portable radios, CD players, calculators etc need rechargeable, light weight batteries or 'cells'. Attempts are being made to increase their energy density by replacing for example the electrode

materials. Some metal hydride nanoparticles like nickel hydrides or high surface area, ultra light weight material like aerogels are found to be better options than the conventional materials in improved batteries.

#### **1.12.1 Significance of Gold Nanoparticles**

It includes Anti-microbial, Biosensor, Diagonosis, Drug delivery, HIV/AIDS, Environment, Technology, Electronics, Photodynamic Therapy, Probes, Catalysis etc.

#### **1.12.2 Significance of Silver Nanoparticles**

Its includes Anti-bacterial agents, Electrochemical properties, Optical properties etc.

#### **1.12.3 Significance of Bimetallic Nanoparticles**

The BNPs have various applications such as catalytic reduction, biosensors, electrochemical, debromination, dechlorination, and remediation. The nanoparticles' size, composition, and structure can offer the ability to tune the activity; hence, catalytic reactions over bimetallic surfaces are of great interest [Sheny *et al.* (2011)].

#### **1.12.4 Significance of Bimetallic (Gold-Silver) Nanoparticles**

Properties of Bimetallic Nanoparticles (BMNPs) are influenced by both the metals; they provide excessive ordinary metallic NPs, which is an advantage [Mohl *et al.* (2011), Huang *et al.* (2006)]. The properties of alloy NPs can be extremely different from those of the elemental monometallic nanoparticles [Mohamed *et al.* (2000)].

Its applications includes Photothermal cancer therapy, Antimicrobial activity, Optical, Catalytic, Electroplating, Fabrication, Potential, Thermal conductivity etc.

#### **Optical Properties**

Plasmonic coupling between NPs is one of the most interesting optical properties; the characteristic improvement of local optical field at particle–particle interface is extremely useful for numerous sensing applications [Lee *et al.* (2006), Wang *et al.* (2007)].

Monometallic Ag and Au NPs have relatively monotonous optical properties due to **surface**

**plasmon resonance** (SPR); the SPR properties of Ag–Au alloy NPs are incessantly tunable because of the possibility of composition changes. SPR excitation within the gold and silver nanostructures greatly enhances the local electric field [Cheng *et al.* (2008), Wang *et al.* (2006)]. The absorption and dispersion of light in NPs rely on the characteristic of the metals, including their chemical composition, morphology, and size. NPs of noble metals, for instance gold and silver, with a size smaller than the wavelength of visible light powerfully scatter and absorb light because of SPR. Au–Ag BNPs show diverse optical responses for alloy and core–shell configurations, even when they have the same Au and Ag contents [Kim *et al.* (2005), Kreibing *et al.* (1995)].

### **Catalytic Properties**

A novel group of materials for catalysis have been densely studied, that is, “bimetallic nanoparticles”. Metal NP catalysts comprising two (or more) different metal components have received attention from both technological and scientific points of view for improving the quality or properties of catalyst [Menezes *et al.* (2013)]. Although the size of Au-NPs is smaller than that of Ag-NPs and AuAg-NPs, equal atomic concentrations of Au-NPs, Ag-NPs, and AuAg-NPs are applied for the catalytic reaction due to their enhanced surface areas and decreased densities [Shin *et al.* (2012)].

The Au-Ag bimetallic nanoparticles have a significant catalytic effect on the reduction between  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$  and Mohr’s salt. All Au-Ag nanoparticles showed a higher catalytic activity than that of the monometallic Au or Ag nanoparticles. The higher catalytic activity of the bimetallic nanoparticles is mainly due to electronic charge transfer from adjacent Ag to Au atoms, which is called **surface Plasmon resonance**. The catalytic activity of Au-Ag bimetallic nanoparticles with a mole ratio of 0.75:0.25 is found to be higher than that of Au nanoparticles of same particle size [Mousumi *et al.* (2013)].

The longitudinal surface plasmon resonance (LSPR) band of bimetallic Au-Ag nanorods is sharper and stronger than that of the Au nanorods and spherical Ag nanoparticles, and these properties lead toward their application in the sensing of biomolecules; hence, bimetallic nanomaterials are preferred [Dash *et al.* (2008)].

### **Electroplating and fabrication**

BNPs allow more than one metal to be used for establishing contact, with or without the expense and complexity of integrating Au alloy into the microelectromechanical (systems) switch fabrication process [Mallin *et al.* (2002), Wang *et al.* (2006)].

### **Potential**

BNPs surrounding the surface regions of glass are of great interest because of their potential application [Kim *et al.* (2007), Wiederrecht (2004)]. Au–Ag NPs in silica glasses with linear and nonlinear optical properties have been achieved [Ditlbacher *et al.* (2000)]. Later, nonlinear field enrichment relying on the laser polarization of single Ag nanobars and nanorice was also reported [Wiley *et al.* (2007)].

### **Thermal conductivity**

It has been demonstrated that nanofluids, consisting of Au–Ag in water, enhances the thermal conductivity of the fluids [Zhong *et al.* (2006), Van Dijk (2007)].

### **Electrical Conductivity**

Among metal filters, Ag flakes are most widely used because Ag has the highest electrical conductivity and, unlike many other metals, their oxides have relatively better conductivity. Approach (i.e., alloying of Au with Ag) that can improve the use of Au as an electrode material by decreasing its inertness [Reddy *et al.* (2006)].

### **1.13 Therapeutic Applications of Nanoparticles**

#### **Therapeutic Applications of Gold Nanoparticles**

It includes Anti-microbial, Biosensor, Diagnosis, Drug delivery & HIV/AIDS applications.

#### **Therapeutic Applications of Silver Nanoparticles**

Its includes Anti-Microbial, Pro-Healing, Anti-Inflammatory & Anti-Viral applications.

#### **Therapeutic Applications of Bimetallic (Gold-Silver) Nanoparticles**

Properties of BMNPs are influenced by both the metals; they provide excessive ordinary metallic NPs, which is an advantage [Mohl *et al.* (2011), Huang *et al.* (2006)]. The properties of alloy NPs can be extremely different from those of the elemental monometallic nanoparticles [Mohamed *et al.* (2000)]. Its applications includes Anti-Microbial & Photo thermal Cancer Therapy.