Chapter 1

Introduction and literature review
1. Introduction to nanomaterials

Nanotechnology and nanoscience is the interdisciplinary science which connects the basic science and engineering for making and using materials, functional structures and devices on the order of nanometer scale. In the recent years, the technology extensively used due to its versatile applications in daily life. Earlier, nanotechnology is defined as the design and fabrication of materials, devices, and systems to control at the nanometer scale up to 100 nanometers while is defined in later as focus towards the observations, study of the phenomenon at nanometer scale and ways of manipulating matter at these scales, at which many properties of matter vary from those of bulk counterpart.\textsuperscript{1} There is an immense elevation in the ratio of surface area to volume at the nanoscale.

As a result of this, materials at the nanoscale exhibit numerous properties when juxtaposed with microscale, which facilitate unique applications.\textsuperscript{2} This technology seldom referred to as ‘converging technology’ as it elucidates the formation/incorporation and consumption of materials, devices, and systems through the control of nanometer-sized materials and their new applications to physics, chemistry, biology, engineering, materials science, medicine and other activities. Sometimes it is called as ‘enabling technology’, due to it permits new scientific and technological developments in an extensive range of disciplines and fields of application.\textsuperscript{2}

Materials at the nanoscale can have diverse properties due to their increased relative surface area and new quantum effects. Nanomaterials comprises large surface area to volume ratio comparatively with their standard form, which can steer to better chemical reactivity and influence their strength. Quantum effects can become much more prominent for defining the materials properties and characteristics, directing to novel optical, electrical and magnetic behaviours. The quantum size effect in metallic nanoparticles (NPs) is well acknowledged in the literature.\textsuperscript{3}

In metal and semiconductor NPs, there is completely an electronic effect. The band structure progresses with increasing particle size, \textit{i.e.} molecular orbital convert into delocalized band states. In a metal, the quasi-continuous density of states in the valence and the conduction bands splits into discrete electronic levels, the spacing between these levels and the band gap increasing with decreasing particle size.\textsuperscript{4,5} The gap noticed in metal NPs can be equivalent in size to that perceived in semiconductors.
(< 2 eV) or even insulators (> 2 eV).\textsuperscript{3} A diagram of the electronic bands in bulk metals, semiconductors, and insulator can be seen in Fig. 1.1.

![Diagram of electronic bands in bulk materials, semiconductors, and insulators.](image)

**Figure 1.1.** Electronic bands in bulk metals, semiconductors and insulator.

The altering of materials on the near-atomic (nanoscale) level has confirmed to be a precious contrivance in the accomplishment of essential properties of bulk materials. For paradigm, to adapt mechanical properties minor changes at the atomic level in bulk materials takes place and in specific such modifications are frequently performed to construct stronger materials. In case of single-phase materials, strengthening can be attained by grain size diminution and solid-solution strengthening or alloying. Grain size diminution acts to strengthen materials by creating it arduous for defects in crystals such as slip planes or dislocations to carry on propagation, because the slip plane or dislocation will have to adjust direction once crossing the grain boundary, as shown in Fig. 1.2.
If the crystal increases in disorientation this becomes more difficult. The existence of smaller grains develops a large grain boundary area to hinder dislocation motion. Nanostructured materials have certainly turned out to be a very dynamic research field in the expanse of materials science containing organic, inorganic and composite materials. Nanostructured materials made of nanosized grains or NPs as building blocks have a substantial segment of grain boundaries with a high degree of disorder of atoms beside the grain boundaries (or particle surfaces), and a large ratio of interface (or surface) area to volume. Chemical composition of the phases and the interfaces, between nano-grains, must be coordinated too for obtaining required properties in the material. One of the most eminent features of nanostructured materials is the significant need of several properties upon the size in the nanoscale region. For example, electronic property, with quantum size effects, instigated by spatial confinement of delocalized valence electrons, is unswervingly reliant on the particle size. Small particle size facilitates usual limitations of phase equilibrium and kinetics to be prevail during the synthesis and processing by the combination of short diffusion distances and high

Figure 1.2. Propagation of a slip plane across a grain boundary in a crystal.
driving forces of accessible large surfaces and interfaces. A wide range of materials, including metals, ceramics and metal oxides in crystalline, quasi crystalline, or amorphous phases have been synthesized as nanosized or nanostructured materials. The large surface area provides higher reactivity and diffusivity. Thus novel properties may result from surface “defects”.6–8

2. Various types of nanostructured materials (NSMs)

Nanostructure is an intermediate size between microscopic and molecular structures. NSMs as a subject of nanotechnology are low dimensional materials comprising of building units of a submicron or nanoscale size at least in one direction and exhibiting size effects. There are four different types of nanostructured materials are given as:

- Zero dimensional nanostructured materials (0D NSMs)
  - For example: Nanoparticles, Colloids, Nanodots, Nanoclusters.
- One dimensional nanostructured materials (1D NSMs)
  - For example: Nanowires, Nanotubes, Nanobelts, Nanorods.
- Two dimensional nanostructured materials (2D NSMs)
  - For example: Quantum wells, Super lattices, Thin films.
- Three dimensional nanostructured materials (3D NSMs)
  - For example: Nanocomposites, Porous materials, Hybrids, Nanocrystal arrays etc.

All the four nanostructures are enclosed with distinct properties.9,10 0D NSMs contain single crystal, polycrystalline and amorphous particles with all possible morphologies such as spheres, cubes and platelets. Normally, the characteristic dimension of NPs ranges from 1-100 nm. If the NPs are single crystalline, they are often referred to as nanocrystals. When the characteristic dimension of the NPs is sufficiently small and quantum effects are observed, they are described as quantum dots. 1D NSMs are ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of functional properties. 1D NSMs contains whiskers, fibers, nanowires and nanorods. Although the whiskers and nanorods are in general considered to be shorter than fibers and nanowires, the definition is slight arbitrary. In addition, one-dimensional structures with diameters ranging from several nanometers to several hundred microns (µ) were referred to as
whiskers and fibers in the early literature, whereas nanowires and nanorods with diameters not exceeding a few hundred nanometers are used predominantly in the current literature. Nanowires in general have a high aspect ratio than that of nanorods. 2D NSMs are ultrathin nanomaterials with a high degree of anisotropy and chemical functionality.\textsuperscript{11} Research on 2D nanomaterials is still in its infancy, with the majority of research focusing on elucidating the unique material characteristics and few reports focusing on biomedical applications of 2D nanomaterials.\textsuperscript{12} Nonetheless, recent rapid advances in 2D nanomaterials have raised important yet exciting questions about their interactions with biological moieties. 2D nanomaterials are highly diverse in terms of their mechanical, chemical and optical properties, as well as in size, shape, biocompatibility and degradability.\textsuperscript{13} These diverse properties make 2D nanomaterials suitable for a wide range of applications, including drug delivery, imaging, tissue engineering and biosensors \textit{etc}.	extsuperscript{14} However, their low-dimension nanostructure gives them some common characteristics. For example, 2D nanomaterials are the thinnest materials known, which means that they also possess the highest specific surface areas of all known materials. This characteristic makes these materials invaluable for applications requiring high levels of surface interactions on a small scale. Owing to the large specific surface area and other superior properties over their bulk counterparts arising from quantum size effect, 3D NSMs have attracted significant research interest and various 3D NSMs have been synthesized in the past 10 years.\textsuperscript{15–25} It is well known that the behaviors of NSMs strongly depend on the sizes, shapes, dimensionality and morphologies, which are thus the key factors to their ultimate performance and applications. Therefore it is of great interest to synthesize 3D NSMs with a controlled structure and morphology. In addition, 3D nanostructures are an important material due to its wide range of applications in the area of catalysis, magnetic material and electrode material for batteries.\textsuperscript{15–25} Moreover, the 3D NSMs have recently attracted intensive research interests because the nanostructures have higher surface area and supply enough absorption sites for all involved molecules in a small space.\textsuperscript{26} On the other hand, such materials with porosity in three dimensions could lead to a better transport of the molecules.\textsuperscript{26–28}
3. Synthesis methods of nanomaterials

The process to manufacture of nanomaterials and nanostructures are the first step in nanotechnology to discover their unique physical properties and phenomena and comprehend potential applications. There are several methods to synthesize the nanomaterials which are classified in two techniques.

- “Top-down” approach
- “Bottom-up” approach

In “top-down” process bulk material is converted to fine particle. This approach comprises of solid state route and ball milling techniques. The second “bottom-up” approach, involves the reduction of atoms or molecular entities in a gas phase or in solution to form the nanomaterial in the nanometer range. The bottom-up approach is more advantageous than the top-down approach because the bottom-up approach has a better chance of producing nanostructures with less defects, more homogenous chemical composition, and better short- and long-range ordering. **Fig. 1.3**, reveals the general summary of the two approaches.

**Figure 1.3.** Schematic representation of top-down and bottom-up approaches for synthesis of nanomaterials.
There are various “bottom-up” methods of synthesizing nanomaterials such as:

- Combustion synthesis
- Gas-phase methods
- Microwave synthesis
- Hydrothermal method
- Solvothermal synthesis
- Sol-gel processing
- Co-precipitation method, etc.

### 1.3.1. Combustion synthesis

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials. Combustion synthesis leads to highly crystalline particles with large surface areas.\(^{29,30}\) The process involves prompt heating of a solution containing redox groups.\(^{31}\) The temperature reaches almost 650 °C for one or two minutes resulted in the formation of crystalline material in combustion synthesis. Therefore, combustion synthesis of nanomaterials are classified on the basis of the physical nature of the initial reaction medium:\(^{32}\)

- Conventional SHS of nanoscale materials, *i.e.* initial reactants are in solid state (condensed phase combustion).
- Solution-combustion synthesis (SCS) of nanosized powders, *i.e.* initial reaction medium is aqueous solution.
- Synthesis of nanoparticles in flame, *i.e.* gas-phase combustion.

### 1.3.2. Gas-phase methods

Gas phase NP preparation methods have attracted huge interest over the years due to number of benefits that they can deliver over other methods.\(^{33,34}\) These techniques are typically characterized by the ability to accurately control the process parameters to be able to tune shape, size and chemical composition of the nanostructures.\(^{35}\) Although, means and methods can differ, almost all gas phase nanomaterial production methods follows following sequence:

- Suspending the precursor materials in a gas phase.
• Transforming the precursor material to small clusters.
• Enforcing the growth of these clusters to a NPs.
• Method to collect prepared NPs.

The growth of small nuclei clusters to NPs is referred to as condensation and it occurs only when the precursor vapor is supersaturated. Condensation process can be driven by both physical and chemical methods and will be discussed in the following:

- **Inert gas condensation:** This method is the most rudimentary of all the gas phase fabrication techniques. The method is simple as heating a material inside a furnace usually under an inert gas such as Nitrogen or Helium.\(^{36}\) This method however, is only appropriate for the materials that have low vapor pressure. An overview of the inert gas condensation process is illustrated in Fig. 1.4.

![Figure 1.4. Schematic diagram of the experimental setup of inert gas condensation process.](image)

- **Pulsed laser ablation:** In pulse laser ablation technique, more confined plume of the material is vaporized instead of the entire sample to produce vapor. To achieve this, high energy laser is focused on to a much localized position.\(^{37,38}\) The laser exposure is made in pulses thus the name pulsed laser. This rapidly heats up a small spot of the material to very high temperature at which the material is vaporized. Due to the small weight size of the sample being vaporized, this generally can be used to make small amount of nanomaterials. However, the technique is quite useful in synthesizing nanomaterials of the
materials that cannot be evaporated otherwise. The method is excessively used to make metal oxide NPs than other types.

- **Chemical vapor synthesis (CVS):** In chemical vapor synthesis (CVS), chemical vapors of precursor materials are brought to reaction in a reaction chamber. The reaction chamber is typically heated using joule heating. The method is similar to chemical vapor deposition (CVD), however instead of deposition of nanomaterial as a thin film, CVS process encourage formation of NPs. Hence, the process parameters are adjusted appropriately during the synthesis in order to suppress film formation and to encourage nucleation of particles in the gas phase. Typically, the resident time of the precursor in the reaction chamber is the most critical parameter to determine whether the film or parameter will be formed.

The main parameters of the CVS process are the residence time of precursors, gas flow rate, pressure different between inlet and the main chamber and temperature of the hot wall. In the simplest form of CVS, metal organic precursor is introduced to the hot wall reactor at a controlled rate. The reactor chamber can be filled with reactive gases to produce the respective metal oxide, halide, nitride or carbide during the process. In other technique, mixtures of NPs of two phases can be fabricated by supplying two or more precursors simultaneously. The same strategy was used to make doped nanomaterials as well. Some researchers have used CVS process to make coated or core shell NPs. This is typically achieved by supplying the second precursor at a later stage of the reactor. CVS is also regarded as a high throughput process as the production is continuous. Even a small scale reactor can produce considerably high amount of nanomaterials compared to other manufacturing techniques. An overview of the chemical vapor synthesis is illustrated in Fig. 1.5.
Figure 1.5. Chemical vapor synthesis process.

- **Flame assisted synthesis**: In flame assisted synthesis process, the energy required to particle nucleation is given by a flame instead of a supplying the energy externally from a secondary heat source. In the flame assisted synthesis method, particle nucleation and the growth will occur inside the flame.\(^{40}\)
- **Sputtering**: Sputtering is a gas phase method of fabrication of nanomaterials that involves vaporizing of a solid precursor material by bombarding with a high velocity ions of an inert gas. This produce a cloud of atoms and atom clusters that get deposited into a substrate subsequently.\(^{41}\) Sputtering is typically carried out under vacuum environment as at higher pressures mobility of sputtered materials are hindered. The most commonly used sputter sources are ion guns or hollow cathode plasma generators. This method is advantages as the composition of the sputtered material is same as the target material.

### 1.3.3. Microwave synthesis

Microwave-assisted synthesis is popular in areas ranging from biochemical processes to nanotechnology.\(^{42-48}\) Chemical reactions are often faster than traditional convection heating methods, and have higher yields and fewer side products.\(^{49,50}\) Using microwave irradiation it is possible to synthesize NPs with exact parameter control in a short time and also change particle properties and particle size as required. Microwave techniques eliminate the use of high temperature calcination for extended periods of time and allow
for fast, reproducible synthesis of crystalline metal oxide nanomaterials. Utilizing microwave energy for the thermal treatment generally leads to a very fine particle in the nanocrystalline regime because of the shorter synthesis time and a highly focused local heating (Fig. 1.6).

![Microwave synthesis instruments](image)

**Figure 1.6.** Microwave (Monowave 300 & Masterwave BTR) synthesis instruments.

### 1.3.4. Hydrothermal method

Hydrothermal synthesis is generally operated in steel pressure vessels called autoclaves with or without Teflon liners under regulated temperature and/or pressure with the reaction in aqueous solutions. The temperature can be elated above the boiling point of water, attaining the pressure of vapor saturation. Hydrothermal synthesis is widely used for the preparation of important inorganic materials, super ionic conductor, chemical sensors, electronically conducting solids, complex oxide ceramics and fluorides, magnetic materials and luminescence phosphors etc. Advantages of the hydrothermal synthesis method over other types of crystal growth include the ability to synthesize crystals of substances which are unstable near the melting point, and the ability to synthesize large crystals of high quality. Disadvantages are the high cost of equipment and the inability to monitor crystals in the process of their growth.
Hydrothermal synthesis can be effected both under temperatures and pressures below the critical point for a specific solvent above which differences between liquid and vapor disappear, and under supercritical conditions. The solubility of many oxides in hydrothermal solutions of salts is much higher than in pure water; such salts are called mineralizers. There is also a group of solvothermal synthesis methods, relational to hydrothermal methods; this group of methods is based on the use of organic solvents and supercritical CO$_2$. One of the most widely known nanomaterials produced by the hydrothermal method are synthetic zeolites. A necessary condition for their production is the presence in the solution of some surface active agents (SAA) that actively influence morphological evolution of oxide compounds in hydrothermal solutions. The choice of synthesis conditions and type of surfactants can ensure the production of targeted porous nanomaterials with given pore size controlled in a fairly wide range of values. Furthermore, with an ever-increasing demand for composite nanostructures, the hydrothermal technique offers a unique method for coating of various compounds on metals, polymers and ceramics as well as for the fabrication of powders or bulk ceramic bodies. It has now emerged as a frontline technology for the processing of advanced materials for nanotechnology. On the whole, hydrothermal technology offered a new perspective which is illustrated in Fig. 1.7. It links all the important technologies like geotechnology, biotechnology, nanotechnology and advanced materials technology.
1.3.5. Solvothermal synthesis

Solvothermal synthesis is a particularly versatile low-temperature route, in which polar solvents, under pressure and at temperatures above their boiling point, are used. Under solvothermal conditions, the solubility of the reactants increases significantly, enabling reaction to take place at considerably lower temperatures than in conventional synthetic techniques. This type of soft-chemistry approach is mild enough to allow “molecular” building blocks such as chains and rings to form and participate in the formation of nanostructures.

1.3.6. Sol-gel processing

The sol-gel technique is a long-established industrial process for the generation of colloidal NPs from liquid phase that has been further developed in last years for the production of advanced nanomaterials and coatings. Sol-gel-processes are well adapted for oxide NPs and composites nanopowders synthesis. The main advantages of sol-gel techniques for the preparation of materials are low temperature of processing,
versatility, and flexible rheology allowing easy shaping and embedding. They offer unique opportunities for access to organic-inorganic materials. The most commonly used precursors of oxides are alkoxides, due to their commercial availability and to the high liability of the M-OR bond allowing facile tailoring in situ during processing. An overview of the sol-gel process is illustrated in Fig. 1.8.

**Figure 1.8.** Schematic representation of the different stages and routes of the sol-gel process.

The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds, which by hydrolysis and polycondensation reactions form the sol. Further processing of the sol enables one to make ceramic materials in different forms. Thin films can be produced by spin-coating or dip-coating. When the sol is cast into a mould, a wet gel will form. By drying and heat-treatment, the gel is converted into dense ceramic or glass materials. If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density aerogel material is obtained. As the viscosity of a sol is adjusted into a suitable viscosity range, ceramic fibres can be drawn from the sol. Ultrafine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques.
Sol-gel derived products have numerous applications. One of the promising application areas is for coatings and thin films used in electronics, optical and electro-optical components and devices, such as substrates, capacitors, memory devices, infrared (IR) detectors and wave guides. Anti-reflection coatings are also used for automotive and architectural applications. Submicron particle size powders of single and multicomponent composition can be made for structural, electronic, dental and biomedical applications. Composite powders can also be used as agrochemicals or herbicides. Optical and refractory fibers are used for fiber optics sensors and thermal insulation, respectively. In addition, sol-gel techniques can be used to infiltrate fiber performs to make composites. Glass monoliths and coating and organic/inorganic hybrids are under development for lenses, mirror substrates, graded index optics, optical filters, chemical sensors, passive and nonlinear active waveguides and lasers. Membranes for separation and filtration processes also are being investigated, as well as catalysts. Biomolecules (such as proteins, enzymes, antibodies, etc.) are incorporated into sol-gel matrices, which can be used for the monitoring of biochemical processes, environmental testing, food processing and drug delivery for medicine or agriculture.

1.3.7. Co-precipitation method

Co-precipitation is the least expensive and the simplest approach for making NPs. This method produces NPs in large quantities (order of grams) in a relatively short interval of time and utilizes inexpensive and readily available chemicals as precursors. The synthesis of NPs by co-precipitation method consists of several steps including\(^{61,62}\):

- Nucleation
- Growth
- Coarsening
- Agglomeration

For the fabrication of monodispersed NPs, the nucleation and growth stages must be under precise control (Fig. 1.9). The rapid nucleation and relatively slow growth will lead to the formation of monodispersed NPs. In the slow growth mode, molecules of NPs generally follow the Oswald ripening process, whereas the rapid growth mode will always lead to an irregular morphology and scattered size distribution for the NPs.\(^ {63}\)
Co-precipitation method gives an amorphous product and subsequent calcinations or annealing is necessary in order to render the crystalline NPs, in which some agglomeration will be unavoidable. The crystalline NPs are rarely precipitated for aqueous solution therefore, the non-aqueous approach using organic solvent may be used to overcome some of these issues of aqueous solutions in the synthesis of metal oxide NPs.\textsuperscript{64,65}

There are three main mechanisms of co-precipitation:\textsuperscript{66}

- Inclusion
- Occlusion
- Adsorption

An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect; this can happen when the ionic radius and charge of the impurity are similar to those of the carrier. An adsorbate is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. An occlusion occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows.
4. Properties of nanomaterials

Nanoparticles have one dimension that measures 100 nanometers or less. The properties of many conventional materials change when formed from NPs. This is typically because NPs have a greater surface area per weight than larger particles which causes them to be more reactive to some other molecules.

There are several properties of nanomaterials follows as:

- Physical properties
- Chemical properties

1.4.1. Physical properties

Nanomaterials displays some characteristic physical properties including electrical, catalytic, magnetic, mechanical, thermal or imaging features as compare to normal bulk particles which make the nanomaterials a significant area in medical, pharmaceutical and different engineering sectors. The nanomaterials acquire some incredible and specific peculiar properties which may be considerably different from the physical properties of bulk materials.\(^3\)\(^6\)\(^7\) The specific features of those physical properties are as follows:

- **Color:** There are some materials which show different color when they are changed to NPs like gold materials which turn into red when they are converted to nanomaterials. Gold NPs in contact with light is powerfully controlled by the particle sizes of the materials. Small particle sizes (~2-150 nm) have high surface electron densities which are called as surface plasmons undergo a collective oscillation when they are excited by light at specific wavelengths.\(^69\)\(^-\)\(^71\) This oscillation is described as a surface plasmon resonance (SPR). For small (~30 nm) monodisperse gold NPs the surface plasmon resonance phenomena is responsible for an absorption of the blue-green portion of the spectrum (~450 nm) while red light (~700 nm) is reflected, producing a rich red color (Fig. 1.10).
Figure 1.10. Suspensions of gold nanoparticles of various sizes.

- **Melting point**: The melting point drastically falls when the particle size of the material approaches to the nanoscale ranges. This phenomenon related to melting point depression is very prominent in nanoscale materials which melt at temperature hundreds of degrees lower than bulk materials. Melting point depression is most evident in nanowires, nanotubes and nanoparticles, which all melt at lower temperatures than bulk form of the same material. Changes in melting point occur because nanoscale materials have a much larger surface to volume ratio than bulk materials, drastically altering their thermodynamic and thermal properties.\(^72\)

- **Mechanical strength**: All the nanomaterials possess high mechanical strength as compared to their conventional counterparts. The mechanical strength of nanomaterials may be one or two times higher in magnitude than that of single crystals in the bulk form. Defects in the form of atomic vacancies can lower the tensile strength of the materials by up to 85 %. Conversion of materials into nanoscale increases crystal perfection or reduction of defects, which would result the enhancement in mechanical strength. Cutting tools which should be harder than the material which is to be cut are made of nanomaterials, such as tungsten carbide, tantalum carbide and titanium carbide. These cutting tools are much more erosion-resistant and durable than their conventional large grained bulk materials. In general, hardness of metals (e.g. Cu) increases linearly with
increase of grain size. However, in case of nanomaterial, the hardness increases linearly with decrease of particle size.\textsuperscript{73}

- **Electrical properties:** This is quite complex phenomenon. Reduction in material’s dimensions would have two different contrasting effects on electrical conductivity. By its property nanoparticle product enhance the crystal perfection and as well as it reduce the defects. As a result electron scattering phenomenon due to crystal defects are also reduced and a reduction in resistivity is experienced. However, at room temperature the defect scattering incident contributes a minor influence on the total electrical resistibility of various metals. On the other hand surface scattering phenomenon which is highly increased due to reduction of particle size is one of the prominent reasons for increase of the total resistivity. In addition a reduction in particle size below a critical dimension, (\textit{i.e.} electron de Broglie wavelength), would result in a modified electronic structure with wide and discrete band gap. The reduction of particle size into this range would result in an increased electrical resistivity.\textsuperscript{74}

- **Optical properties:** Optical properties exhibited by nanomaterials are quite different from their bulk counterpart. The reason behind this change in property is mainly due to the effect of the surface plasmon resonance. In addition, the increased energy level spacing is also an important criterion for this changing behavior. Due to increased band gap for semiconductor NPs absorption edge is shifted toward shorter wavelengths. Surface plasmon resonance effect changes due to change in particle size which in turn changes the color of metallic NPs.\textsuperscript{70} The coherent excitation of entire free electrons in the conduction band may produce an in-phase oscillation, called surface plasmon resonance. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface plasmon resonance is generated. On resonance, light is tightly confined to the surface of the nanostructure, until it gets eventually absorbed inside the metal, or scattered back into photons.\textsuperscript{74}

- **Magnetic properties:** Reducing the size of the magnetic systems changes the electronic properties by reducing the symmetry of the system and by introducing a quantum confinement.\textsuperscript{75} The strength of a magnet is measured in terms of coercivity and saturation magnetization value. These values increase with decrease in the grain size and an increase in specific surface area (surface area per unit volume) of the grain.
Nanoparticles exhibit magnetic properties that are different from bulk materials. These are due to the following reasons:

- As the size of these system reaches the typical lengths of few nanometers, it is expected that the response of the system depends on the boundary conditions (which no longer periodic, but determined by the particle size) and therefore, to be different from bulk materials.
- Because of the large ratio of surface to volume atoms in NPs, the surface energy becomes important when compared with volume energy, and therefore, the equilibrium situation can be different that for bulk materials. In the case of NPs, the volume is so small, therefore the thermal energy (k_B T) is enough to invert the magnetization with relaxation times as low as few seconds. Thus, the material loses coercivity and remanence, giving rise to the so-called super paramagnetic behavior.

### 1.4.2. Chemical properties

Chemical properties of the materials are also changed when it converts to nano range. Due to increase of exposed surface area of the NPs as compared with conventional bulk objects, reactivity of those particles increase enormously.

Some important chemical properties of the NP are as follows:

- In case of NPs 50% of all the atoms are surface atoms and as a result electric transport properties of these particles are no longer dependent on solid state bulk phenomenon. Electrical properties are directly related to chemical properties.
- Due to larger proportion of surface atoms, the atoms present in nanomaterials posses a higher energy as compare to atoms present in bulk structure.
- The interactions between NPs depend on the chemical nature of the surface. Due to large surface area high quantity charge species defects and impurities may be easily attracted to surfaces and interfaces of NPs and thus chemical nature of the surfaces changes abruptly as compare to their bulk counterpart.
- Surface properties of the NPs and their interaction can be modified or altered by using molecular monolayer.
.5. Ni-Co nanoferrites: A brief review

Ferrites are chemical compounds obtained as powder or ceramic bodies with ferrimagnetic properties formed by iron oxides as their main component, Fe₂O₃ and FeO, which can be partly changed by other transition metal oxides. Spinel ferrites have general formula AB₂O₄, where A is divalent and B is trivalent metal cations, respectively (Fig. 1.1). The Oxygen forms an fcc crystal lattice with 32O²⁻, which has 64 tetrahedral and 32 octahedral vacancies, wherein, 1/8 of tetrahedral and 1/2 of octahedral sites are occupied by A and B metal cations. The magnetic and electrical properties of ferrites are highly sensitive to the cation distribution among tetrahedral and octahedral sites, which in turn can be governed by the choice of synthesis route and sintering conditions. Super paramagnetism, spin canting, core/shell structure, metastable cation distribution etc. are some of the phenomena, which have been observed in NPs of various ferrites.

Cobalt ferrite is a well-known hard magnetic material with relatively high coercivity and saturation magnetization while nickel ferrite is a soft material with low coercivity and saturation magnetization. These (hard and soft magnetic) properties make them very promising candidates for a variety of applications in biomedical, electronic as well recording technologies. Many technological applications require magnetic NPs to be embedded in a nonmagnetic matrix. Over the past few years, increased attention has been focused on the preparation of various nanostructures with magnetic nanoparticulate components and on understanding the magnetic behavior of NPs due to new possible surface, interparticle, and exchange interactions in magnetic/nonmagnetic matrix.

Encapsulating magnetic NPs in silica is a promising and important approach in the development of magnetic NPs for technological and biomedical applications. For magneto-electronic applications, silica-coated NPs could be used to form ordered arrays with interparticle magnetic couplings controlled through the silica shell thickness. The rich and well documented biocompatible chemistry of silica colloids may allow for practical implementation of magnetic NPs in magnetically guided drug delivery, tumor targeting, and magnetically assisted chemical separation of cells and/or protein.
1.5.1. Applications of ferrite

- Spinel ferrites ceramic are widely used in microwave devices to control transmission path, frequency, amplitude and phase of microwave signals.
- The structured magnetic materials have an interesting area of study because of its possible applications in a variety of widely areas ranging from information technology to biotechnology.
- Ferrites are excellent soft magnetic materials in high-frequency devices due to their low cost, high resistivity and low eddy current losses, which have been studied extensively for multilayer chip inductor application.

.6. Tin oxide (SnO$_2$) NPs: A brief review

SnO$_2$ is a wide band-gap metal oxide semiconductor (Table 1.1) in which inherent oxygen vacancies act as $n$-type dopants.$^{92,93}$ It belongs to a class of materials that combines high electrical conductivity with optical transparency and thus constitutes an important component for optoelectronic applications.$^{94}$ The
study of SnO$_2$ is motivated by its applications as a solid state gas sensor material, oxidation catalyst, and transparent conductor. The key for understanding many aspects of SnO$_2$ surface properties is the dual valency of Sn. The dual valency facilitates a reversible transformation of the surface composition from stoichiometric surfaces with Sn$^{4+}$ surface cations into a reduced surface with Sn$^{2+}$ surface cations depending on the oxygen chemical potential of the system. SnO$_2$ has the rutile type tetragonal structure belonging to the $P42/mnm$ space group (Fig. 1.2). The lattice parameters are $a = b = 4.7382$ Å and $c = 3.1871$ Å, and the band-gap energy is in the ultraviolet range between 3.5 and 3.8 eV as estimated from experimental results and theoretical calculations. Its high optical transparency, electrical conductivity, and chemical stability make it a very attractive material for solar cells, heat mirrors, catalysis and gas sensing applications.

Figure 1.2. The schematic diagram of rutile type tetragonal structure and powder form of SnO$_2$ nanoparticle.
Table 1.1. Properties of SnO$_2$ NPs.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Chemical formula</td>
<td>SnO$_2$</td>
</tr>
<tr>
<td>2.</td>
<td>Molar mass</td>
<td>150.71 g mol$^{-1}$</td>
</tr>
<tr>
<td>3.</td>
<td>Melting point</td>
<td>1630 °C</td>
</tr>
<tr>
<td>4.</td>
<td>Boiling point</td>
<td>1900 °C</td>
</tr>
<tr>
<td>5.</td>
<td>Density</td>
<td>6.95 g cm$^{-3}$</td>
</tr>
<tr>
<td>6.</td>
<td>Appearance</td>
<td>White or light grey powder</td>
</tr>
<tr>
<td>7.</td>
<td>Odor</td>
<td>Odorless</td>
</tr>
<tr>
<td>8.</td>
<td>Solubility in water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>9.</td>
<td>Solubility</td>
<td>Soluble in hot concentrated alkalis, concentrated acids, insoluble in alcohol</td>
</tr>
<tr>
<td>10.</td>
<td>Magnetic susceptibility ($\chi$)</td>
<td>-4.1×10$^{-5}$ cm$^3$ mol$^{-1}$</td>
</tr>
<tr>
<td>11.</td>
<td>Refractive index</td>
<td>2.006</td>
</tr>
<tr>
<td>12.</td>
<td>Crystal structure</td>
<td>Rutile tetragonal</td>
</tr>
<tr>
<td>13.</td>
<td>Electronic configuration</td>
<td>Tin [Kr] 4d$^{10}$ 5s$^2$ 5p$^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxygen [He] 2s$^2$ 2p$^4$</td>
</tr>
</tbody>
</table>

1.6.1. Applications of SnO$_2$ NPs

- SnO$_2$ NPs, as one of the most important semiconductor oxides, has been used as photocatalyst for photodegradation of organic compounds.

- SnO$_2$ NPs also used as catalysts, energy-saving coatings and anti-static coatings, in the making of optoelectronic devices and resistors.

- SnO$_2$ layers have been used as transparent and electrically conducting coatings on glass. These films have a high mechanical and chemical stability. Due to the mechanical stability of the SnO$_2$ they are used in hot end coatings on bottles.

- SnO$_2$ NPs has very good transparent mirror properties, due to this property they are used as electrodes and anti-reflection coatings in solar cells, as heat shields in electronic devices, in thermal insulation, in solar head collectors, in photovoltaic cells, in double glazing lamps.

- SnO$_2$ NPs are widely used in sensing applications due to its semiconductor properties like in smoke sensors, humidity sensors, gas sensors etc. The transparent electrical conduction property of SnO$_2$ NPs are mostly used in transparent ovens and in liquid crystal displays.
Silica coated nickel oxide (NiO) NCs: A brief review

NiO NPs are one such momentous metal oxide that tend to be p-type semiconductor with a wide band-gap (Fig. 1.13). It has tremendous application in science and technology (Table 1.2). It can be used as a transparent p-type semiconducting layer and as an antiferromagnetic film and can also be extensively used in smart windows, electrochemical supercapacitor, and dye-sensitized photocathode. It exhibits anodic electrochromism. Due to excellent durability and electrochemical stability, low material cost as an ion storage material, large-spin optical density, and various manufacturing possibilities, NiO semiconductors become interesting topics for scientists. Different methods have already been reported for the synthesis of NiO NPs such as evaporation, magnetron sputtering, and sol-gel. Particularly, the optical behavior of NiO under different circumstances is becoming one of the prime searches of the scientists. Professor Guerra et al. investigated the cathodoluminescence and photoluminescence of NiO whereas Professor Kuzmin and his group examined the effect of doping in the origin of visible photoluminescence in NiO. Even the NiO nanowires are also under observation for their emission property. However, the complexity remains in the synthesis technique as well as in the limitation of tailoring the optical properties of NiO NPs. Especially the optical response of bare NiO NPs cannot be tailored much for their large band-gap energy. Keeping this in mind, scientists have proposed to oxidize Ni nanoparticle within insulating medium by ion implantation method in search of better stability and novel optical properties. Effort has been also delivered to synthesize NiO NPs within insulating silica matrix to form nanocomposite (NC) films leading toward optical gas sensor.

Figure 1.13. The schematic diagram and powder form of NiO nanoparticles.
Table 1.2. Properties of NiO NPs.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Chemical formula</td>
<td>NiO</td>
</tr>
<tr>
<td>2.</td>
<td>Molar mass</td>
<td>74.6928 g mol⁻¹</td>
</tr>
<tr>
<td>3.</td>
<td>Appearance</td>
<td>Green crystalline solid</td>
</tr>
<tr>
<td>4.</td>
<td>Density</td>
<td>6.67 g cm⁻³</td>
</tr>
<tr>
<td>5.</td>
<td>Melting point</td>
<td>1955 °C</td>
</tr>
<tr>
<td>6.</td>
<td>Solubility in water</td>
<td>Negligible</td>
</tr>
<tr>
<td>7.</td>
<td>Solubility</td>
<td>Soluble in KCN</td>
</tr>
<tr>
<td>8.</td>
<td>Magnetic susceptibility (χ)</td>
<td>660×10⁻⁶ cm³ mol⁻¹</td>
</tr>
<tr>
<td>9.</td>
<td>Refractive index</td>
<td>2.1818</td>
</tr>
</tbody>
</table>

1.7.1. Applications of NiO NPs

The key applications of NiO NPs are as follows:

- In preparation of Ni cermet for the anode layer of solid oxide fuel cells.
- In lithium NiO cathodes for lithium ion microbatteries.
- In electrochromic coatings, plastics and textiles.
- In nanowires, nanofibers and specific alloy and catalyst applications.
- As a catalyst and as anti-ferromagnetic layers.
- In light weight structural components in aerospace.
- Adhesive and coloring agents for enamels.
- In active optical filters.
- In ceramic structures.
- In automotive rear-view mirrors with adjustable reflectance.
- In cathode materials for alkaline batteries.
- Electrochromic materials.
- Energy efficient smart windows.
- P-type transparent conductive films.
- Materials for gas or temperature sensors, such as CO sensor, H₂ sensor, and formaldehyde sensors.
- As a counter electrodes.
8. Characterization techniques

There are several techniques used to understand these characterization parameters in NPs. They include:

- X-ray diffraction (XRD)
- Scanning electron microscopy (SEM)
- Energy dispersive X-ray analysis (EDS)
- X-ray photoelectron spectroscopy (XPS)
- Transmission electron microscopy (TEM)
- High resolution transmission electron microscopy (HR-TEM)
- Optical spectroscopy
- UV-Visible (UV-Vis) spectroscopy
- Differential thermal analysis (DTA)/Thermogravimetric analysis (TGA)
- Infrared spectroscopy (IR)

1.8.1. X-ray diffraction (XRD)

The X-ray diffraction is a conventional technique for determination of crystallographic structure and compositional analysis of the materials. There is increase or decrease in intensity with the amount of constituent. This technique is used to establish the metallic nature of particles gives information on translational symmetry size and shape of the unit cell from peak positions and information on electron density inside the unit cell, namely where the atoms are located from peak intensities.\textsuperscript{124}

The interaction of X-ray radiation with crystalline sample is governed by Bragg’s law, which depicts a relationship between the diffraction angles (Bragg angle), X-ray wavelength, and interplanar spacing of the crystal planes. According to Bragg’s law, the X-ray diffraction can be visualized as X-rays reflecting from a series of crystallographic planes as shown in Fig. 1.14. The path differences introduced between a pair of waves travelled through the neighboring crystallographic planes are determined by the interplanar spacing. If the total path difference is equal to \( n\lambda \) (\( n \) being an integer), the constructive interference will occur and a group of diffraction peaks can be observed, which give rise to X-ray patterns. The quantitative account of Bragg’s law can be expressed as:

\[
2d_{hkl} \sin \theta = n\lambda
\]

Where \( d \) is the interplanar spacing for a given set of \( hkl \) and \( \theta \) is the Bragg angle.
The XRD measurements were carried out using Rigaku X-ray diffractometer with Cu Ka ($\lambda = 1.54187\text{Å}$) radiation at room temperature, shown in Fig. 1.15 and Fig. 1.16, and operated at a voltage of 30 kV and filament current of 40 mA.

The diffraction method is based on the effect of broadening of diffraction reflections associated with the size of the particles (crystallites). All types of defects cause displacement of the atoms from the lattice sites. M.A. Krivoglaz\textsuperscript{125} in 1969 derived an equation for the intensity of the Bragg reflections from a crystal defect, which enabled all the defects to be derived conventionally into two groups. The defects in the first group only lower the intensity of the diffraction reflections but do not cause the reflection broadening. The broadening of the reflections is caused by the defects of second group. These defects are micro-deformations, inhomogeneity (non-uniform composition of the substance over their volume) and the small particle size. The size of nanomaterials can be derived from the peak broadening and can be calculated by using the Scherrer equation, provided that the nanocrystalline size is less than 100 nm.

$$D = \frac{k\lambda}{\beta\cos\theta}$$

Where $D$ is the average crystallite dimension perpendicular to the reflecting phases, $\lambda$ is the X-ray wavelength, $k$ is the Scherrer constant which equals to 0.9 for spherical particles, whose value depends on the shape of the particle (crystallite, domain) and on diffraction reflection indices ($hkl$), and $\beta$ is the full width half maximum of the peaks.

The Scherrer formula is quite satisfactory for small grains (large broadening) in the absence of significant microstrain. A microstrain describes the relative mean square deviation of the lattice spacing from its mean value. Based on the grain size dependence
of the strain it is reasonable to assume that there is a radial strain gradient, but from X-ray diffraction only a homogeneous, volume averaged value is obtained.

![X-ray Diffraction (XRD) machine.](image1)

**Figure 1.15.** X-ray Diffraction (XRD) machine.

![Schematic details of X-ray Diffraction (XRD).](image2)

**Figure 1.16.** Schematic details of X-ray Diffraction (XRD).
Therefore, X-ray diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

Other applications include:

- Characterization of crystalline materials
- Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- Determination of unit cell dimensions
- Measurement of sample purity

With specialized techniques, XRD can be used to:

- Determine crystal structures using Rietveld refinement
- Determine modal amounts of minerals (quantitative analysis)
- Characterize thin films samples by:
  - Determining lattice mismatch between film and substrate and to inferring stress and strain
  - Determining dislocation density and quality of the film by rocking curve measurements
  - Measuring superlattices in multilayered epitaxial structures
  - Determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements
- Make textural measurements, such as the orientation of grains, in a polycrystalline sample.

1.8.2. Scanning electron microscopy (SEM)

The scanning electron microscope (Fig. 1.17) is an electron microscope that determines the size, shape and surface morphology with direct visualization of the NPs. Therefore scanning electron microscopy offer several advantages in morphological and sizing analysis. However they provide limited information about the size distribution and true population average. During the process of SEM characterization, solution of NPs should be initially converted into a dry powder. This dry powder is then further mounted on a sample holder followed by coating with a conductive metal (e.g. gold) using a sputter coater. Whole sample is then analyzed by scanning with a focused fine beam of
electrons. Secondary electrons emitted from the sample surface determine the surface characteristics of the sample. This electron beam can often damage the polymer of the NPs which must be able to withstand vacuum. Average mean size evaluated by SEM is comparable with results obtained by dynamic light scattering (DLS). In addition these techniques are time consuming, costly and frequently need complementary information about sizing distribution.

The basic principle behind the SEM is that when the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons, back scattered electrons and characteristic X-rays are generated that contain information about the sample’s surface topography, composition, etc. The SEM can produce very high-resolution images of a sample surface, revealing details about 1-5 nm in size in its primary detection mode i.e. secondary electron imaging. Characteristic X-rays are the second most common imaging mode for an SEM. These characteristic X-rays are used to identify the elemental composition of the sample by a technique known as energy dispersive X-ray (EDS). Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic X-rays as clues to the elemental composition of the sample.

In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. Electronic devices are used to detect and amplify the signals and display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of the microscope. The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

SEM requires that the specimens should be conductive for the electron beam to scan the surface and that the electrons have a path to ground for conventional imaging. Non-conductive solid specimens are generally coated with a layer of conductive material by low vacuum sputter coating or high vacuum evaporation. This is done to prevent the accumulation of static electric charge on the specimen during electron irradiation. Non-conducting specimens may also be imaged uncoated using specialized SEM instrumentation such as the “Environmental SEM” (ESEM) or in field emission gun (FEG) SEM operated at low voltage, high vacuum or at low vacuum, high voltage.
1.8.3. Energy dispersive X-ray analysis (EDS)

EDS analysis is a technique to analyze near surface elements and estimate their proportion at different position, thus giving an overall mapping of the sample. This technique is used in conjunction with SEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20 keV. This causes X-rays to be emitted from the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns (µ) in depth, and thus EDS is not truly a surface science technique. By moving the electron beam across the material an image of each element in the sample can be obtained. Due to the low X-ray intensity, images usually take a number of hours to acquire.

The composition or the amount of NPs near and at the surface can be estimated using the EDS, provided they contain some heavy metal ions. Elements of low atomic number are difficult to detect by EDS. The Si-Li detector protected by a beryllium (Be) window cannot detect elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) can be detected. EDS spectra have to be taken by focusing the beam at different regions of the same sample to verify spatially uniform composition of the bimetallic materials.
1.8.4. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (Fig. 1.18) also known as electron spectroscopy for chemical analysis (ESCA) is the most widely used surface analysis technique because it can be applied to a broad range of materials and provides valuable quantitative and chemical state information from the surface of the material being studied. The average depth of analysis for an XPS measurement is approximately 5 nm. XPS is typically accomplished by exciting a samples surface with monoenergetic Al kα X-rays causing photoelectrons to be emitted from the sample surface. An electron energy analyzer is used to measure the energy of the emitted photoelectrons (Fig. 1.19). From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of a detected element can be determined.

Figure 1.18. Schematic view of XPS.

Figure 1.19. Ejection of photoelectrons.
As the demand for high performance materials increases, so does the importance of surface engineering. Many of the problems associated with modern materials can be solved only by understanding the physical and chemical interactions that occur at the surface or at the interfaces of a material’s layers. The surface chemistry will influence such factors as corrosion rates, catalytic activity, adhesive properties, wettability, contact potential and failure mechanisms.

The material’s surface is the point of interaction with the external environment and other materials. Therefore, surface modification can be used in a wide variety of applications to alter or improve the performance and behavior of a material. XPS can be used to analyze the surface chemistry of a material after an applied treatment such as fracturing, cutting or scraping. From non-stick cookware coatings to thin film electronics and bioactive surfaces, XPS is the standard tool for surface material characterization.

1.8.5. Transmission electron microscopy (TEM)

Transmission electron microscopy (Fig. 1.20) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen and interacts as passes through the sample. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a charge-coupled device (CCD).
TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology and semiconductor research.

The TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope.

Modern TEMs are equipped with specimen holders that allow to tilt the specimen to a range of angles in order to obtain specific diffraction conditions. Therefore, a high contrast image can be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through. This produces a variation in the electron intensity that reveals information on the crystal structure. This technique, particularly sensitive to extended crystal lattice defects, is known as ‘bright field’ or ‘light field’. It is also possible to produce an image from electrons deflected by a particular crystal plane which is known as a dark field image.

Figure 1.20. Schematic representation of transmission electron microscope (TEM).
The specimens must be prepared as a thin foil so that the electron beam can penetrate. Materials that have dimensions small enough to be electron transparent, such as powders or nanotubes, can be quickly produced by the deposition of a dilute sample containing the specimen onto support grids.

The TEM is used widely both in material science/metallurgy and biological sciences. In both cases the specimens must be very thin and able to withstand the high vacuum present inside the instrument. For biological specimens, the maximum specimen thickness is roughly 1 µm. To withstand the instrument vacuum, biological specimens are typically held at liquid nitrogen temperatures after embedding in vitreous ice, or fixated using a negative staining material such as uranyl acetate or by plastic embedding. The properties of nanocomposites (NCs) depend to a large extent on successful nano-level dispersion or intercalation/exfoliation of nanoclays, therefore monitoring their morphology and dispersion is very crucial.

1.8.6. High resolution transmission electron microscopy (HR-TEM)

HR-TEM is an imaging mode of the transmission electron microscope that allows the imaging of the crystallographic structure of a sample at an atomic scale.\textsuperscript{129,130} HR-TEM is a powerful tool to study properties of materials on the atomic scale, such as semiconductors, metals, nanoparticles and sp\textsuperscript{2}-bonded carbon (e.g. graphene, carbon nanotubes). While HR-TEM is often also used to refer to high resolution scanning TEM (STEM, mostly in high angle annular dark field mode), this article describes mainly the imaging of an object by recording the 2D spatial wave amplitude distribution in the image plane, in analogy to a “classic” light microscope. For disambiguation, the technique is also often referred to as phase contrast TEM. At present, the highest point resolution realized in phase contrast TEM is around 0.5 Å (0.050 nm).\textsuperscript{131} At these small scales, individual atoms of a crystal and its defects can be resolved. For 3-dimensional crystals, it may be necessary to combine several views, taken from different angles, into a 3D map. This technique is called electron crystallography.

One of the difficulties with HR-TEM is that image formation relies on phase contrast. In phase-contrast imaging, contrast is not necessarily intuitively interpretable, as the image is influenced by aberrations of the imaging lenses in the microscope. The largest contributions for uncorrected instruments typically come from defocus and
astigmatism. The latter can be estimated from the so-called “Thon ring pattern” appearing in the fourier transform modulus of an image of a thin amorphous film.

As opposed to conventional microscopy, HR-TEM does not use absorption by the sample for image formation, but the contrast arises from the interference in the image plane of the electron wave with itself. Each imaging electron interacts independently with the sample. As a result of the interaction with the sample, the electron wave passes through the imaging system of the microscope where it undergoes further phase change and interferes as the image wave in the imaging plane. It is important to realize that the recorded image is not a direct representation of the samples crystallographic structure.

1.8.7. Optical spectroscopy

Optical spectroscopy has been extensively used for the characterization of nanomaterials and the techniques can be generally categorized into two groups:

- Absorption and emission spectroscopy
- Vibrational spectroscopy.

The former determines the electronic structures of atoms, ions, molecules or crystals through exciting electrons from the ground to excited states (absorption) and relaxing from the excited to ground states (emission). The vibrational techniques may be summarized as involving the interactions of photons with species in a sample that results in energy transfer to or from the sample via vibrational excitation or de-excitation. The vibrational frequencies provide the information of chemical bonds in the detecting samples. IR and Raman spectroscopy are the examples of vibrational spectroscopy.

1.8.8. UV-Visible (UV-Vis) spectroscopy

Ultraviolet spectrophotometers (Fig. 1.21) consist of a light source, reference and sample beams, a monochromator and a detector. The ultraviolet spectrum for a compound is obtained by exposing a sample of the compound to ultraviolet light from a light source, such as a Xenon lamp (Fig. 1.22).
The reference beam in the spectrophotometer travels from the light source to the detector without interacting with the sample. The sample beam interacts with the sample exposing it to ultraviolet light of continuously changing wavelength. When the emitted wavelength corresponds to the energy level which promotes an electron to a higher molecular orbital, energy is absorbed. The detector records the ratio between reference and sample beam intensities ($I_0/I$). The computer determines at what wavelength the sample absorbed a large amount of ultraviolet light by scanning for the largest gap between the two beams. When a large gap between intensities is found,
where the sample beam intensity is significantly weaker than the reference beam, the computer plots this wavelength as having the highest ultraviolet light absorbance when it prepares the ultraviolet absorbance spectrum.

UV-Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

- Solutions of transition metal ions can be colored (i.e. absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another. The color of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the color of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the color and changes the wavelength of maximum absorption ($\lambda_{\text{max}}$).

- Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water-soluble compounds, or ethanol for organic-soluble compounds. Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths. Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.

- While charge transfer complexes also give rise to colors, the colors are often too intense to be used for quantitative measurement.

1.8.9. **Differential thermal analysis (DTA)/Thermogravimetric analysis (TGA)**

Thermal analysis is the analysis of a change in a property of a sample, which is related to an imposed change in the temperature. The sample is usually in the solid state and the changes that occur on heating include melting, phase transition, sublimation, and decomposition.

The analysis of the change in the mass of a sample on heating is known as thermogravimetric analysis (TGA). TGA measures mass changes in a material as a
function of temperature (or time) under a controlled atmosphere. Its principal uses include measurement of a materials thermal stability and composition. TGA is most useful for dehydration, decomposition, desorption and oxidation processes.\textsuperscript{132} Common applications of TGA are:

- Materials characterization through analysis of characteristic decomposition patterns.
- Studies of degradation mechanisms and reaction kinetics.
- Determination of organic content in a sample.
- Determination of inorganic (e.g. ash) content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis.

It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings and paints.

The most widely used thermal method of analysis is DTA. In DTA, the temperature of a sample is compared with that of an inert reference material during a programmed change of temperature. The temperature should be the same until thermal event occurs, such as melting, decomposition or change in the crystal structure. In an endothermic event takes place within the sample, the temperature of the sample will lag behind that of the reference and a minimum will be observed on the curve. On the contrary, if an exothermal event takes place, then the temperature of the sample will exceed that of the reference and a maximum will be observed on the curve. The area under the endotherm or exotherm is related to the enthalpy of the thermal event, $\Delta H$. Fig. 1.23, shows a typical TGA/DTA system.
For many problems, it is advantageous to use both DTA and TGA, because the DTA events can then be classified into those which do or do not involve mass change. TGA-DTA modes can be used to determine the following:

- Melting points
- Glass transition temperatures
- Crystallinity
- Moisture/volatile content
- Thermal and oxidative stability
- Purity
- Transformation temperatures

### 1.8.10. Infrared spectroscopy (IR)

Measures infrared intensity vs wavelength of light, it is used to determine the nature of associated functional groups and structural features of NPs. IR spectroscopy (Fig.1.24) is a popular characterization technique in which a sample is placed in the path of an IR radiation source and its absorption of different IR frequencies is measured. Solid, liquid and gaseous samples can all be characterized by this technique. IR photons
energies, in a range between 1 to 15 kcal mol\(^{-1}\), are insufficient to excite electrons to higher electronic energy states, but transitions in vibrational energy states.

Each molecule has its own unique signatures. Therefore, IR spectroscopy may be employed to identify the type of bond between two or more atoms and consequently identify functional groups. IR spectroscopy is also widely used to characterize the attachment of organic ligands to organic/inorganic NPs and surfaces. Because IR spectroscopy is quantitative, the number of a type of bond may be determined. Virtually all organic compounds absorb IR radiation, but inorganic materials are less commonly characterized, as heavy atoms show vibrational transitions in the far IR region, with some having extremely broad peaks that hampers the identification of the functional groups. Furthermore, the peak intensities of some ionic inorganic compounds may be too weak to be measured.\(^{134,135}\) The covalent bonds that hold molecules together are neither stiff nor rigid, but rather they vibrate at specific frequencies corresponding to their vibrational energy levels. The vibration frequencies depend on several factors including bond strength and the atomic mass. The bonds can be modified in different ways, in a similar manner to a spring. Chemical bonds may be contorted in six different ways:

- Stretching (both symmetrical and asymmetrical)
- Scissoring
- Rocking
- Wagging
• Twisting

Absorption of IR radiation causes the bond to move from the lowest vibrational state to the next highest, and the energy associated with absorbed IR radiation is converted into these types of motions.\textsuperscript{136–138} Other rotational motions usually accompany these individual vibrational motions. These combinations lead to absorption bands, not discrete lines, which are commonly observed in the mid IR region.\textsuperscript{138} Weaker bonds require less energy to be absorbed and behave as though the bonds are springs that have different strengths. More complex molecules contain dozens or even hundreds of different possible bond stretches and bending motions, which implies the spectrum may contain dozens or hundreds of absorption lines. This means that the IR absorption spectrum can be its unique fingerprint for identification of a molecule.\textsuperscript{139} The fingerprint region contains wavenumbers between 400 and 1500 cm\textsuperscript{-1}. A diatomic molecule, that has only one bond, can only vibrate in one direction. For a linear molecule (e.g. hydrocarbons) with \(n\) atoms, there are \(3n-5\) vibrational modes. If the molecule is non-linear (such as methane, aromatics etc.), then there will be \(3n-6\) modes. Samples can be prepared in several ways for an IR measurement. For powders, a small amount of the sample is added to KBr, after which this mixture is ground into a fine powder and subsequently compressed into a small, thin, quasi-transparent disc. For liquids, a drop of sample may be sandwiched between two salt plates, such as NaCl, KBr and NaCl are chosen as neither of these compound shows an IR active stretch in the region typically observed for organic and some inorganic molecules.

\subsection{Applications of nanomaterials}

The nanomaterials possessed exceptional, useful chemical, physical and mechanical properties, which can be exploited for a broad spectrum of applications in diverse fields such as:\textsuperscript{140}

\begin{itemize}
  \item Medicine and drug
  \item Electronics
  \item Food
  \item Fuel cells
  \item Solar cells
  \item Batteries
  \item Space
\end{itemize}
1.9.1. Medicine and drug

Researchers are developing customized NPs the size of molecules that can deliver drugs directly to affected cells in human body. When its perfected, this method should greatly reduce the damage treatment such as chemotherapy does to a patient’s healthy cells.

- **Drug delivery:** Nanotechnology in medicine currently being developed involves employing NPs to deliver drugs, heat, light or other substances to specific types of cells (such as cancer cells). Particles are engineered so that they are attracted to affected cells, which allows direct treatment of those cells. This technique reduces damage to healthy cells in the body and allows for earlier detection of disease. For example, NPs that deliver chemotherapeutic drugs directly to cancer cells are under development.

- **Therapy techniques:** In this techniques researchers have developed "nanosponges" that absorb toxins and remove them from the bloodstream. The nanosponges are polymer NPs coated with a red blood cell membrane. The red blood cell membrane allows the nanosponges to travel freely in the bloodstream and attract the toxins.

- **Diagnostic techniques:** Researchers have developed a sensor using carbon nanotubes embedded in a gel; that can be injected under the skin to monitor the level of nitric oxide in the bloodstream. The level of nitric oxide is important because it indicates inflammation, allowing easy monitoring of inflammatory diseases.
1.9.2. Electronics
Nanoelectronics holds some answers for how we might increase the capabilities of electronics devices while we reduce their weight and power consumption. Electrodes made from nanowires that would enable flat panel displays to be flexible as well as thinner than current flat panel displays. Semiconductor nanowires to build transistors and integrated circuits. Transistors built in single atom thick graphene film to enable very high speed transistors.\textsuperscript{141}

1.9.3. Food
Nanotechnology is having an impact on several aspects of food science, from how food is grown to how it is packaged. Companies are developing nanomaterials that will make a difference not only in the taste of food, but also in food safety, and the health benefits that food delivers.
Clay NCs are being used to provide an impermeable barrier to gases such as O\textsubscript{2} or CO\textsubscript{2} in lightweight bottles, cartons and packaging films. Storage bins are being produced with silver NPs embedded in the plastic. The silver NPs kill bacteria from any material that was previously stored in the bins, minimizing health risks from harmful bacteria. ZnO NPs can be incorporated into plastic packaging to block UV rays and provide antibacterial protection, while improving the strength and stability of the plastic film. Nanosensors are being developed that can detect bacteria and other contaminates, such as salmonella, at a packaging plant. This will allow for frequent testing at a much lower cost than sending samples to a lab for analysis. This point-of-packaging testing, if conducted properly, has the potential to dramatically reduce the chance of contaminated food reaching grocery store shelves.

1.9.4. Fuel cells
Nanotechnology is being used to reduce the cost of catalysts used in fuel cells to produce hydrogen ions from fuel such as methanol and to improve the efficiency of membranes used in fuel cells to separate hydrogen ions from other gases such as oxygen. Catalysts are used with fuels such as hydrogen or methanol to produce hydrogen ions. Platinum, which is very expensive, is the catalyst typically used in this process. Companies are using NPs of platinum to reduce the amount of platinum needed, or using NPs of other materials to replace platinum entirely and thereby lower
costs. Fuel cells contain membranes that allow hydrogen ions to pass through the cell but do not allow other atoms or ions, such as oxygen, to pass through. Companies are using nanotechnology to create more efficient membranes; this will allow them to build lighter weight and longer lasting fuel cells. Fuel cells that can replace batteries in electric cars are also under development. Hydrogen is the fuel most researchers propose for use in fuel cell powered cars. In addition to the improvements to catalysts and membranes, it is necessary to develop a lightweight and safe hydrogen fuel tank to hold the fuel and build a network of refueling stations. To build these tanks, researchers are trying to develop lightweight nanomaterials that will absorb the hydrogen and only release it when needed.

1.9.5. Solar cells

Companies have developed nanotech solar cells that can be manufactured at significantly lower cost than conventional solar cells. Researchers at Michigan Technological University have developed a honeycomb like structure of graphene in which the graphene sheets are held apart by lithium carbonate (Li₂CO₃). They have used this “3D graphene” to replace the platinum in a dye sensitized solar cell and achieved 7.8 % conversion of sunlight to electricity. Researchers are studying solar cells made from single molecule thick sheets of graphene and materials such as molybdenum diselenide (MoSe₂). They are predicting that this type of solar cells could produce up to 1000 times as much more power for a given weight of material than conventional solar cells. They have completed computer modeling and are working on building the solar cells.

1.9.6. Batteries

Companies are currently developing batteries using nanomaterials. One such battery will be a good as new after sitting on the shelf for decades. Researchers have demonstrated the use of silicon coated carbon nanotubes for in anodes for Li-ion batteries. They are predicting that the use of silicon can increase the capacity of Li-ion batteries by up to 10 times.

Using nanotechnology in the manufacture of batteries offers the following benefits:

- Reducing the possibility of batteries catching fire by providing less flammable electrode material.
Increasing the available power from a battery and decreasing the time required to recharge a battery. These benefits are achieved by coating the surface of an electrode with NPs. This increases the surface area of the electrode thereby allowing more current to flow between the electrode and the chemicals inside the battery. This technique could increase the efficiency of hybrid vehicles by significantly reducing the weight of the batteries needed to provide adequate power.

Increasing the shelf life of a battery by using nanomaterials to separate liquids in the battery from the solid electrodes when there is no draw on the battery. This separation prevents the low level discharge that occurs in a conventional battery, which increases the shelf life of the battery dramatically.

1.9.7. Space

Nanotechnology may hold the key to making space-flight more practical. Advancements in nanomaterials make lightweight spacecraft and a cable for the space elevator possible. By significantly reducing the amount of rocket fuel required, these advances could lower the cost of reaching orbit and traveling in space.

1.9.8. Better air quality

Nanotechnology can improve the performance of catalysts used to transform vapors escaping from cars or industrial plants into harmless gases. That’s because catalysts made from NPs have a greater surface area to interact with the reacting chemicals than catalysts made from larger particles. The larger surface area allows more chemicals to interact with the catalyst simultaneously, which makes the catalyst more effective.

1.9.9. Cleaner water

Nanotechnology is being used to develop solutions to three very different problems in water quality. One challenge is the removal of industrial wastes, such as a cleaning solvent called TCE (trichloroethylene), from groundwater. NPs can be used to convert the contaminating chemical through a chemical reaction to make it harmless. Studies have shown that this method can be used successfully to reach contaminates dispersed in underground ponds and at much lower cost than methods which require pumping the water out of the ground for treatment.


1.9.10. Chemical sensors

Nanotechnology can enable sensors to detect very small amounts of chemical vapors. Various types of detecting elements, such as carbon nanotubes, ZnO nanowires or Pd NPs can be used in nanotechnology based sensors. Because of the small size of nanotubes, nanowires, or NPs, a few gas molecules are sufficient to change the electrical properties of the sensing elements. This allows the detection of a very low concentration of chemical vapors.

1.9.11. Fabric

Making composite fabric with nano-sized particles or fibers allows improvement of fabric properties without a significant increase in weight, thickness, or stiffness as might have been the case with previously used techniques.

1.9.12. Enzyme immobilization

The definition of immobilization is to fix something preventing it from moving. In enzyme technology, this term refers to the physical confinement or localization in a certain region of space with retention of their catalytic activities. By immobilizing an enzyme, some structural changes can occur, thereby changing its properties and activity to some extent. Immobilized proteins and enzymes have also been found useful in many bioanalytical and biomedical applications. These applications include the use of immobilized antibodies or antigens in bioaffinity chromatography, immobilized receptors or ligands in the study of their interactions and immobilized cells in biosensors. Irreversible immobilizations involve the covalent attachment of the enzyme to the surface, or the entrapment within a matrix or micro-encapsulation. For the covalent attachment, the support must have a reactive group (i.e. amine, carboxylate, thiol) or must be activated in order to perform the immobilization. The immobilization procedure gives rise to a stable amide bond between the support and the enzyme (i.e. carbodiimide). When the support is aminated, a cross-linker such as glutaraldehyde, is commonly used, forming imine bonds between the biomolecule and the support.

1.9.12.1. Salient features of enzyme immobilization

- The enzyme phase is called as carrier phase which is water insoluble but hydrophilic porous polymeric matrix, e.g. agarose, cellulose, etc.
The enzyme phase may be in the form of fine particulate, membranous, or microcapsule.

The enzyme in turn may be bound to another enzyme via cross linking.

A special module is produced employing immobilization techniques through which fluid can pass easily, transforming substrate into product and at the same time facilitating the easy removal of catalyst from the product as it leaves the reactor.

The support or carrier utilized in immobilization technique is not stable at particular pH, ionic strength or solvent conditions. Hence, may be disrupted or dissolved releasing the enzyme component after the reaction.

1.9.12.2. Advantages of enzyme immobilization

♦ Multiple or repetitive use of a single batch of enzymes.
♦ Immobilized enzymes are usually more stable.
♦ Ability to stop the reaction rapidly by removing the enzyme from the reaction solution.
♦ Product is not contaminated with the enzyme.
♦ Easy separation of the enzyme from the product.
♦ Allows development of a multi-enzyme reaction system.
♦ Reduces effluent disposal problems.

1.9.12.3. Disadvantages of enzyme immobilization

♦ It gives rise to an additional bearing on cost.
♦ It invariably affects the stability and activity of enzymes.
♦ The technique may not prove to be of any advantage when one of the substrate is found to be insoluble.
♦ Certain immobilization protocols offer serious problems with respect to the diffusion of the substrate to have an access to the enzyme.

1.9.12.4. Technique of enzyme immobilization

■ Carrier binding
  ▪ Physical adsorption
  ▪ Covalent bonding
  ▪ Ionic bonding
■ Cross linking
■ Entrapment
- Occlusion within a cross linked gel
- Microencapsulation

- **Carrier binding**

  - **Physical adsorption:** This method is based on the physical adsorption of enzyme protein on the surface of water-insoluble carriers. Examples of suitable adsorbents are ion-exchange matrices, porous carbon, clay, hydrous metal oxides, glasses and polymeric aromatic resins.

  The bond between the enzyme and carrier molecule may be ionic, covalent, hydrogen, coordinated covalent or even combination of any of these. Immobilization can be brought about by coupling an enzyme either to external or internal surface of the carrier. The external surface binding method is advantageous as it does not involve conditions like pore diffusion. The disadvantages, however, include exposure of enzymes to microbial attack, physical abrasion of enzyme due to turbulence associated with the bulk solution. The major disadvantage of the internal immobilization method is the pore diffusion.

  - **Advantages of adsorption**
    - Little or no confirmation change of the enzyme.
    - Simple and cheap.
    - No reagents are required.
    - Wide applicability and capable of high enzyme loading.

  - **Disadvantages of adsorption**
    - Desorption of the enzyme protein resulting from changes in temperature, pH and ionic strength.
    - Slow method.

- **Covalent bonding:** Covalent binding is the most widely used method for immobilizing enzymes. The covalent bond between enzyme and a support matrix forms a stable complex. The functional group present on enzyme, through which a covalent bond with support could be established, should be non-essential for enzymatic activity.
The protein functional groups which could be utilized in covalent coupling include:

- Amino group
- Carboxylic group
- Phenol ring
- Indole group

**Advantages of covalent coupling**

- The strength of binding is very strong, so, leakage of enzyme from the support is absent or very little.
- This is a simple, mild and often successful method of wide applicability.

**Disadvantages of covalent coupling**

- Enzymes are chemically modified and so many are denatured during immobilization.
- Only small amounts of enzymes may be immobilized (about 0.02 grams per gram of matrix).

**Cross linking**

This method is based on the formation of covalent bonds between the enzyme molecules, by means of multifunctional reagents, leading to three dimensional cross linked aggregates.

The most common reagent used for cross-linking is glutaraldehyde.

**Advantages of cross linking**

- Very little desorption (enzyme strongly bound).
- Best used in conjunction with other methods.

**Disadvantages of cross linking**

- Cross linking may cause significant changes in the active site.

**Entrapment**

In entrapment, the enzymes or cells are not directly attached to the support surface, but simply trapped inside the polymer matrix. Entrapment is carried out by mixing the biocatalyst into a monomer solution, followed by polymerization initiated by a change in temperature or by a chemical reaction.
Polymers like polyacrylamide, collagen, cellulose acetate, calcium alginate or carrageenan etc. are used as the matrices.

➢ **Advantages of entrapment**
  - Loss of enzyme activity upon immobilization is minimized.

➢ **Disadvantages of entrapment**
  - The enzyme can leak into the surrounding medium.
  - Another problem is the mass transfer resistance to substrates and products.
  - Substrate cannot diffuse deep into the gel matrix.

❖ **Occlusion within a cross linked gel**: In this entrapment method, a highly cross-linked gel is formed as a result of the polymerization which has a fine “wire mesh” structure and can more effectively hold smaller enzymes in its cages. Amounts in excess of 1 g of enzyme per gram of gel or fibre may be entrapped. Some synthetic polymers such as polyarylamide, polyvinylalcohol, etc. and natural polymer (starch) have been used to immobilize enzymes using this technique.

❖ **Microencapsulation**: This entrapment involves the formation of spherical particle called as “microcapsule” in which a liquid or suspension of biocatalyst is enclosed within a semi permeable polymeric membrane.

### 1.9.12.5. Applications of enzyme immobilization

- **Industrial production**: Industrial production of antibiotics, beverages, amino acids etc. uses immobilized enzymes or whole cells.

- **Biomedical applications**: Immobilized enzymes are widely used in the diagnosis and treatment of many diseases. Immobilized enzymes can be used to overcome inborn metabolic disorders by the supply of immobilized enzymes. Immobilization techniques are effectively used in drug delivery systems especially to oncogenic sites.

- **Food industry**: Enzymes like pectinases and cellulases immobilized on suitable carriers are successfully used in the production of jams, jellies and syrups from fruits and vegetables.

- **Research**: A research activity extensively uses many enzymes. The use of immobilized enzyme allow researcher to increase the efficiency of different
enzymes such as Horse Radish Peroxidase (HRP) in blotting experiments and
different proteases for cell or organelle lysis.

- Production of biodiesel: From vegetable oils.
- Waste water management: Treatment of sewage and industrial effluents.
- Textile industry: Scouring, biopolishing and desizing of fabrics.
- Detergent industry: Immobilization of lipase enzyme for effective dirt removal
  from cloths.

1.9.13. Protein-nanoparticle interaction

Nanoparticles and other nanomaterials are increasingly considered for use in
biomedical applications such as imaging, drug delivery, and hyperthermic therapies.
Thus, understanding the interaction of nanomaterials with biological systems becomes
key for their safe and efficient application. It is increasingly being accepted that the
surface of nanomaterials would be covered by protein corona upon their entrance to the
biological medium. The biological medium will then see the achieved modified surface
of nanomaterials, and therefore further cellular/tissue responses depend on the
composition of corona.\textsuperscript{157}

In a biological medium, NPs may interact with biomolecules such as proteins, nucleic
acids, lipids and even biological metabolites due to their nano-size and large surface-
to-mass ratio. Of particular importance is the adsorption of proteins on the NP surface.
The formation of NP-protein complexes is commonly referred to as the nanoparticle-
protein corona (NP-PC). A number of consequences of protein adsorption on the NP
surface can be speculated. Overall, the NP-PC can influence the biological reactivity of
the NP.\textsuperscript{158,159} The protein corona may influence cellular uptake, inflammation,
accumulation, degradation and clearance of the NPs. Furthermore, the NP surface can
induce conformational changes in adsorbed protein molecules which may affect the
overall bio-reactivity of the NP. In depth understanding of such interactions can be
directed towards generating bio-compatible nanomaterials with controlled surface
characteristics in a biological environment.\textsuperscript{160,161} Adsorption of proteins at the nano-bio
interface is aided by several forces such as hydrogen bonds, solvation forces, Van der
Waals interactions, \textit{etc}. The overall NP-PC formation is a multifactorial process and
not only depends on the characteristics of the NP, but also on the interacting proteins
and the medium. Specific association and dissociation rates for each protein decide
longevity of their interaction with the NP surface. Irreversible (or at least long-term) binding of proteins on the NP leads to formation of a “hard corona” whereas quick reversible binding of proteins that have faster exchange rates defines a “soft corona”.162–166

1.9.14. Catalysis

During the twentieth century, chemists have made considerable achievements in heterogeneous catalysis,167–178 whereas homogeneous catalysis179–182 progressed after world war-II (hydroformylation) and especially since the early 1970s (hydrogenation). Heterogeneous catalysis that benefits from easy removal of catalyst materials and possible use of high temperatures suffered for a long time from lack of selectivity and understanding of the mechanistic aspects that are indispensable for parameter improvements. Homogeneous catalysis is very efficient and selective, and is used in a few industrial processes, but it suffers from the impossibility of removal of the catalyst from the reaction media and its limited thermal stability. Green catalysis aspects now obviously require that environmentally friendly (for example phosphine-free) catalysts be designed for easy removal from the reaction media and recycling many times with very high efficiency. These demanding conditions bring a new research impetus for catalyst development at the interface between homogeneous and heterogeneous catalysis, gathering the sophisticated fulfilment of all the constraints that were far from being fully taken into account by the pioneers and even the specialists in each catalytic discipline in the former decades. Yet the considerable knowledge gained from the past research in homogeneous, heterogeneous, supported and biphasic catalysis, including also studies in non-classical conditions (solvent-free, aqueous, use of ionic liquids, fluorine chemistry, micro-emulsions, micelles, reverse micelles, vesicles, surfactants, aerogels). In this context, the use of transition-metal NPs in catalysis183,184 is crucial as they mimic metal surface activation and catalysis at the nanoscale and thereby bring selectivity and efficiency to heterogeneous catalysis. Transition-metal NPs are clusters containing from a few tens to several thousand metal atoms, stabilized by ligands, surfactants, polymers or dendrimers protecting their surfaces. Their sizes vary between the order of one nanometer to several tens or hundreds of nanometers, but the most active in catalysis are only one or a few nanometers in diameter, *i.e.* they contain a few tens to a few hundred atoms only.185–187 This approach is also relevant to homogeneous
catalysis, because there is a full continuum between small metal clusters and large metal clusters, the latter being also called colloids, sols or NPs. NPs are also well soluble in classic solvents (unlike metal chips in heterogeneous catalysis) and can often be handled and even characterized as molecular compounds by spectroscopic techniques that are well known to molecular chemists, such as $^1$H and multinuclear NMR, IR and UV-Vis spectroscopy and cyclic voltammetry. Molecular mechanisms involving the NP surfaces in catalytic reactions are much more difficult to elucidate, however, than those of monometallic catalysts, and the size and shape of the NP catalysts are key aspects of the catalytic steps. NPs themselves can also be used as catalysts in homogeneous systems or alternatively they can be heterogenized by fixation onto a heterogeneous support such as silica, alumina, other oxides or carbon, for example carbon nanotubes. Thus, the field of nanoparticle catalysis involves both the homogeneous and heterogeneous catalysis communities, and these catalysts are sometimes therefore called “semi-heterogeneous”.

1.9.15. Photocatalysis

Photocatalysis is a branch of science which employs catalyst that is utilized for speeding up chemical reactions that requires or engages light. A photocatalyst is defined as a material that is capable of absorbing light, producing electron-hole pairs that enable chemical transformations of the reaction participants and regenerate its chemical composition after each cycle of such interactions. There are two types of photocatalytic reactions.

- Homogeneous photocatalysis
- Heterogeneous photocatalysis

The significant features of the photocatalytic system are the desired band gap, suitable morphology, high surface area, stability and reusability. Metal oxides such as oxides of vanadium, chromium, titanium, zinc, tin and cerium having these characteristics follow similar primary photocatalytic processes such as light absorption, which induces a charge separation process with the formation of positive holes that are able to oxidize organic substrates. In this process, a metal oxide is activated with either UV light, visible light or a combination of both, and photoexcited electrons are promoted from the valence band to the conduction band, forming an electron/hole pair ($e^-/h^+$). The photogenerated pair ($e^-/h^+$) is able to reduce and/or oxidize a
compound adsorbed on the photocatalyst surface. The photocatalytic activity of metal oxide comes from two sources: (i) generation of ‘OH radicals by oxidation of OH\(^-\) anions, (ii) generation of O\(_2\)\(^-\) radicals by reduction of O\(_2\). Both the radicals and anions can react with pollutants to degrade or otherwise transform them to lesser harmful byproducts (Fig. 1.25).\(^{196,198,200}\)

\[\text{Figure 1.25. The mechanism of photocatalysis.}\]

There are many catalysts reported in the literature for this exciting process. Among these metal oxides (TiO\(_2\), ZnO, SnO\(_2\) and CeO\(_2\)), which are abundant in nature, have also been extensively used as photocatalysts, particularly as heterogeneous photocatalyst since several decades.\(^{196,200,201}\) This is because of their biocompatibility, exceptional stability in a variety of conditions and capability to generate charge carriers when stimulated with required amount of light energy. The favourable combination of electronic structure, light absorption properties, charge transport characteristics and excited lifetimes of metal oxides has made it possible for their application as photocatalyst.\(^{195–198,200,202}\) Heterogeneous photocatalysis employing metal oxides such as TiO\(_2\), ZnO, SnO\(_2\) and CeO\(_2\) has proved its efficiency in degrading a wide range of distinct pollutants into biodegradable compounds and eventually mineralizing them to harmless CO\(_2\) and H\(_2\)O.\(^{203–209}\)
1.10. Aim of the present work and thesis outlines

The goal of the present work was to study physical properties for different types of nanomaterials with different synthetic routes (i.e. sol-gel auto-combustion and co-precipitation) and various characterization techniques. In the present work the structural analysis, morphology and magnetic properties of selected system will be studied using XRD, SEM, EDS, VSM, HR-TEM and FT-IR spectroscopy. First chapter is dealing with the general introduction of nanomaterials, second chapter is concerned with the synthesis of Ni-Co nanoferrites by sol-gel auto-combustion method to study their structural, optical, morphological and magnetic properties and to provide magnetic support for immobilization of yeast alcohol dehydrogenase enzyme (YADH), and third chapter is accredited to the synthesis of Co doped SnO\textsubscript{2} NPs by co-precipitation technique to determine their particle size, structure, morphology, elemental composition and its interaction with human serum albumin (HSA) via various spectroscopic techniques and their antimicrobial and photocatalytic activities while as the fourth chapter is associated with the synthesis of silica supported NiO nanocomposite via sol-gel auto-combustion method to investigate their particle size, structure, morphology and elemental composition and its catalytic performance for one-pot multicomponent synthesis of benzodiazepine derivatives under microwave irradiation. The fifth chapter is concerned with the synthesis of silica coated Ni-Co ferrite nanocomposites via sol-gel auto-combustion method to study their structural, optical and morphological properties and immobilization of glucose oxidase enzyme as a magnetic support.
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