Chapter 1

A brief account of nanoparticles and related optoelectronic properties

Abstract

In this chapter, a brief account of the history, property and significant applications of nanoparticles (NPs) in modern life has been described. A concise description about the synthesis of NPs using various methods is presented here. In this part, the synthetic routes in colloidal methods are focused. The current status, conditions and advances of the micelle and microemulsion templates based methods are depicted schematically. Different characterization methods that are usually followed by experimental setups are described precisely. In parallel with the experimental methods the theoretical approach from the perspective of electronic structure theory has been described also for proper understanding of the properties of NPs. In this connection, the synergy among the two aspects (experimental and theoretical) has been given a special attention which is further elaborated to the field of plasmonics as its relevant application.

1. Introduction

1.1 Brief account of nanoparticles:

The rapid progress and significant advances of nanoparticles (NPs) is one of the major scientific developments and breakthroughs that are expected to affect our daily lives in near future. The past decades have witnessed new industrial revolutions, based on nanotechnologies. Nanoscience is a multidisciplinary field ranging from photonics to microelectronics, from biochemistry to medical science in global research activity. Overall, the whole science community is indebted to Nanoscience and technology for plenty of new scientific discoveries. On this account it is essential to define the basic object of the whole nanoscience i.e. nanoparticles. Nanoparticle is as an object with dimension between 1 to 100 nanometers that behaves as an entire entity in terms of its unique properties. The prefix 'nano' comes from the Greek word *νᾶνος* which means literally dwarf or very small according to the Latin nomenclature *nanus*. Nanometer scale is one billionth of a meter or 10 ^{9} meter. Nanoparticle is further known as ultra fine particles (UFP) below 100nm size range. [1, 2] The diverse nature of this field is not only attributed to size, but also depends on wide range of shapes. According to internal structure, it can be homogeneous material throughout the whole structure or hetero-structured with two materials or more. In materials the nanoparticles can be made of metals, semiconductors or dielectrics.

The history of nanoparticle from ancient times to middle ages has been summarized by Daniel and Astruc.[3] The earliest existence of preparation and application of nanoparticles date back to Byzantine Empire 4 century AD and has been reported.[4] In order to generate coloring and glittering effects on the surface of glass and pottery, or on the church windows, artisan created and utilized gold or copper nanoparticles.[5, 6] These applications can be found in the glass windows of many Gothic European Cathedrals, among which the León Cathedral (in Spain) is one of the masterpieces. Since the middle ages, the soluble gold has been very well-known owing to its curative powers of various diseases like heart and venereal diseases, dysentery, epilepsy, and tumors. In 1618, the publication of Francisci Antonii depicted the details about the formation of colloidal gold sols and their medical uses, including successful practical cases. In 1728, an article based on gold by Helcher[7] explored that the stability of drinkable gold preparation enhanced noticeably when boiled starch was used. Once more in same decade, Fuhlame explored the process of dying silk with colloidal gold (1794).[8] In 1818, Jeremias Benjamin Richter, explained the origin of colors shown by various gold preparations. Finally in 1857, the pioneering work of Michael Faraday[9] had explored the luminous optical nature of colloidal gold which motivated thousands of scientific investigations including synthesis, modifications, properties and applications.

Particles of controlled size within the range 1 to 100 nm acquired intermediate properties between the atomic or molecular entity and the macroscopic bulk materials. This size dependent intrinsic property is the key feature of rapidly extending area of nanoscience and nanotechnology. Therefore it is crucial to find out the origin of these unique properties of nanoparticles. It is observed that two main factors are responsible for nanomaterials to behave significantly differently from bulk materials. The first one is surface effect that is attributed for large surface area of NPs. It smoothly scales the properties of NPs.

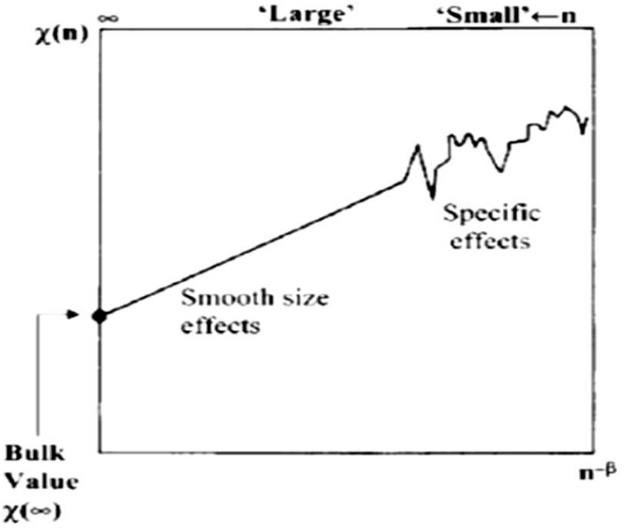


Figure 1.1 **$\chi(n)$** vs. **$n^{-\beta}$** Plots where $\beta = 0$. Small nanoparticles reveal specific size effects, while larger particles are expected to exhibit smooth size dependence, converging to the bulk value.[10]

The fraction of atoms at the surface of the nanomaterials increase compared to the bulk materials. The fraction of atoms on the surface is known as dispersion (*F*) and it measures with surface area divided by volume. Atoms at the surface of a material are loosely bound, while the atoms in the bulk are rigidly attached to the neighboring atoms. Therefore with increase of fraction of atoms at the surface the mean coordination numbers (number of nearest neighbour) of the particles decrease. The high coordination number of the bulk atoms of a cluster results more cohesive force than the surface atoms.

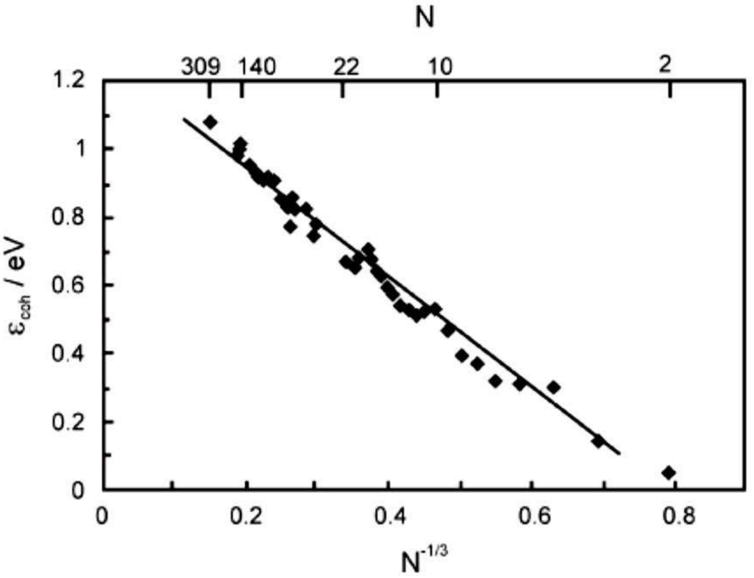
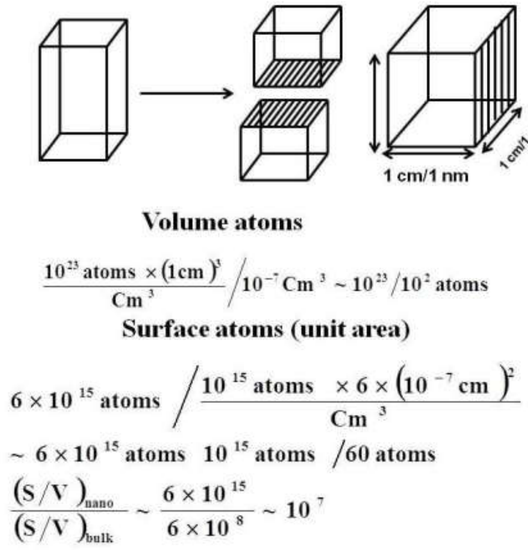


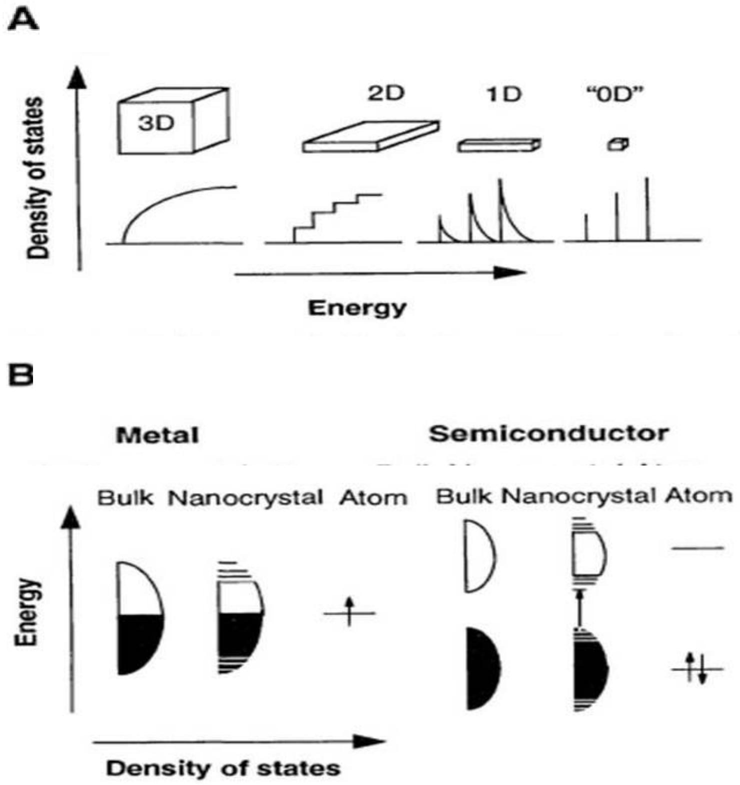
Figure 1.2 Calculated cohesive energies of various size magnesium clusters in their most stable geometry as function of $\mathbf{N^{-1/3}}$.[11]

This results the higher stabilization energy of the bulk atoms than the surface atoms. As a consequence the total surface energy increases along the surface of nanoparticles. When the particles vary from centimeter to nanometer size range the surface energy increases seven order of magnitude.[12]



Scheme 1.1 Two new surfaces have been created by breaking a rectangular solid into two pieces. Multiplication of atoms (10^7) times in nanocrystal as compared to the surface atoms in bulk.[12]

On this account the particles are thermodynamically unstable or metastable. Thus a small nanocrystal with higher surface is chemically more reactive than the bulk. The other one is the quantum effect. The electronic states of any bulk structure are considered as a continuum and are described in terms of their band structure. In the band structure each atom participates with its atomic orbital. With reduce of size of bulk structure the electronic energy levels are no more continuous and become discrete due to confinement of the electron wave function. In nanostructures the electronic states are transferred to band like extended states and are described in terms of density of states (DOS). These bands are proportional to the number of atoms in an ensemble. The average electronic energy level spacing of successive quantum levels are known as Kubo gap. The energy required to cross the Kubo gap for electronic excitation is known as thermal energy.[13] There has been significant difference between metal and semiconductor nanocrystals relative to their band structures and accompanied electronic transitions. In each case, the density of states is discrete at the band edges. The Fermi energy level lies in the center of the band in metal. Consequently with reduction of size the energy levels can easily exceeds the thermal energy at room temperatures. In contrast in semiconductors, the Fermi level lies in between two bands. As a result the relevant Kubo gaps remain large even at small sizes. Therefore at a given temperature, the transition occurs for relatively large size in case of semiconductors NPs.[14] The band width or the band gap can be tuned by manipulating the size of the nanoclusters. This discreteness is of fundamental importance for the properties of nanoparticles.



Scheme 1.2 **(A)** Density of states in one band of a semiconductor as a function of dimension. **(B)** Schematic illustration of the density of states in metal and semiconductor clusters.[14]

Most of the properties such as intrinsic conductivity, optical transitions or electronic transitions, depends on it. Furthermore the qualitative change in the electronic structure arising due to quantum confinement also bestows unusual catalytic and magnetic properties on these particles, totally different from the bulk. Some of the properties are illustrated with few examples from recent literature.

1.1.1 Conductivity:

The collective motion of electrons in a bulk metal obeys Ohm's law $U = RI$, where U is the applied voltage, R is the resistance of the material, and I is the current.[15] As the band becomes discrete levels, the above Ohm's law is no longer valid. An idealized "staircase", current-voltage characteristic for an ideal quantum dot occurs if the Coulomb energy of the quantum dot is compensated by an external voltage of $U = \pm ne/(2C)$. The step height I corresponds to current [e/(RC)], and the width U corresponds to voltage [e/(2C)].

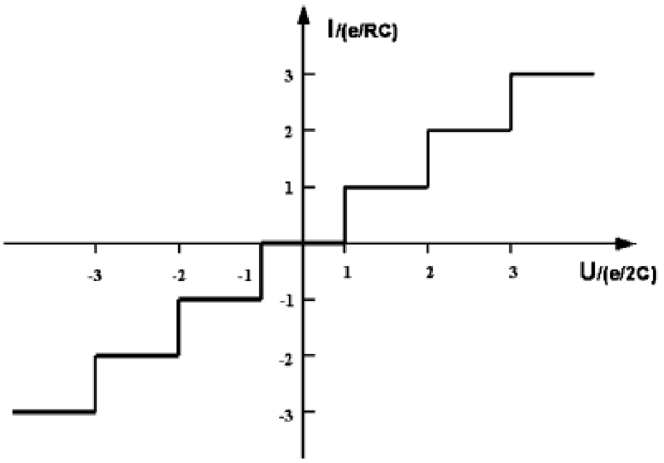
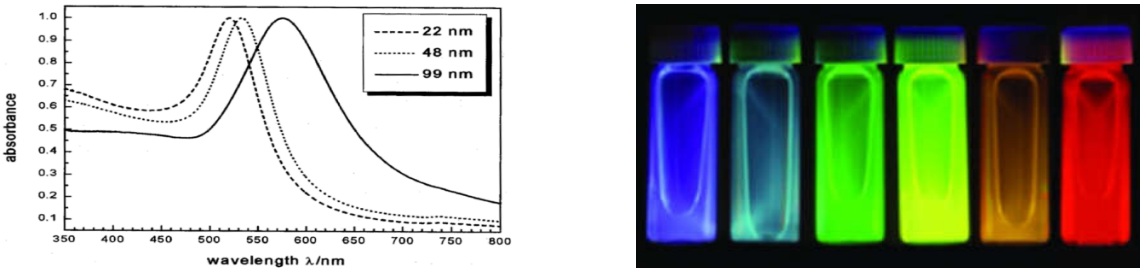


Figure 1.3 *I-U* characteristic of ideal single electron transport, where Coulomb blocked is shown as the step function.[16]

1.1.2 Optical Properties:

The optical properties of nanomaterials are significantly different from bulk materials. The electronic absorption spectra of metal NPs in the visible region are dominated by the plasmon bands. This surface plasmon excitations impart characteristic colors to the colloidal metal sols.[16] On the other hand, the optical absorption peak of a semiconductor NP shifts to a short wavelength, due to an increased band gap. Besides this, semiconductor NPs also exhibit interesting luminescence behavior. The luminescence is generally dependent on the size of the NP and the surface structures.



(a) (b)

Figure 1.4 (a) Absorption spectra of colloidal metal NPs with different size **(b)** Luminescent colloidal semiconduntor NPs.[17]

1.1.3 Magnetic Property:

The dependence of magnetism on the size of NPs is well-established. For magnetic NPs, the maximum magnetization is known as saturation magnetization.[18] The typical magnetization curve for different magnetic systems shows the characteristic curves associated with saturation magnetization (Ms, maximum induced magnetization), remanent magnetization (Mr, induced magnetization remaining after an applied field is removed),and coercivity (H,the intencity of an external coercive field needed to force the magnetizationto zero).

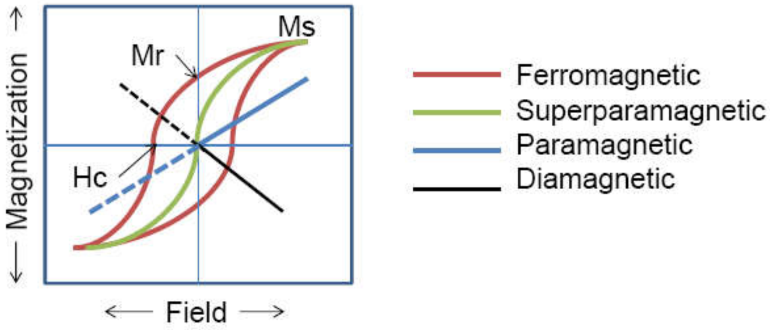


Figure 1.5 Magnetic behavior under an applied field.[18]

With increase of size against coercivity, a critical size r_c appears. This point corresponds to the transition from single domain to multi domain regime. The other transition point is r_0, where superparamagnetic regime transforms to single domain regime. These changes are attributed to the variation Ms with size.

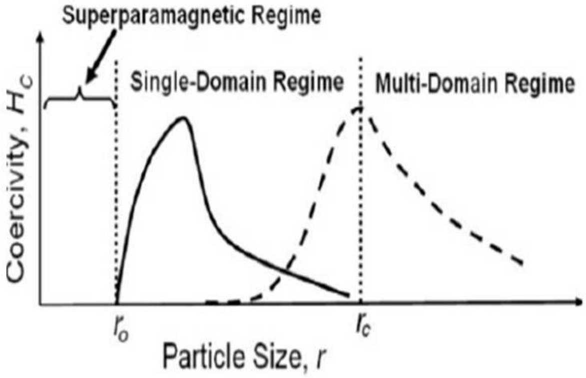


Figure 1.6 Transition from superparamagnetic to single to multi-domain regimes.[18]

1.1.4 Chemical Reactivity:

The surface area of nanocrystals increases markedly with the decrease in size. Thus a small metal nanocrystal of 1 nm diameter will have ~ 100% of its atoms on the surface. A small nanocrystal with a high surface area would be expected to be more reactive than bulk. Furthermore, the qualitative change in the electronic structure arising due to quantum confinement in small nanocrystals will also bestow unusual catalytic properties on these particles, totally different from those of the bulk metals.

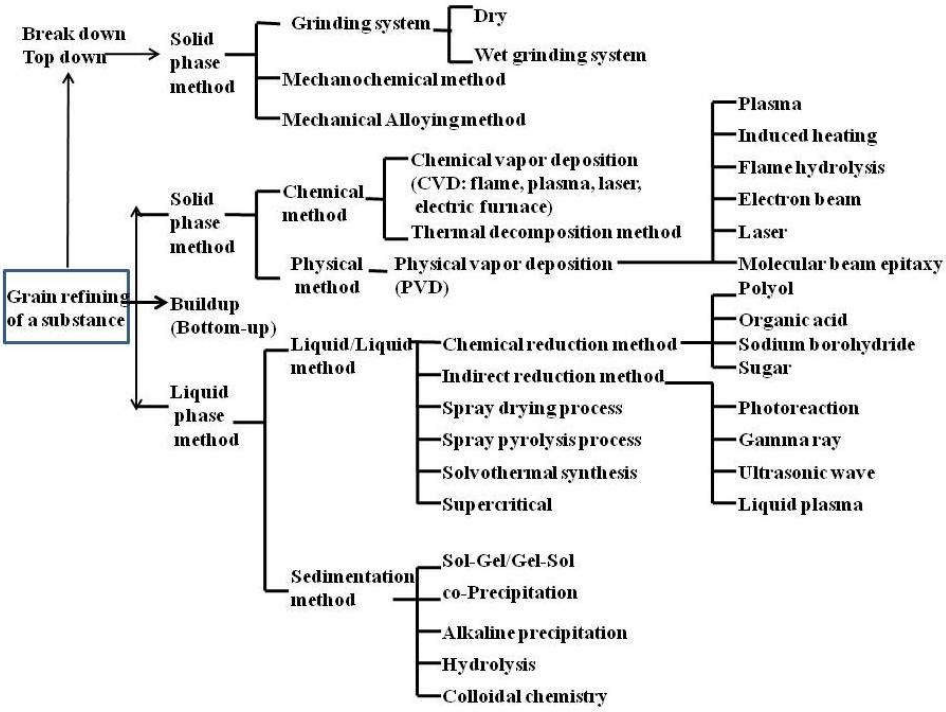
1.2 Applications of NPs:

It is necessary to outline the importance of nanomaterials in our daily life. The unique properties of nanomaterials enable them to be applied in a wide range of fields, from medical applications to environmental sciences. Nanotechnology has enormous prospects in the applied field of nano-electronics. The fabrication of nano-scopic electronic circuit elements serve faster micro processors (or better said nano-processors) that make computation at far higher speed.[19] The use of nanocrystalline materials can greatly enhance resolution of a television or a monitor with reduction of pixel size.[20] Disks and tapes constructed with engineered nanomaterials can store huge amounts of information. The future aspects of inclusion of spintronics or spinelectronics (intrinsic spin of the electron and its associated magnetic moment) will drastically increase the capability of data storage.[21] The standard redox potential for Ag/Ag^+ is 0.799 V. [22] This magnitude decrease with decrease of size. At a very fine state of dispersion, the sign of potential may change to –ve. Thus, a metal or its salt in fine dimensions can function towards both oxidation and reduction processes based on its degree of fineness. Due to having higher capacity and better cycle life than the conventional electrodes, nanomaterials can be used cathodes and anodes in lithium-ion batteries.[23] Nanomaterials can be used as sensors to detect parameters like electrical resistivity, magnetic permeability, chemical activity, thermal conductivity, capacitance etc. In electron microscopy it is used as probe tips.[24] Not only electronics, in biomedical applications also nanoparticles have the leading role in early diagnosis and treatment of diseases. Nanofiber scaffolds are employed to regenerate central nervous system cells and possible other organs.[25] Nanoparticles with biochemical activity can be assessed as coatings for surgical masks owing to antimicrobial properties.[26,27] One of the most pronounced biomedical applications is the development of nanoparticles based drug delivery systems. The other medical applications including nucleic acid sequence and protein detection, medical imaging, smart nanophase extractors, nasal vaccination and many more are influenced by unique properties of nanoparticles.[28-33] Nanotechnology can be applied in pollution remediations also.

For enhanced chemical activity, nanomaterials are used as catalysts to react with toxic gases in catalytic converters. In cosmetic industry, titanium dioxide and zinc oxide are currently used in sunscreens to absorb and reflect UV light.[34] Nanoparticles are used for very thin coatings.[35] Besides these, semiconductor nanocrystals (NCs) or quantum dots (QDs) are well known for their special physico-chemical and optical properties including size tunable absorption, emission and stability against photo bleaching which allows novel applications in bio-analytical research.[36-38] These properties offer significant advances in the field of biosensing platforms. The colloid QDS are the excellent source of fluorescence and very stable in nature, that improves sensitivity and extended lifetime in their use as optical labels.[39] Iron oxide NCs are very good contrast agent for Magnetic Resonance Imaging (MRI) and gold NCs are competent for Computed Tomography (CT).[40] The size controlled luminescence allow colloidal QDs to be used in light emitting devices (LEDs) and modify LEDs to wider color gamut, larger color rendering inde.[41, 42, 43] Furthermore due to the broad absorption band the thin films of colloidal QDs have high absorption cross section. This characteristic makes the QDs suitable for solar cells.[43, 44] The colloidal QDs perform as photo catalysis also in the solar energy conversion. The thorough studies on structural properties of nanomaterials reveal that the comprising elements from the periodic groups II–VI, III–V, or IV–VI, *i.e.*, the transition elements have been most widely used as precursors. Detail analysis have been carried out on their morphology and size dependent properties such as physical, optical, chemical and so forth. During the last two decades, the fabrication of semiconductor nanomaterials has received tremendous attention due to their applications in biodiagnosis, bioimaging, photonics, optoelectronics and sensors.[16]

1.1.5 Synthesis of nanoparticles

Owing to possess a huge surface energy, the greatest challenge in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the NPs from growth in size by reducing the overall surface energy. Studies of Nanotechnology and nanoscience provide opportunities for the developments of new nano-sized materials, including those for medical applications. Pharmaceutical NPs are biodegradable. The largest activity in the field of nanoscience is to optimize certain specific properties such as size (diameter, volume, length) granulometric distribution, surface properties, purity, and surface coverage, ease of manipulation or performance in a mass production approach. Self-assembly of these NPs by different techniques either from the bottom-up techniques (assembling particles synthesized in solution) or from the top-down techniques (different lithographic methods), is being pursued. Thus the major goal of nanotechnology is to manipulate atoms and molecules in a user defined and repeatable manner to build objects with certain desired properties. Various preparation techniques for nanoparticles (nanomaterials) are summarized in Scheme.1.3



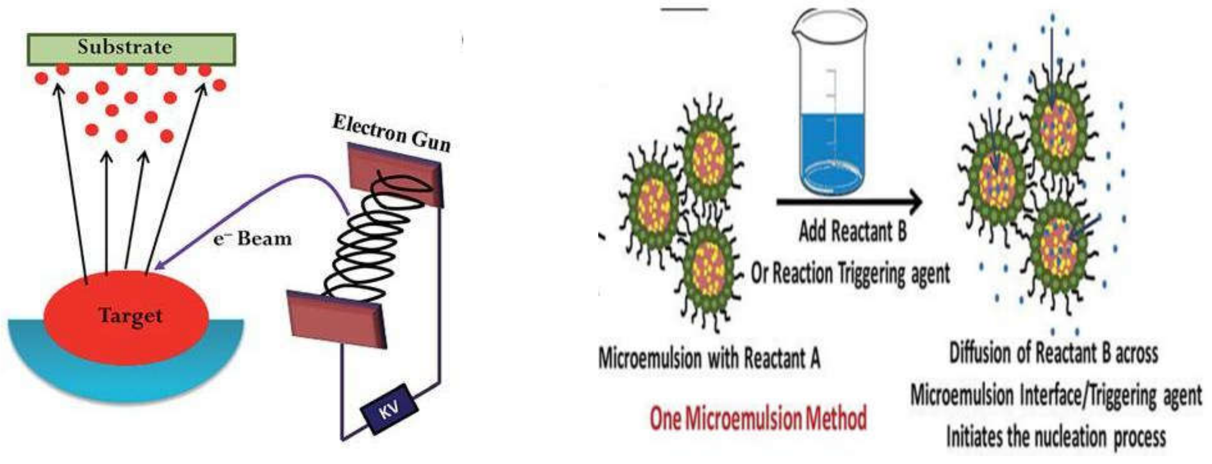
Scheme 1.3 Typical synthetic methods for nanoparticles for the top-down and bottom-up approaches.

1.3.1 Top-down Method:

The synthesis of nanoparticles can be generally categorized into the bottom-up and top-down methods. The first is breakdown or (top-down) method by which a large structure is gradually scaled down until nanometric dimensions are reached. This method consists of the common approaches like etching, precision, engineering lithography and grinding.

1.3.2 Bottom-up methods:

In the bottom-up approach Nanoparticles are constructed atom by atom or molecule by molecule. The bottom-up approach is also divided into solid phase methods and liquid phase methods. Depending on synthetic route nanoparticles are divided in “Colloidal” and “Epitaxial” QDs.



(a) **(b)**

Scheme 1.4 Schematic representation of **(a)** epitaxial route (pulsed laser deposition) and **(b)** colloidal route (one microemulsion method) of synthesis of NPs.

Epitaxial NPs are synthesized in vapor phase methods such as chemical vapor deposition method (CVD) and physical vapor deposition method (PVD). The former involves a chemical reaction, whereas the later uses cooling of the evaporated material. These methods require relatively high energy input, ultra-high vacuum environments and extremely high purity chemical precursors. Moreover, epitaxial technique does not offer size and shape selection and provide relatively large lateral dimensions (>10 nm).[45] In contrast, liquid phase methods have been the major synthetic routes of Nanoparticles from the past decades. This method is further subdivided into liquid/liquid methods and sedimentation methods. Several methods such as chemical reduction method, spray drying, spray pyrolysis, solvothermal synthesis and the supercritical method are engaged in this method.[16] The sedimentation method is also carried out by some well known processes like sol-gel, co-precipitation, alkaline precipitation, hydrolysis and colloidal methods.[16] Among all these methods colloidal method is a solution based approach which is relatively inexpensive, facile, scalable and less sensitive to impurities. The size and shape may be well controlled in colloidal synthesis. In addition the surface of colloidal NCs can be easily functionalized with molecules while epitaxial NCs are not available for their substrate-bound nature. Keeping all these features in consideration, the colloidal method is designated as the leading route of NP synthesis by experimentalists. Regarding this, a brief account of the colloidal method is dicussed in the next section.

1.3.2.1 Colloidal method:

Through the past decade, chemists have come to appreciate that, the low cost processing and simplicity of this preparative route of nanocrystal has been made impressive progress toward the tailored synthesis of colloidal nanocrystal. Among all the chemical processes, colloidal methods have been established as very versatile and reproducible method. In recent times, several processes have been developed in colloidal methods. These processes are distinct in nature by different dispersion media such as microemulsions, micelles. These methods are superior to many others as because of their ability to deliver homogeneous and monodispersed NPs of variety of metals,[46,47] oxides,[48] and chalchogens.[49] The reaction takes place in aqueous cores of the reverse micelles or microemulsions which are dispersed in an organic solvent and are stabilized by capping agents. The dimensions of these aqueous cores are in the nanoregimes and are being referred to as nanoreactors. [50] The fundamental mechanism of formation of NPs takes place in the nanoreactors through several steps. The consequential steps are displayed in the following Figure 1.7. The first step is the fast reaction of the precursor ions. This reaction would lead to presence of high amount of single atoms in solution. In the second step these atoms tend to bind each other and form small clusters. In the third or final step the clusters undergo aggregation and coalescence process until the particles becomes sufficiently stable.[51]

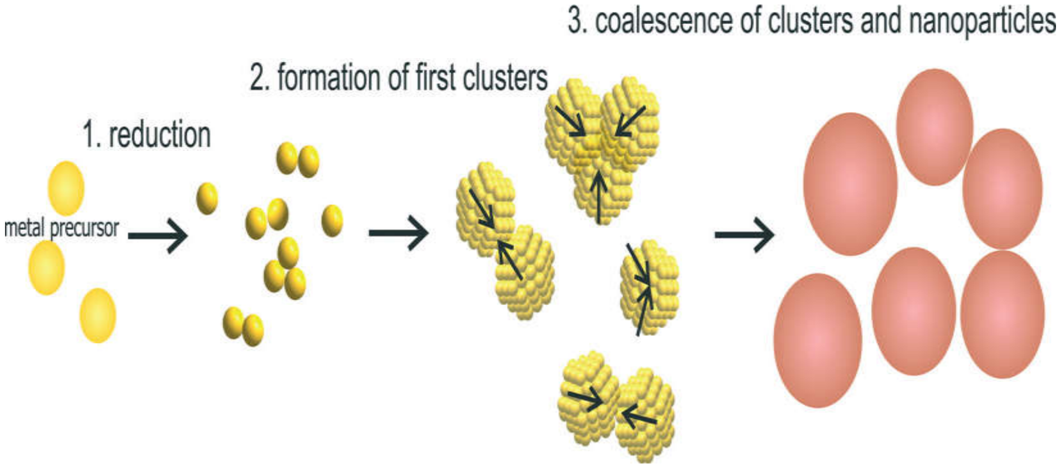


Figure 1.7 Mechanistic steps of nanoparticle formation.[51]

The final step where aggregation and coalescence or dissolution occurs simultaneously is known as Ostwald Repening.[51] This Ostwald Repening has significant influence on the NP stabilization in the dispersing medium. The continuous growth after nucleation and subsequent precipitation of NPs from the dispersion medium can be prevented by using surface stabilizing agents. The surface stabilizing agents used are of various types for different mediums. In case of NP synthesis based on polymer matrix PVA (poly(vinyl alcohol)), PVP (poly (vinylpyrrolidone)) etc.[16] Organic ligands are effective to suppress the NP aggregation via phosphine or thiol functionalities.[52] For colloidal medium, the surfactants and cosurfactants are used to inhibit Ostwad Repening. Surfactants are surface-active and microstructure-forming molecules with strong chemical dipoles. They can be ionic (cationic or anionic), nonionic and zwitterionic. The most common cationic surfactants are cetyltrimethylammonium bromide (CTAB), di-n-didodecyldimethylammoniumbromide (DDAB) etc., while bis(2-ethylhexyl)sulfosuccinate (AOT), sodium dodecyl benzene sulfonate (SDBS), lauryl sodium sulfate (SDS) are the well known anionic surfactants.[36] The nonionic surfactants are Triton X-100, sorbitan monooleate, Span 80, nonylphenyl ether (NP-5) or polyoxyethylene (9) nonylphenyl ether (NP-9).[50] Again co-surfactants are generally used in conjugation with surfactants for the sake of increase of stability of microemulsions and thus facilitate the formation. The medium chain alcohols are the well known co-surfactants.[53]

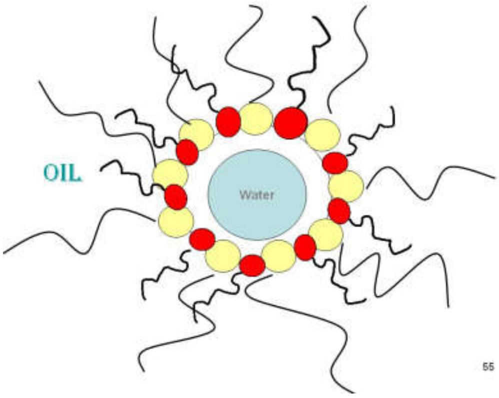


Figure 1.8 Surfactants (long chain) and cosurfactants (short chain alkanols) are essential for stable microemulsion

Surfactants are significantly important in the context of colloidal route of NP synthesis. They can form various shaped micelles, reverse micelles, microemulsion, reverse microemulsions etc.[46] Normal micelles are oil droplets in water. The size of the droplets is controlled by the length of surfactant alkyl chain. The hydrophobic hydrocarbon chains of the surfactants are oriented toward the core of the micelles while the hydrophilic groups are directed to the surface of the micelles. Above CMC the surfactant molecules aggregate and form micelles. Normal micelles can solubilize more oil in the hydrocarbon core. It is possible to tailor the size of the droplets in the range 1- 100 nm approximately by varying the concentration of the dispersed phase and the surfactant (ω).[47] On the other hand, reverse micelles are water in oil microemulsions in which polar head groups of surfactant molecules are attracted by aqueous core. It consists of nanometer sized monodispersed water droplets. (Figure 1.9) The reverse micelle formed at a particular ratio of aqueous phase to the surfactant (ω) leads to uniform sized nanoreactors with an aqueous core of 5-10 nm (Luisi et al., 1986).[48] The use of reverse micelles is valid for both water and oil - soluble substrates to convert into products.

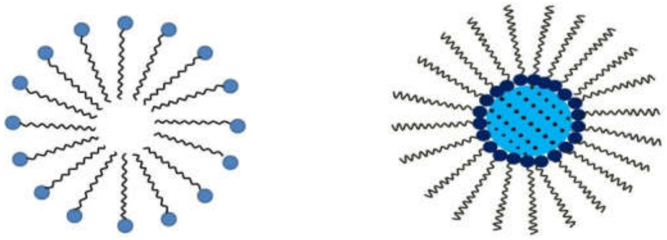


Figure 1.9 Schematic representations of micelle and reverse micelles

In contrast, microemulsions or μ-emulsions are isotropic mixtures of oil, water and surfactants with greater thermodynamic stability than ordinary emulsions. Microemulsions do not require high energy inputs or sear conditions for their formation. The droplet sizes of microemulsions in the dispersed phase are generally in the magnitude of ~ 10 nm.[47] The normal microemulsions are oil-in-water microemulsions, In this system the oil droplets are surrounded by surfactant (or possibly co-surfactant) film. Conversely the reverse microemulsions are water-in-oil system, where water droplets are captured by surfactant layers. The schematic representations are displayed in the following Figure 1.10.

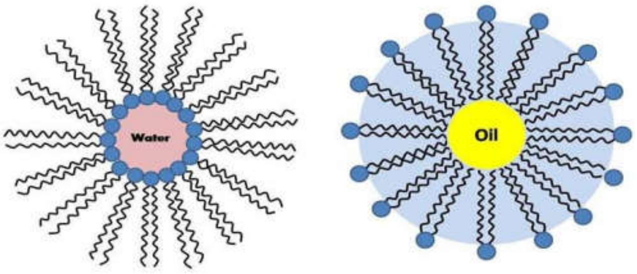


Figure 1.10 Schematic representation of reverse and normal microemulsions

Synthesis of NPs in different colloidal mediums is of considerable importance. At the core of the colloidal systems various reactions such as reduction, precipitation, hydrolysis, polymerization etc can take place during the very first stage of mechanism.[16] Based on these reactions versatile methods have been proposed under colloidal condition. Among such methods reduction method is one of the most common methods to prepare metal NPs.[57] The precipitation method is usually used to prepare NPs of metal salts like halides,[58] sulphates,[59] carbonates.[60]

Monodisperse Nanoparticles can be synthesized by careful control of the kinetics of the precipitation. The pH and the concentration of the reactants and ions are the major factors that influence the precipitation process.[16] Based on the solubility of almost all inorganic substances in water at elevated temperatures and pressure the hydrothermal method is used to synthesis zeolite/molecular sieve crystals.[16] The method also depends on the subsequent crystallization of the dissolved material from the fluid. The NPs of metal oxides are usually produced by hydrolysis method. The organic NPs are prepared through polymerization method. The advantage of this method is fast polymerization rates and high molar mass of polymers. On the other hand, the high weight ratio of surfactant to polymer is the key drawback. The schematic representations of some of the methods are displayed in the following.

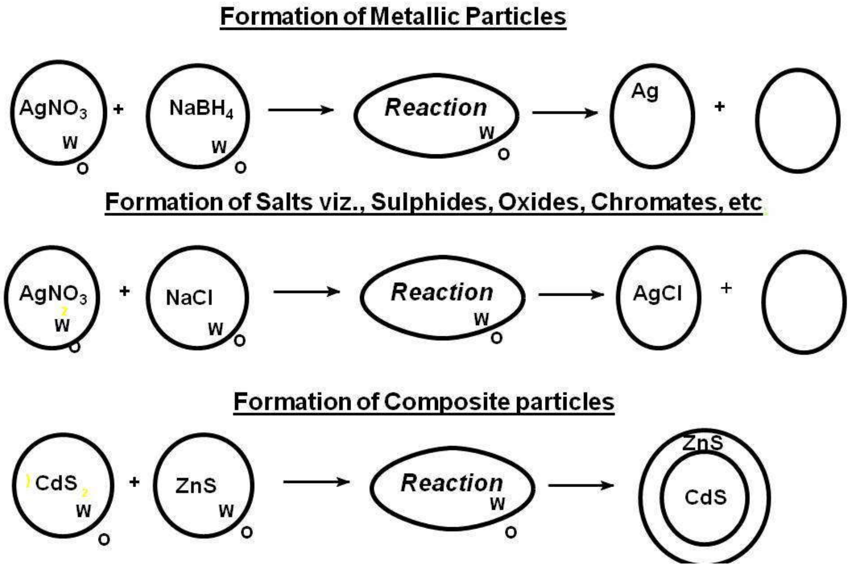


Figure 1.11 Various methods to synthesis different NPs

Although various synthetic methods have been summarized in the above discussion, there are some features to consider that are common to all the methods. For synthesis of nanoparticles the following conditions to fulfill:

- Control of particle size, size distribution, shape, crystal structure and composition distribution
- Improvement of the purity of nanoparticles (lower impurities)
- Control of aggregation
- Stabilization of physical properties, structures and reactants
- Higher reproducibility
- Higher mass production, scale-up and lower costs

It is widely accepted that the route of microemulsion or Micellar medium have a pivotal role in generalizing the fabrication of nanoparticles in a precisely controlled manner. The above conditions are found to be best fitted in these routes. These routes are discussed in the following section.

1.3.2.2 Synthetic routes:

A wide range of NPs can be prepared using micellar route. Reverse micelle is an established platform for synthesis of metal NPs like platinum, palladium, rhodium, iridium through reduction of their salt solutions by appropriate reducing agents.[61] Colloidal NPs of Ag and Au are also reported to be synthesized in water/cyclohexane/PEGDE or PEGDE/water/n-hexane reverse micelles, when $AgNO_3$ and $HAuCl_4$ is reduced by $NaBH_4$.[62] Other metal NPs such as Cu, Ni, Fe and further for metal alloys like Fe-Ni, Cu-Au, Co-Ni etc reverse micelle is an effective synthetic tool.[63] Besides metal NPs colloidal semiconductor NPs like CdS, PbS, CuS, Cu_2S, CdSe etc. may be synthesized in reverse micelles using AOT, Triton surfactants. [64] By the hydrolysis of metal alkoxide, metal oxide NPs such as ZrO_2, TiO_2, SiO_2, GeO_2, Fe_2O_3 etc.[65, 66] Reverse micelle is also an important medium for synthesizing the composite NPs. The composite NPs such as CdS-ZnS, CdS-Ag2S, CdSe-ZnS, CdSe-ZnSe have been successfully synthesize.[69] Magnetic NPs i.e. Fe_3O_4, γ-Fe_2O_3,[45, 67] different ferrite materials like (Mn, Zn) Fe_2O_4, (Ni, Zn) Fe_2O_4, $ZnFeO_4$, and $BaFe_{12}O_{19}$ [68] can be synthesized using normal micelle. On the other hand, synthesis of NPs in microemulsion is of considerable importance too due to its lower energy requirements, potential as drug delivery in pharmaceutical applications and in the petrochemical industries. In general there are two methods for nanoparticle synthesis using microemulsion techniques (Osseo-Asare and Arriagada, 1990).[69] The first method is the one microemulsion method, that includes "energy triggering" and the "one microemulsion plus reactant" method. The next method is the two micro emulsion methods. In microemulsion templates various methods can be carried like micelles. In addition to the synthesized NPs in reverse micelles, an extended range of NPs can be achieved from microemulsions. Metal salts like metal halides (AgCl, AgBr), metal sulphates and metal carbonates ($BaCO_3$, $CaCO_3$, $SrCO_3$) are reported to be obtained using W/O microemulsions.[70,71] Besides inorganic nanomaterials organic NPs such as Cholesterol, Retinol, Rhodiarome, Rhovanil [72] can be prepared by polymerization using oil in water microemulsion. This leads to hydrophobic NPs (10 – 40 nm) dispersed in water.[73] Finally, it will be incomplete if it is not acknowledged about the synthesis of NPs of pharmaceutical interest. Solid NPs of nimesulide, amoxicillin have been reported to be obtained from using water in oil microemulsion templates.[74] A scale up of the synthetic route in microemulsion is presented in the following description.

1.3.2.3 Mechanistic steps:

Reverse micelles as well as microemulsions are dynamic in nature. These methods rely on fusion-fission events between the nanodroplets. Due to Brownian motion, micelles frequently collide and coalesce to form dimmers, which may exchange contents, then break apart again. [55] Any inorganic precursors encapsulated inside the micelles will become mixed. As the chemical reaction has taken place at the nanodroplets, critical number of molecules is produced (N_{crit}). This results the nuclei formation and furthermore leads to the formation of nanoparticles. In some cases, where reaction rates are very rapid, the overall reaction rate is governed by the intermicellar exchange rate. Thus the inter micellar exchange rate plays a significant role in the nanoparticle formation.- Although the formation process involves diffusion, collision, exchange, reaction nucleation, and growth of nuclei, yet again the time scale analysis of these processes leads to different models. The following figure (Figure 1.12) shows, as the reaction proceeds, the growth initially take place at the interface and then the core of the micelle developes. The reverse micelles form the encounter pair (EP) which changes to fused diameter (FD) after collision. The surface tension of the FD becomes very high due to large surface area and it is unable to sustain its geometry. The FD breaks down into two stable smaller droplets containing the precipitated material.

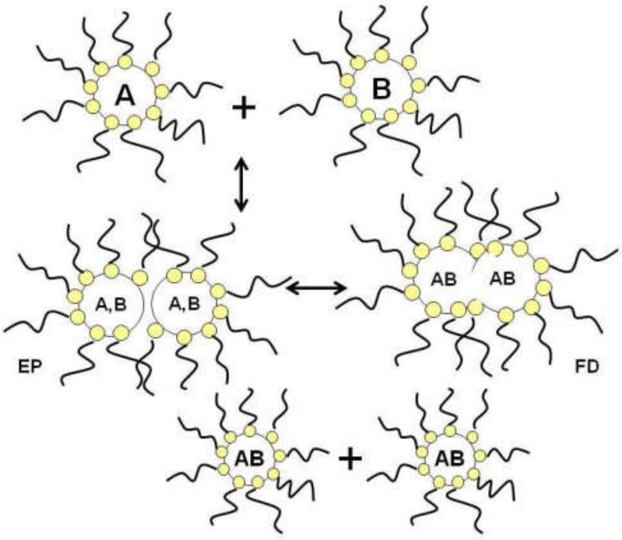


Figure 1.12 Schematic representation of steps of formation of NPs in reverse micelle templates

According to Nagy (1989), [75] all the reactions and nucleations are completed initially and the remaining non nucleated micelles contribute to the growth of the already formed nuclei in the case of the single-micro emulsion method. Natarajan et al. (1996)[76] extended this model by considering fusion-fission mechanisms for the intermicellar exchange process. This leads to nuclei formation in micelles having atoms greater than the critical nucleation number and also subsequent growth of the nucleus. Bandyopadhyaya et al. (1997)[77] explored a model to describe the formation of $CaCO_3$ nanoparticles considering finite rates for the nucleation and diffusion of gas into a micelle.

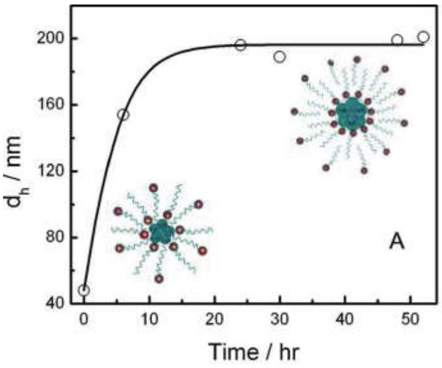


Figure 1.13 Growth of AgBr NPs in CTAB colloidal dispersion. [78]

The product obtained after the reaction is homogeneous. The main advantage of using this methodology is that the morphology of the product can also be controlled as the surfactant aggregates form a variety of structures which are used as templates. The size of the core can also be controlled by changing ω ([water/surfactant]).

1.4 Characterizations of nanoparticles:

Several methods have been applied detecting, measuring and characterizing nanoparticles. The experimental characterization techniques are UV-Visible absroption /emission, FTIR, XRD, Raman, TEM/SEM, EDXA, DLS, AFM, calorimetry.

1.4.1 Optical absorption:

This is a very effective method based on the well-known phenomenon of light absorption by a sample. It can be used to probe the size of the nanoparticles through their optical absorption spectra.[79] Using optical absorption spectroscopy band gap energy of nano materials can be estimated by several proposed methods. The information obtained on the band gap energy is extremely useful to evaluate the dispersion and local structure of the Nanoparticles.[80]

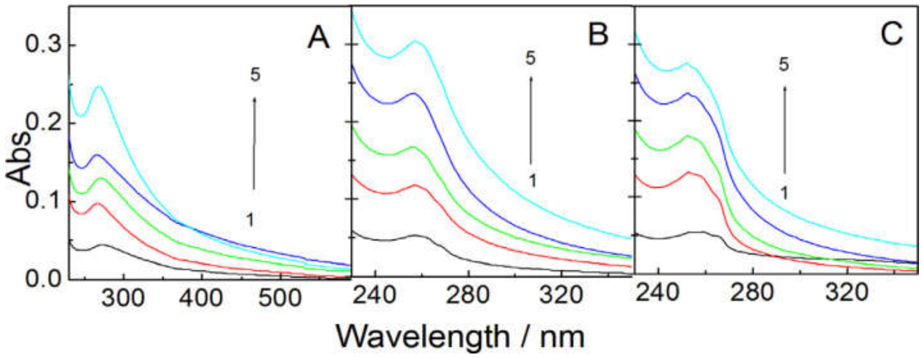


Figure 1.14 Absorption spectra of surfactant stabilized silver chloride NPs.[81]

1.4.2 Emission spectra:

Emission spectroscopy is a spectroscopic technique that examines the wavelength of photons emitted by atoms or molecules due to their transition from an excited state to lower energy state. The characteristic set of discrete wavelengths corresponds to the electronic structure of each element. Analyzing the wavelengths the elemental composition of a sample can be determined.

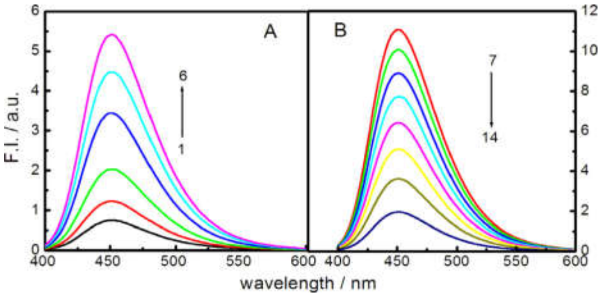


Figure 1.15 (**A**) Absorption and (**B**) emission spectra of 7-HC in presence of Ludox®.[82]

1.4.3 Fourier transform infrared spectroscopy (FTIR):

In nanotechnology the FTIR spectroscopy can effectively be used to measure the particle formation.[83] Owing to high surface to volume ratio nanoparticles exhibit distinguished features compared to bulk form in the IR spectrum.[84] The number of atoms that constitute the surface can influence the vibrational spectra of Nanoparticles.[85] FTIR spectroscopy is widely applied to identify the elements and the phase of the elements. For example, when water is in liquid phase, the fundamental vibrational modes are at 3219 (ν_1), 1645 (ν_2) and 3405(ν_3) cm^{-1} whereas in vapor phase the infrared modes appear at 3652 (ν_1), 1595 (ν_2) and 7765 (ν_3) cm^{-1}.[86] It is found that width and intensity of peaks in an IR spectrum have explicit dependence on the particle size. As particle size increases, the width of the peak decreases and intensity increases.

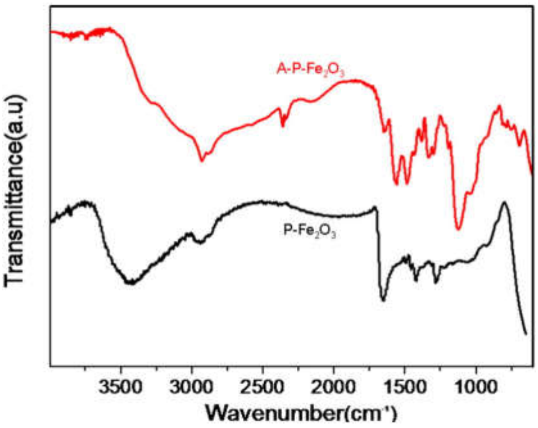


Figure 1.16 FTIR spectra of Fe_3O_2 NPs.[87]

1.4.4 X-Ray Diffraction (XRD):

XRD can be used to explore the structure of single crystal as well as polycrystalline materials. X-rays are electromagnetic radiation with a very shorter wavelength (few Angstrom). When an incident X-ray beam encounters a crystal lattice, general scattering occurs. Diffraction occurs when scattering in a certain direction is in phase with scattered rays from other atomic planes. The diffraction follows Bragg's law or equation. X-ray diffraction data generally provide information about crystallinity, orientation of the crystallites and phase composition in semi crystalline polymers (Figure 1.17). According to the Debye-Shcerrer formula crystallite size the D_{hkl} for a sample can be determined.[88]

$$D_{hkl} = \frac{0.9\lambda}{\beta Cos\theta} \tag{1.1}$$

Where β is the full width at half maxima (FWHM) of XRD lines, λ is the wavelength and θ is the half diffraction angle of 2θ. The use of XRD is often compared to the microscopy techniques. With the aid of molecular modeling X-ray diffraction instrumentation can be used to determine the structure of crystalline polymer.

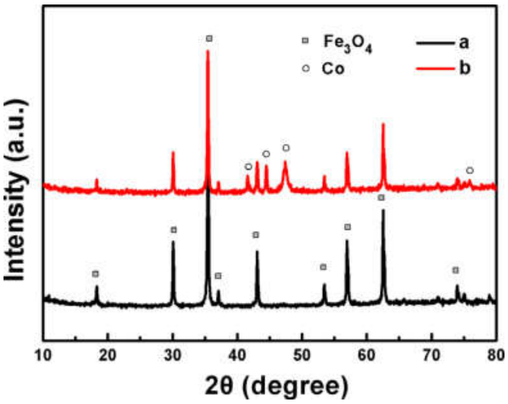


Figure 1.17 XRD patterns of Co and Fe_3O_4 nanoparticles.[89]

1.4.5. Raman spectra:

Raman spectroscopy is useful for providing the information about the chemical bonds in molecules and regarding symmetry. From the fingerprint analysis a molecule can be identified. The incident laser light interacts with the molecular vibrations, phonons or other excitations in the systems. Hence the energy of the laser photons are shifted up and down. This shift in energy gives the information about the vibrational modes of the system.

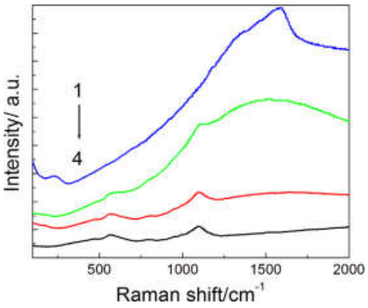


Figure 1.18 Raman spectra of surfactant stabilized AgCl NPs in aqueous media.[81]

1.4.6 Microscopic analysis:

Optical microscopes are generally used for observing micron level materials with reasonable resolution. Nanoparticles are generally characterized by their size, morphology and surface charge, using such advanced microscopic techniques as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Electron microscopy techniques are very useful in ascertaining the overall shape of polymeric nanoparticles. Basic principles and applications of all these imaging techniques used in nanotechnology research are described below.

1.4.6.1 Scanning Electron Microscopy (SEM):

By scanning the sample surface with a high energy beam of electrons Scanning electron microscopy (SEM) provides morphological examination with direct visualization (Figure 1.19). The scanning electron microscope creates the magnified images by using electrons instead of light waves in conventional method. The SEM can produce high resolution image up to 1-5 nm size in its primary detection mode. The surface characteristics of the sample are obtained from the secondary electrons emitted from the sample surface.

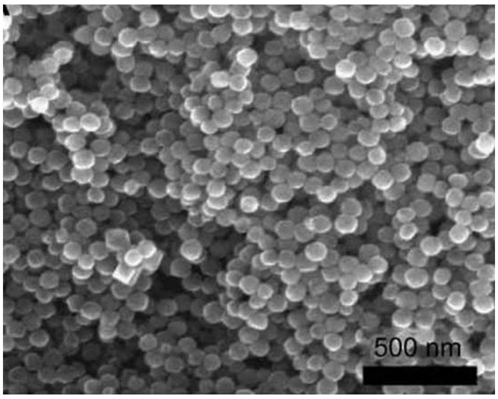


Figure 1.19 SEM image of monodispersed superparamagnetic single-crystal magnetite NPs with mesoporous structure.[90]

1.4.6.2 Transmission electron microscope:

TEM is a microscopy technique that operates on different principle than SEM, yet it often brings same type of data. The beam of electrons is transmitted through an ultra thin specimen and interacts as passes through the sample. The nanoparticle dispersion is deposited onto support grids or films. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen (Figure 1.20). The TEM is used widely both in

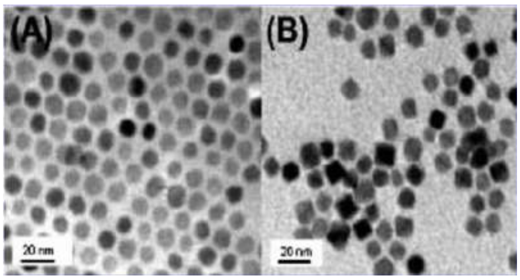


Figure 1.20 Tranmission electron microscopy image of Fe_3O_4 NPs.[91]

High resolution transmission electron microscopy allows the imaging of the crystallographic structure of a sample at an atomic scale. For image formation by HRTEM, absorption by the sample occurs and the contrast arises due to interference in the image plane of the electron wave with itself. This is an essential technique to explore nanoscale properties of crystalline material due to high resolution. At the small scale, individual atom and crystalline defects can be imaged. A typical HRTEM image of nanomaterials is shown in the following Figure 1.21.

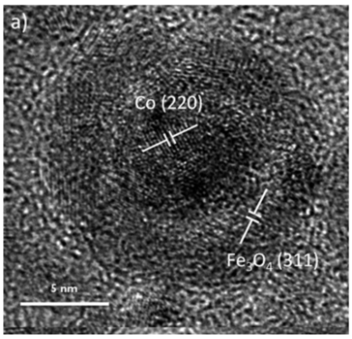


Figure 1.21 HRTEM image showing fringes in the core and shell of a particle.[92]

1.4.6.3 Atomic force microscopy:

Atomic force microscopy (AFM) offers ultra-high resolution in particle size measurement. It is ideal for quantitatively measuring the nanometerscale surface roughness and for visualizing the surface nano texture. The prime advantage of AFM is its ability to explore the nanostructures, properties of surfaces. AFM provides the most accurate description of size and size distribution and requires no mathematical treatment. The use of this new tool is of importance in fundamental and practical research and development for a variety of applications.

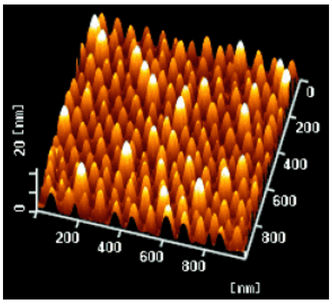


Figure 1.22 AFM image of the transferred films of Au nanoparticles-PMMA hybrids.[93]

1.4.7. Energy Dispersive X-ray Analysis (EDX):

The estimation of surface elements with their proportion at different position including overall mapping of the sample can be achieved by Energy Dispersive X-ray Analysis. This technique is done in conjunction with SEM. An electron beam with energy range of 10 – 20 keV (Figure 1.23) strikes the surface of a conducting sample. This causes X-rays to be emitted from the material and provide the image of each element at the surface of the sample [87]

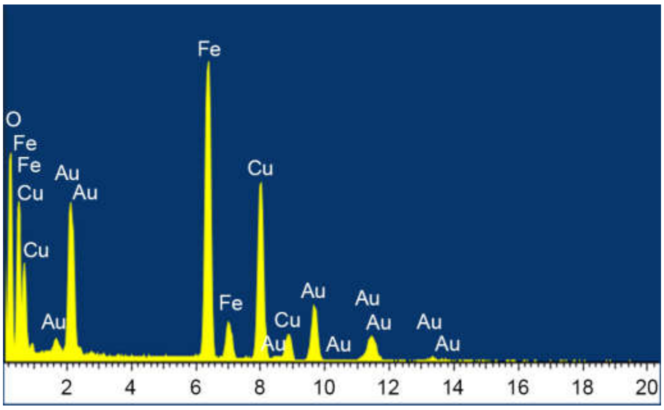


Figure 1.23 EDX spectrum Nanoparticle grafted on Dendritic α-Fe_2O_3.[94]

1.4.8. Particle size analysis

1.4.8.1 Dynamic light scattering measurement

There are different techniques for measurement of particle size and its distribution (PSD). Currently the most popular method of determining particle size is photon-correlation spectroscopy (PCS) or Dynamic Light Scattering (DLS). It is widely used to determine the size of Brownian nanoparticles in colloidal suspensions. Shining monochromatic light (laser) on to a solution of spherical particles causes a Doppler shift. The change in the wavelength of the incoming light is related to the size of the particle. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size (radius r_k) using the Stokes-Einstein relationship,[95] as shown below:

$$r_k = \frac{kT}{6\pi\eta D} \tag{1.2}$$

Where, k is the Boltzmann's constant; T, the temperature in K; η, the solvent viscosity; and D, the diffusion coefficient.

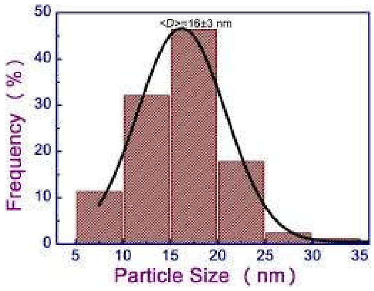


Figure 1.24 The size distribution of recoil-implanted Au NPs.[96]

1.4.8.2 Surface charge:

The nature and intensity of the surface charge of nanoparticles is very essential to determine their interaction with the biological environment as well as their electrostatic interaction with bio active compounds. The colloidal stability is measured through zeta potential of nanoparticles.

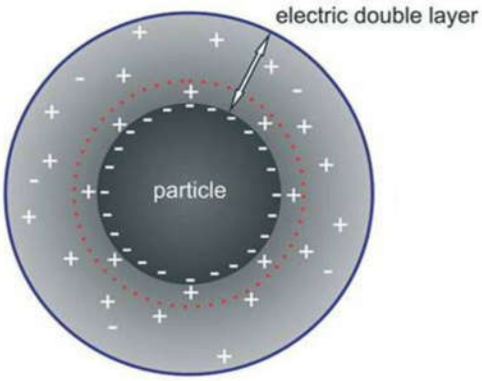


Figure 1.25 Schematic representation of electric double layer formation arround NPs

It corresponds to potential difference between the outer Helmholtz plane and the surface of shear. High zeta potential values, either positive or negative, ensure the stability and prevention of aggregation of the particles. The extent of surface hydrophobicity can then be predicted from the values of zeta potential. The zeta potential can also provide information regarding the nature of material encapsulated within the nanocapsules or coated onto the surface.

Table 1.1 Hydrodynamic diameter and zeta potential data for thermally treated colloidal silica NPs.[82]

Wt % of colloidal silica	**d_h / nm**		**Z.P. / mV**	
	Silica	Silica-7HC	Silica	Silica-7HC
0.004	25	25	-35	-23
0.008	27	27	-35	-29
0.012	25	27	-34	-33
0.016	-	26	-	-35
0.02	-	28	-	-35

1.4.8.3 Hydrophobicity:

Surface hydrophobicity is measured by several techniques such as hydrophobic interaction chromatography, biphasic partitioning, adsorption of probes, contact angle measurements etc. X-ray photon correlation spectroscopy allows the identification of specific chemical groups on the surface of the Nanoparticles.

1.5 Basis of Theoretical investigation of optoelectronic properties:

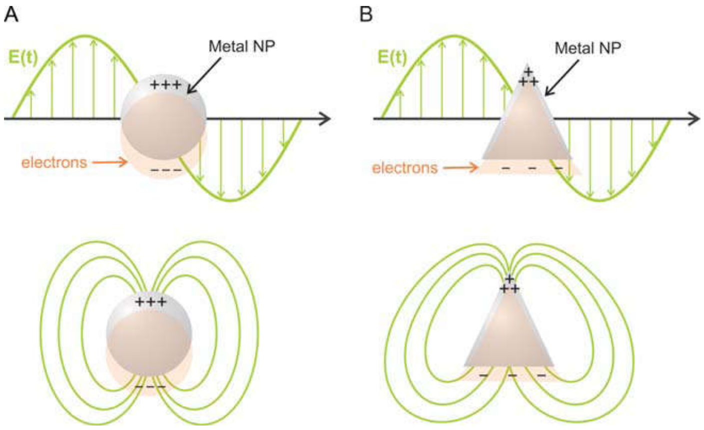
Although characterizing NPs experimentally using various aforementioned techniques is of utmost importance for understanding their properties, yet this approach has some limitations. The underlying mechanisms responsible for the experimental observations cannot be quantified through these methods. Hence it is desirable to find a strategy to compensate the limitations and explore the science in a more definitive fashion. Combining the experimental observations with the theoretical analysis has come out to be the major goal of the present work, spanning a bridge between the gap of experimental and theoretical outcomes. By virtue of evolution of computational modeling and simulations theoretical chemistry has become a powerful tool for understanding and manipulating nanoscale chemical and physical processes for desired applications.

Recently this computational chemistry has been envisaged to predict the structural informations as well as the nature of several properties like mechanical, chemical, electrical, magnetism, toxicity, optical properties of NPs. The simulations carried out in the theoretical studies are based on various techniques, such as quantum mechanical (QM) calculations, force field based methods, classic and *ab initio* quantum dynamics (QD), classical electrodynamics etc. The mechanical property of NPs has been well quantified by applying the theoretical paradigms. The QD approaches have been found to be efficient for modeling the mechanical properties of NPs. Cornwell et al used molecular dynamics to predict the elastic properties of single walled carbon nanotubes.[97] This method is also expanded to several systems like nanotube reinforced compounds,[98-100] graphite/epoxy nanocomposites,[101-103] etc. This nanomechanics-based computer modeling and simulation of mechanical properties of nanocomposites is crucial to predict property relationship in material design and optimization. The enhanced catalytic properties of NPs can be predicted by theoretical paradigms like quantum mechanical (QM) methods and kinetic models.[104,105] Regarding this context the transition metal NPs are considered mainly for superior catalytic properties. Parallel with the MD simulation, the Density functional theory (DFT) calculations are performed to monitor the change of electronic structures during chemical reactions. The structure of single wall Platinum nanotube (SWPtN) has been optimized for providing catalytic activity by coupling MD simulation and DFT calculation.[106] The catalytic activity of Pt and Ir in the process of methane dehydrogenation has been compared by DFT study.[107] This study revealed a easier or barrierless pathway for Ir. As a whole this catalytic property analysis has been found to be supportive for efficient catalyst selection in the design of hydrogen fuel cells theoretically. Computational models for toxicity prediction are important to support risk assessment. The model, such as Quantitative structure-activity relationships (QSARs) had been used by Puzyn *et al* (2011) to describe the cytotoxicity of metal oxide NPs like ZnO, CuO, V_2O_3, Bi_2O_3, Fe_2O_3, Cr_2O_3 etc.[108] Surface reactivity is another measure of toxicity of NPs. The characterization of surface reactivity of gold NPs and nanotoxicological implications of oxygen adsorption at silver surfaces [109] by DFT study provide a rational way to optimize NPs with less toxicity.

The photophysical property of colloidal QDs is the center of attraction among the other properties for multifarious applications in the field of optics and biosensing as depicted in the earlier section. The optical properties are generally characterized by different experimental techniques (like absorption spectroscopy, fluorescence spectroscopy) with evaluation of various parameters (such as band gap, half life time etc). However these techniques are not enough to predetermine their optical nature for the best suited application. The optical properties of NPs are influenced by various geometric parameters of NPs. Hence it is very demanding to find out the appropriate analytical techniques that decides how to tune these parameters to gain optimum efficiency for desired opportunity. In this dearth, the theoretical studies of electronic structures of NPs have been found to be the exclusive way to predict the optoelectronic nature before their fabrication. Once the optoelectronic nature is identified, the extent of manipulation of geometric parameters becomes settled for certain application. Therefore theoretical investigations are the way out of the experimental techniques (i.e. synthesis and characterizations) to make the goals simpler and more precise.

1.5.1 Optoelectronic property and Surface Plasmon Resonance:

The research community has coined the new term ‘plasmonics’ to designate the interactions of light with nano-structured materials. The optical property of NPs is dominated by a unique effect known as plasmonic effect. This effect has a significant contribution to optoelectronic property of NPs due to its tunable features for desired applications. The plasmonic effect includes two main issues. First is the Surface Plasmon Polariton (SPP) that is the charge density wave propagation on the interface of the metal and dielectric. Second is the Localized Surface Plasmon Resonance (LSPR) that is the collective oscillation of electrons of NPs coupled to electromagnetic field. When an electromagnetic field with sufficient frequency, propagates in a bulk material medium, an oscillatory motion of charged particles is coupled to the electromagnetic field oscillations. These coupled mechanical-electromagnetic waves are known as Polaritons. When the wavelength of the electromagnetic field is coupled to the collective motion of the valence electrons of a metal then the resonating electrons form surface plasmon polaritons (SPPs). The generation of plasmon resonance is accompanied by restoring forces exerted by the positive nuclei. When SPPs are confined to NP geometry, the plasmon resonances are defined as localized surface plasmon resonances (LSPRs). In case of semiconductors the charge carriers are electrons or holes. Photoexcitation of semiconductor NPs deals with the transfer of electrons from valence to conduction band creating electron-hole pair. The short lived electron-hole pairs are known as excitons.[110] Excitation and recombination of the excitons are the fundamental factors for LSPR to occur in semiconductor NPs. The LSPR frequencies are highly dependent on density of free charge carriers, the effective mass of charge carriers and the geometric factors. Metal NPs hold very high density of free electrons inherently while the density is low for semiconductor and metal oxide NPs. Hence the LSPR of semiconductor NPs appears in the lower energy or longer wavelength.[14] Besides this, the resonant conditions also depend on the geometric parameters of NPs, i.e. size and shape, and on the polarization of the field with respect to the NP. Each plasmon forms different surface charge distribution (***n***) on the NP. According to the number of opposite surface charges induced, ***2n***th multipole and different plasmon modes like dipole, quadrupole, octupole are formed by varying the resonant conditions. Scheme 1.5 shows schematically the influence of time varying electric field to produce different surface charge and electric field distributions on a NP with the shape of a sphere and a triangular prism.



Scheme 1.5 Schematic representation of the LSPR of NPs with the shape of a sphere (**A**) and a triangular prism (**B**).[111]

1.5.2 Characteristics of LSPR:

For NPs of noble metals and semiconductors, the resonant frequencies lie in the middle of optical spectrum and therefore LSPR interact strongly with light. The following characteristics of LSPRs are essential to their applications:

1.5.2.1 Spectral response:

Each LSPR mode corresponds to a certain eigenfrquency i.e. each mode will interact with a certain color of light. The factors such as the material, size, shape and the dielectric feature of the immediate surroundings of the NP plays a vital role to tune the spectral position of a plasmon mode.

1.5.2.2 Enhanced absorption:

Resonant NPs show strong absorption of light with specific range of wavelength. Thus they are very efficient light absorbers. At the LSPR frequency, the absorption cross-section becomes several times greater than the actual physical cross-section of the NPs.

1.5.2.3 Heat generation:

The energies absorbed by metallic NPs turn into heat due to their inability to decay the absorbed energy in the form of emission. In combination with the enhanced resonant absorption, it is possible to heat different NPs selectively by tuning the color of light to their main LSPR modes.

1.5.2.4 Enhanced Scattering:

The scattering cross-section of a metallic NP is also enhanced at the LSPR frequency. Depending on the size of NP, either scattering or absorption may dominate. For small NP sizes (roughly below 15 nm) absorption dominates while scattering occurs for larger NPs.

1.5.2.5 Specific electric field distribution around the NP:

Each plasmon mode is associated with a specific electric field around the NP with two significant characteristics. First is the exponential decay of the intensity of the electric field from the NP surface to the surrounding medium. Second is the presence of some regions (usually called hotspots) where the field intensity is several time stronger than the incident field.

1.5.2.6 Directionality:

Plasmon modes interact to light with specific angular patterns. Depending on the typical angular pattern of a dipole light, it will be absorbed or scattered with varying efficiencies. Other LSPR modes may show more complex angular patterns. This directional property defines the suitability of metallic NPs for various applications.

1.5.3 Applications of plasmonics

Since 1990s, the research on plasmonics has turned to be more application oriented. The concept of plasmonic waveguide of metal nanowire or nanoslit was introduced and implemented to explore the transmission in sub-wavelength dimensions[112-115] with the basic of SPP. The performance of plasmonic waveguides is still limited by over optical losses. The dimensions of the waveguides are of several hundreds of nanometers which are usually smaller than the wavelength of the light to guide. Therefore they are not categorized as nanoparticles in a strict sense. The situation is also applied for SPP-based photodetectors.[116-118] On the other hand the LSPR of, metal nanoparticles (especially the colloidal ones) smaller than 100 nanometers shows outstanding performance in an expansive space for applications. The radiative decay engineering is one of the significant applications where nanoparticles of noble metals (e.g. gold and silver) are introduced in the vicinity of fluorophores to modify the fluorescence properties of the latter.[119-121] The manipulation is based on several interactions between the nanoparticles and the fluorophores such as excitation enhancement, radiative decay rate alteration, energy transfer, etc, leading to fluorescence peak shift, fluorescence intensity enhancement and quenching, light emission redirection and other effects. This technique is widely manifested in bio- labeling, imaging and detection.[122-124]

Another prevailing application shown by metal nanoparticles (mostly gold nanoparticles) using LSPR is the plasmonic photo thermal therapy.[125-128] Metal nanoparticles absorb electromagnetic radiation of high energy using LSPR and release the energy in the form of heat dissipation, resulting local temperature increase. The enhanced temperature can be precisely tuned to kill cancer cells without effecting health tissues in their certain safe range. The LSPR band is tuned in such a way so that it is within the near infrared window in biological tissues (650 nm to 900nm). This is the key condition for the technique to become promising for *in vivo* therapy. The gold nanorods are more efficient than the spherical gold nanoparticles due to their ability for tunable peak absorption from 550 nm up to 1 μm depending on the aspect ratio of the rods. Other potential applications with metal nanoparticles include nonlinear optics (nano-antennas and second harmonic generation),[129-130] near-field scanning optical microscopy (to overcome the diffraction limit of light),[131] thermal emitters,[132] thermal control in catalysis (another application of the photothermal effect),[133] photovoltaics,[134] metamaterials,[135] etc. Certainly the demand for devices with compact dimension and superior performance for industrial and military application is also the main driving force for the intensive research on this topic.

Apart from metal NPs, the semiconductor NPs or the quantum dots (QDs), have also attracted extensive attention from the scientific (especially the photonics) community and experienced rapid development in the recent years. The quantum confinement of electrons occurs when the size decreases down to nanometer scale, thus alignment of the energy levels can be tuned by altering the size and shape of the QDs like metal NPs. These features allow for abundant freedom in tailoring the optical properties, e.g. absorption and fluorescence, of quantum dots. Therefore quantum dots are widely utilized in optical applications such as photodetectors, [136] photovoltaics,[137] bio-labeling and imaging[138] and light emitting devices.[139]

1.6 Aims and scopes of the present study:

The fabrication of NPs of desired application is one of the challenging deeds in active nano-research. Though plethora of synthetic routes of NP fabrication has been found in literature, yet the colloidal routes are thought to be beneficial for experimentalists due to the user-friendly and candid approach of the methods. Moreover the methods are not only popular for their prudent skill of tuning NPs to preferred size and shape but also functionalizing the surface of NP to make it biocompatible. The quality and the structure of nanoparticles play a pivotal role in determining their functions. Therefore comprehensive characterizations are essential to determine the potentiality of NPs. On this account advanced instrumentations and techniques are required for characterization. In parallel with the experimental techniques theoretical methods have their unique perspectives for precise understanding of the properties that is required for development of new preparation methods for a wide variety of NPs of specific applications. Regarding this, study of electronic structures of NPs to predict their behavior toward various properties is in need. The present study bestows the synergy among the previous aspects that is extended to the field of plasmonics and enlightens the simpler way to achieve the executions. The specific aims and scopes of the present work are highlighted below: Need to do the theoretical investigation.

1. Development of novel properties in reduced dimension render nanoparticles excellent candidates for use in the domain of information technology, medical therapies, environmental science etc. Synthesis of $ZnCrO_4$ NP in microemulsion medium is an effective method to tune its size and shape in various orders. Different parameters such as concentration of surfactants, concentrations of precursors, sonication, temperature etc have pronounced effect in manipulating the size and shapes. Thus it has been found significant study to dig out the excellent route for fabrication of NP with imperative band gap values.

2. Ferromagnetic cobalt and iron oxide NPs offer unique opportunities for cell tracking *in vivo*. Both types of NPs have their individual effectiveness in NP based imaging studies. These NPs have been found to be effectively used as contrast agents in magnetic resonance imaging (MRI). Cobalt NPs show much higher saturation magnetization than the iron oxide NPs; while the later are promising agent for their low toxicity and biocompatibility. Therefore it would be significant if the both NPs can be combined in an ensemble to augment the effectiveness that support better imaging. In this regard, synthetic routes in micellar medium have been found essential for such manipulation. This manipulation not only leads to unique magnetic properties but also optical properties with significant applications.

3. The unique characteristics of nanoparticles compared to the bulk, are basically the outcome of surface effect and quantum confinement effect. These

factors have been encouraging for investigation of the variation of surface plasmon resonance (SPR), which is the focal feature of optoelectronic properties, with the shape and size of NPs. This study is performed on Cu_2O nanoclusters using classical electrodynamics and time-dependent density functional theory (TDDFT). The results of classical electrodynamics has revealed exalted scattering in the larger dimension while increased absorption in the smaller. A blue shift of the SPR peak with decreasing cluster size validates the quantum confinement effect in the nanoclusters. While, the highest blue shift of SPR peak for Cu_2O nanocylinder due to its maximum surface/volume (S/V) demonstrates the influence of surface effect. The TDDFT study on $(Cu_2O)_n$ clusters for n =1, 2, and 3 describes the origin of absorption peaks to be ligand to metal charge transfer (LMCT) and metal to metal charge transfer (MMCT) processes.

4. The information about the correlation between the size and symmetry of NPs with their optoelectronic properties is further applied on retinal-gold nanoconjugate, which is conclusively proved to be excellent vision-enhancer. The absorption wavelength of retinal is found to shift from visible to infrared region when attached to gold nanoclusters of O_h, D_{2h} and C_{4v} symmetries. The constructive interference of the transition dipole moments (TDMs) in retinal-gold nanoconjugates makes the rod shaped gold nanocluster most efficient vision enhancer among these three shapes. The conjugation of isolated retinal with gold probes makes the process of 11-*cis* to all-*trans* isomerization thermodynamically more favourable, as evidenced through thermochemical and vibrational frequency analysis. Thus this total investigation bestows upon an effective algorithm to optimize the particle topography for targeted application.