Chapter 1

Introduction

This chapter gives an insight to this thesis and briefly summarizes the different aspects of nanomaterials in terms of its properties, applications and modes of synthesis. The chapter emphasizes the importance of a ligand in the synthesis of nanoparticles. It also highlights the effect of ligand on the size, shape, crystalline phase and formation of assembly of nanomaterials.
1.1 Introduction:

“Nano” today is considered as most happening field and is attracting many researchers to turn towards nanoscience and nanotechnology. The term nanotechnology was coined by Tokyo Science University Professor Taniguchi in 1974 and was popularized in mid 80’s by Dr. K. Eric Drexler, through his books *Engines of Creation: The Coming Era of Nanotechnology* and *Nanosystems: Molecular Machinery, Manufacturing, and Computation.*

Term ‘Nano’ can be traced to a Greek root which means dwarf. On the length scale, nano is one billionth of a meter. The use of nanomaterials is documented from the times of Romans. Some of the examples that show use of nanoparticles are the Lycurgus Cup, which consists of gold and silver alloy nanoparticles and the ‘Damascus Sword’ containing the nanoscale carbon particles etc (Figure 1.1). Michael Faraday had demonstrated the synthesis of gold nanoparticles in 1857 in his paper titled ‘Experimental relations of gold (and other metals) to light’ published in Philosophical Transactions. But in last few decades this field has scaled new heights for many reasons including invention of revolutionary imaging methods and techniques that made the characterization of the materials at nanoscale very easy.

**Figure 1.1:** Examples of use of nanomaterials in ancient times. (A) The Lycurgus Cup, (B) the Damascus Sword and (C) the gold colloids prepared by Michael Faraday (The pictures are taken from ref 2, 3 and 4).

Materials in the micrometer scale exhibit physical properties mostly similar to that of bulk form; however materials in the nanometer scale exhibit properties distinctively different from their bulk counterpart. At nanolevel, number of surface
atoms or ions becomes a significant fraction of the total number of atoms or ions and the surface energy plays significant role in the properties of such materials.\textsuperscript{5} The change in the properties is due to the increase in this surface to volume ratio. At nanoscale the electronic structure of materials also gets modified resulting in development of the discrete energy levels in contrast to continuous energy level in bulk materials (Figure 1.2).\textsuperscript{6,7} This leads to dramatic modification of many fundamental properties of nanomaterials such as electrical and thermal conductivity, band gap, density of states, electron affinity, mechanical, magnetic and optical properties etc. These properties are a strong function of size and shape of the particles for a given composition of the nanomaterial.

![Energy Diagram](image)

**Energy Diagram**

*Figure 1.2: Electronic energy levels depending on the number of bound atoms. By binding more number of atoms, the discrete energy levels of the atomic orbital merge into energy bands as shown in the figure. The above figure has been adapted from ref no 6 and 7. Above picture is for semiconductors.*

Other properties of materials that are greatly affected by reduction in size to nanolevel are lowering of melting point of the material, reduced lattice constant and the stabilization of crystallographic phases different from the bulk. It is also observed that metal become semiconductors and semiconductors turn insulators at
nanolevel. Figure 1.3 illustrates examples of variation of properties of materials at nanoscale. The fields where nanoparticles are used have a wide spectrum. A partial (not extensive) list of fields they are being used include catalysis,\textsuperscript{8-16} sensors,\textsuperscript{17-20} electronic devices,\textsuperscript{21-26} as photocatalyst,\textsuperscript{27-30} for separation,\textsuperscript{31-36} optics,\textsuperscript{37-44} data storage,\textsuperscript{45-47} surface enhanced Raman spectroscopy substrate,\textsuperscript{48-54} etc. Nanoparticles are also widely used in medical applications like drug and gene delivery,\textsuperscript{55-62} biosensors,\textsuperscript{63} in MRI scanners,\textsuperscript{64-68} hyperthermia\textsuperscript{68-75} etc.

**Figure 1.3:** Variation of properties of material at nanolevel. (A) Gold at nano-scale possessing different shapes and size. Accordingly, colour of the solution changes with shape and size. (B) Magnetic data as a function of size. (C) Gold nanoparticles acting as a catalyst. Bulk gold does not possess catalytic property.\textsuperscript{76} The images have been taken from reference.\textsuperscript{77,78}

Due to such wide variety of applications, nanoparticles have gained importance and various protocols for synthesis of nanoparticles have been reported. Two classifications that are generally used to distinguish the synthesis of
nanomaterials are i) top down approach which involves slicing or successive cutting of bulk material to obtain nanosize\textsuperscript{5,79,80} and ii) bottom up that involves building up the material atom by atom, molecule by molecule or cluster by cluster.\textsuperscript{80} Figure 1.4 shows the schematics representing these two methods.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1_4.png}
\caption{Two different approaches for the synthesis of nanoparticles top down and bottom up (taken from ref no.5).}
\end{figure}

Synthesis of nanoparticles are further broadly classified into three major types
1. Physical Method
2. Chemical Method
3. Biological Method

More detailed classification of the above three methods are summarized in the table 1.1.
Table 1.1: Method for synthesis of nanoparticles

<table>
<thead>
<tr>
<th>Physical Method</th>
<th>Chemical method</th>
<th>Biological methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation method (Physical vapour deposition, PVD) and (Chemical vapour deposition, CVD)</td>
<td>Sol-gel method&lt;sup&gt;83-86&lt;/sup&gt;</td>
<td>Biosynthesis&lt;sup&gt;87-89&lt;/sup&gt;, Bacteria, Fungi&lt;sup&gt;89,90&lt;/sup&gt; DNA/RNA&lt;sup&gt;91,92&lt;/sup&gt;</td>
</tr>
<tr>
<td>Solvated Metal Atom Dispersion (SMAD)&lt;sup&gt;93,94&lt;/sup&gt;</td>
<td>Chemical precipitation&lt;sup&gt;86,95&lt;/sup&gt;</td>
<td>Plants and plant extracts&lt;sup&gt;96-98&lt;/sup&gt;</td>
</tr>
<tr>
<td>Laser ablation&lt;sup&gt;102-104&lt;/sup&gt;</td>
<td>Hydrothermal synthesis&lt;sup&gt;86,105&lt;/sup&gt;</td>
<td>Amino acids&lt;sup&gt;106&lt;/sup&gt;</td>
</tr>
<tr>
<td>Sonochemical methods&lt;sup&gt;108,109&lt;/sup&gt;</td>
<td>Micelles or micro-emulsion based synthesis&lt;sup&gt;86,110,111&lt;/sup&gt;</td>
<td>Peptides&lt;sup&gt;112,113&lt;/sup&gt;</td>
</tr>
<tr>
<td>Photolytic and Radiolytic methods&lt;sup&gt;114,115&lt;/sup&gt;</td>
<td>galvanic replacement reaction&lt;sup&gt;86,116,117&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

As mentioned before, the properties of nano-materials depend highly on size and shape of nano-materials. Of the above mentioned procedures, chemical methods have proved to be the most reliable ones to produce different sizes and shapes of nanomaterials. As is well known, main ingredient of the chemical synthesis of nanoparticle are the ligands that are used as capping and/ or shape
directing agents. Ligands not only help in achieving stable nanoparticles but also help in achieving nanoparticles of desired shape and size. Custom made ligands perform multiple tasks like capping and reducing the metal ions to metal nanoparticles. Use of ligands which can perform multiple tasks reduces the number of steps involved in the synthesis, thus making the task easy and manageable. Moreover, usage of molecules with multiple functional groups enables the preparation of functional nanoparticles that can be used for targeted drug delivery, selective sensitivity and multi valent expositions that can be used for specific applications. In the following section we briefly summarize the different roles played by the ligands in the synthesis of nanomaterials.

1.2 Role of Ligands/surfactant in synthesis of nanoparticles:

1.2.1 Stabilization of Nanoparticles:

Stability is one important factor that determines the application potential of the nanoparticles. Stability of nanoparticles especially as dispersion can be achieved by two methods

a) Electrostatic repulsion.

b) Steric repulsion (using ligand/surfactants).

1.2.1.1) Electrostatic interaction.

![Scheme illustrated stabilization of nanoparticles via electrostatic interaction](image)

**Figure 1.5:** Scheme illustrated stabilization of nanoparticles via electrostatic interaction.
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In metals, especially noble metals, stabilization of nanoparticles can occur through two modes: electrostatic repulsion and steric repulsion. In the first scenario, subsequent to their reductive preparation, the particles are surrounded by an electric double layer arising due to adsorption of reactant ions on the surface of nanoparticles. This results in two forces acting on nanoparticles, 1) van der Waals force of attraction between metal cores and, 2) electrostatic force of repulsion (potential energy) due to charged ions on the surface. Stability of nanoparticles is dependant on the combination of these two forces. Figure 1.5 shows graph of potential energy versus distance from the surface of spherical particle. At a distance far from the surface, both van der Waals attraction potential and electrostatic repulsion potential is zero. Near the surface, a minimum is observed in potential energy due to van der Waals attraction. At a distance not very far away from the surface where electric repulsion dominates the van der Waals attraction potential and the combination of these two opposing forces leads to a maxima in the energy curve. This maximum is known as repulsive barrier. If the barrier is greater than certain value, two particles cannot overcome the barrier and thus agglomeration is prevented.\(^5,120\) Electrostatic stabilization is kinetic stabilization process and it is useful only in the case of dilute solutions. Addition of electrolytes screens the double layer charge leading to aggregation. As can be noticed, such stabilization occurring due to electronic repulsion is highly dependent on several factors and the ideal condition for most stable dispersion can be achieved in a very narrow window.

1.2.1.2) Stabilization of nanoparticles using ligands/surfactants:

![Steric Stabilization](image)

*Figure 1.6: Steric stabilization of metal nanoparticles.*\(^{120}\)
Steric stabilization of nanoparticles can be achieved by co-ordination of organic molecules on the surface of nanoparticles, which act as capping ligands. In this way nanoparticle cores are separated from each other and agglomeration is prevented. In case of metal nanoparticles system, ligands that are commonly used as stabilizing agent include thiols, amines, silane, phosphines, carboxylic acid (especially for transition metals) etc.

**Table 1.2: Ligand used in synthesis of different nanoparticles**

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Remarks</th>
</tr>
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<tbody>
<tr>
<td>Thiols</td>
<td>used to capped Gold (Au), Silver (Ag), Platinum (Pt), Palladium (Pd) and semiconductor nanoparticles.</td>
</tr>
<tr>
<td>Amines</td>
<td>Au, Ag, Pt, Pd</td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td>Ag, magnetic nanoparticles (Co, Ni, Fe),</td>
</tr>
<tr>
<td>Phosphines</td>
<td>Au, magnetic nanoparticles</td>
</tr>
<tr>
<td>Silanes</td>
<td>Metals, Metal oxide</td>
</tr>
</tbody>
</table>

One of the major reasons why these ligands are preferred for capping is due to their binding ability with the surface of nanoparticles. Thiol containing ligands are most widely used as stabilizing agent for metal nanoparticles as the metal-sulfur interaction in known to be strongest as compared to other surfactants. The chemisorption energy between gold and sulfur is estimated to be ~126 kJ. Extensive studies have been carried out to study the interaction between gold and thiol using various techniques. The thiol-metal bond is most commonly described as a surface bound thiolate. Evidence for thiol being present as it is (without leaving hydrogen) can also be found in literature. Andreoni et al. have carried out detailed experiments to probe the presence and absence of the sulphur bound hydrogen. It was found that apart from presence of thiolates at the bridge sites, intact thiols are also present at “atop” sites and thiolate along with atomic hydrogen adsorbed to the metal surface. Murray and co-workers have based their
argument on ligand place exchange reaction where the hydrogen of the incoming thiol is removed during the replacement step by binding to the leaving thiolate ligand. Brust and co-workers through detailed NMR studies concluded that both the situations (thiolate and thiol binding to gold nanoparticle surface) are possible.  

Amines are also known to impart stability to nanoparticles. In depth analysis of interaction of amines with nanoparticle surface has been carried out. Amine-nanoparticle interactions were studied for Au and Ag by recording FTIR, XPS and NMR measurements. Two possibilities of amines binding to gold surface have been proposed: either though co-ordination bond formation or weak co-valent interaction. The analysis carried out by Sastry and co-workers points towards two different modes of binding of alkylamines with nanoparticle surface. The weakly bound component is attributed to the formation of an electrostatic complex between protonated amine molecule and surface bound AuCl$_4^-$ ions, while the strong bound entities are assigned to a complex [AuCl(NH$_2$)]. Work by Heath and co-workers also suggests that amines form partially covalent bond with gold nanoparticles and that the stability of amine capped gold nanoparticles is a finite size effect which is largely kinetic rather than thermodynamic in origin. Sastry and co-workers showed that gold nanoparticle surface-bound alkanethiols may be replaced by alkylamines by a place-exchange mechanism while the converse process, i.e., exchange of surface bound alkylamines with alkanethiols, does not occur. On the contrary many researchers claim that amines on nanoparticles can be easily replaced by thiols. While the debate goes on, it is a fact that amines are also found to cap nanoparticles and can help stabilizing nanoparticles.

Carboxylic acids are one of the important class of ligand that is used in synthesis of nanoparticles. The carboxylic acid that is being mostly used is oleic acid, which plays a major role in synthesis of magnetic nanoparticles. Interactions of oleic acid with surface of nanoparticles have been discussed in detail. Carboxylic acids generally binds to the metal surface in two different types either a bidentate bond through two equivalent oxygen atoms or a monodentate bond with inequivalent oxygen atoms. In case of the monodentate bond, the C=O bond is still present and the acid hydrogen is substituted by metal atoms. However, through detailed FTIR and XPS analysis, Dravid and co-
workers have concluded the bidentate chelating is the type of bonding present in Co nanoparticles case.

It has also been shown that oleic acid can be used to prepare aqueous dispersions of nanoparticles. This aspect is surprising because if the carboxylic acid group binds to the nanoparticle surface then the nanoparticles would not be dispersible in aqueous medium. To address this issue Prasad and co-workers and Efrima and co-workers have studied interaction of oleic acid with silver nanoparticle surface in the aqueous medium. The studies carried out using FTIR and \(^1\)H NMR reveals that in aqueous medium, oleic acid binds to nanoparticles surface through the double bond. This results in carboxylic acid moiety being exposed to the water medium.

Interaction of phosphine with nanoparticle surfaces has been studied by Hyeon and co-workers. Triphenylphosphine (TPP), trioctylphosphine (TOP) were investigated in detail using NMR. The NMR peak of TOP stabilized palladium nanoparticles appeared at 2.89 ppm while free TOP exhibited a peak at -30.43 ppm. The NMR results indicated that TOP binds weakly to the surface of nanoparticles.

Silanes also are one of the important ligands that are being used for capping surface of nanoparticles. Binding of different silanes like n-hexylsilane (H\(_{13}\)C\(_6\)SiH\(_3\)), n-octylsilane (H\(_{17}\)C\(_8\)SiH\(_3\)), octadecylsilane (H\(_{37}\)C\(_{18}\)SiH\(_3\)) to the surface of nanoparticles are analyzed using reflection-absorption infrared spectroscopy (RAIRS). From RAIRS and XPS results it is proved that the three Si-H bonds of the alkylsilane are broken and a monolayer of the ligand on nanoparticle surface is formed through weak covalent bonds.
1.2.2: Influence of ligand on shape and size of nanoparticles

Factors like temperature of reaction, concentration of reaction, rate of reaction, pH of the reaction solution etc are known to affect the size and shape of the nanoparticles. Another major factor that plays an important role in governing the shape and size of nanoparticles is the ligands/surfactants that are present during the formation of nanoparticles. Using the celebrated Brust protocol Heath and co-workers could vary the size of gold nanoparticles ranging from 1.5 to 20 nm. The variation in size of gold nanoparticles was achieved by controlling the initial AuCl₄⁻/thiol ratio. Reactivity was controlled by varying the chain length and concentration of the ligands. Concentration of surfactants like sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) were varied and their effects on the size and shape of resulting nanoparticles were investigated in detail. Change in concentration of these surfactants resulted in formation of different micelle structures which are responsible for control of shape and size of nanoparticles. Using of different concentrations of oleic acid ligand during the cobalt carbonyl decomposition results in the formation of either large nanocrystals
or small clusters. More dramatically, it was shown that by adding or removing free oleic acid ligand from the final reaction product, nanocrystal colloid was turned into a cluster complex solution and vice versa.\textsuperscript{170} In order to gain more knowledge on the role of ligands played during the synthesis of nanoparticles, ligand-metal interaction was studied in detail during the growth of nanoparticles. Concentrations of ligand are found to control the size and shape of nanoparticles. At different concentrations, interaction of ligands with metal precursor differs. This results in variety of reaction product formation which ultimately decides the final products.\textsuperscript{171} Similar ligand effects on particle size were studied in detail by Challa Kumar and co-workers. They demonstrated that usage of different ligands leads to different reaction pathways. This in turn controls the nanoparticle dimensions.\textsuperscript{172,173} The variation in size and shape occurs due to interaction of ligands with the precursor even prior to the nucleation.

Ligands are also known to direct the shape of nanoparticles leading to formation of anisotropic nanoparticles. Murphy and co-worker have extensively synthesized gold nanorods of different aspect ratio using a method called ‘seed mediated method’. Based on the systematic studies, they concluded that CTAB is the most suitable surfactant for the formation of gold nanorods and nanowires.\textsuperscript{174-177} Detail study on role of CTAB on formation of nanorods/wires reveal that CT\textsuperscript{+} head group binds to the side surface of nanorods with some preference. The preferential binding is based on steric argument - the Au atom spacing on the side faces is more comparable to the size of the CT\textsuperscript{+} headgroup than the close-packed \{111\} face of gold, which is at the end of the nanorods. Such binding stabilizes the side faces, which have relatively large surface energy and stress (tension) compared to other faces. This allows material addition along the [110] common axis on \{111\} faces, which do not contain the CT\textsuperscript{+} headgroups.\textsuperscript{177}
Detailed investigation of formation of different shapes on nanoparticles has been carried out by Sau and co-workers.\textsuperscript{178} Methods like preformed-seed-mediated growth method,\textsuperscript{179-181} high-temperature reduction method,\textsuperscript{182,183} spatially confined medium/template approach,\textsuperscript{184,185} electrochemical synthesis,\textsuperscript{186-188} photochemical method\textsuperscript{189,190} and biosynthesis\textsuperscript{97} which result in different anisotropic nanoparticles in presence of various ligands have been demonstrated. They have concluded that among the many factors that govern the shape of nanoparticles additives like surfactants and ligands play a major role.\textsuperscript{191-195}

1.2.3: Influence of ligand on the crystalline phase of nanoparticles

Properties of nanoparticles are also known to be function of their crystalline phase. This is more prominent in case of magnetic nanoparticles and their magnetic properties.\textsuperscript{196,197} Interestingly the type of crystallographic phase a nanoparticle adopts also has been seen to depend on the type of ligand used. Challa Kumar and co-workers showed formation two different crystal structures when combination of surfactants is used. The two crystal structures obtained in case of cobalt nanoparticles are the hcp phase and the fcc phase.\textsuperscript{173} A new phase $\varepsilon$-phase of cobalt nanoparticles was obtained by Bawendi and co-worker when trioctylphosphane oxide (TOPO) was used as capping surfactant. Use of oleylamine at different temperature resulted in formation of different crystalline phases of Ni nanoparticles.
(hcp and fcc). Hans et al. have synthesized Ni nanoparticles using dodecylamine (DDA) and octadecene (OD) as surfactants. When they used only DDA, cubic phase formation was seen, while the mixture of DDA and DA lead to formation of hexagonal phase. Magnetic measurements were carried out for these two different phases which showed vast difference in nature of magnetic characteristics such as field cooled and zero field cooled curves, Curie temperature etc.198

Crystal structure of CdTe nanoparticles formed using phosphonic or fatty acid is observed to vary strongly. The nanocrystals grown in presence of the fatty acids had a wurtzite structure, and the reaction in presence of phosphonic acids tended to yield nanocrystals with a zinc blend structure.199 The exact reason for formation of different crystallographic phases when different ligands are used is not known but one of the reasons cited is binding of ligand and change in aggregation state that can cause phase transformation without particle coarsening.200

1.2.4: Role of ligand in assembly formation

One of the key steps towards the application of nanoparticles in various fields is their assembly into desired architecture.201 There are various techniques like i) self assembly of nanoparticles202-204 ii) template directed self assembly205-207 iii) assembly by lithography or patterning,208-211 that can lead to the assemblies of nanoparticles. Application of these small clusters in devices requires them to be arranged in one, two or three dimensions (1D, 2D and 3D). Here again, the ligands play an important role.86,212-217 In the following we will discuss the assembly of nanoparticles formed by usage of different ligands. Assemblies obtained by usage of ligand depend on various factors like size, stability, solubility of the nanomaterials. Other factors like electrostatic attractions, covalent bonding between the ligands and dipole-dipole interaction incase of magnetic nanoparticles also govern the formation of the assemblies.218,219 One of the simplest methods to achieve ligand capped nanoparticle assemblies is to drop coat the nanoparticle solution on a substrate and allow the solvent to evaporate.

The factors that govern the formation of assemblies have been summarized by Prasad and co-workers.220 The factors that govern the assembly formation include size, ligands used, chain length of the ligand, substrate used for formation of assemblies etc.
We will restrict our discussion to the ligand and capping here. As discussed in earlier section, nanoparticle stabilization can be achieved in two ways electrostatic/ligand capping. But the nanoparticles stabilized by electrostatic forces can be destabilized by minor changes. Therefore nanoparticles stabilized by ligands (stearic force) are more preferred to obtain reliable assemblies. In this case, stability is imparted by combination of forces viz van der Waals attractive forces between the metal core and the stearic repulsive force of the ligand. Expressions for these two forces have been reported by Korgel et al.221

\[
E_{\text{steric}} = \frac{100R\delta_{\text{SAM}}^2}{(C-2R)\Pi\sigma_{\text{thiol}}^3} KT \exp\left(-\frac{\Pi(C-2R)}{\delta_{\text{SAM}}}\right) \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

Where \( \delta_{\text{SAM}} \) is the thickness of brush and \( \sigma_{\text{thiol}} \) is the diameter of the area occupied by the thiol on the particle surface.

\[
E_{\text{vdW}} = -\frac{A}{12} \left\{ \frac{4R^2}{C^2 - 4R^2} + \frac{4R^2}{C^2} + 2\ln\left[\frac{C^2 - 4R^2}{C^2}\right] \right\} \ldots \ldots \ldots (2)
\]

Where \( A \) is the Hamaker’s constant and \( C \) is the center to center distance between the particles. The above two forces are opposite in nature. When these two are combined a minimum in the total energy can be seen where nanoparticle assemblies can be formed. It can be seen that apart for the above forces, attractive interaction between ligand molecules (interdigitation or bundling) also plays a dominant role.

Figure 1.9: Interparticle potential (2) between two nanocrystals: This curve results from a summation of two different forces namely \( E_{\text{steric}} \) (3) plotted using (eq.1); \( E_{\text{vdW}} \) (1) plotted using (eq.2) as described in the text. Figure taken from ref no. 220
One of the requisite for formation of assemblies is super saturated solution resulting in formation of assemblies either in solution or on a substrate. Though detail information about the forces responsible for assembly formation is available most of the assemblies obtained are on substrate. There are also examples where assemblies are obtained in solution.\textsuperscript{222-224}

Type of ligands and variation in the chain length also govern the formation of nanoparticle assemblies. One of the early reports where assembly of nanoparticles was observed is by Shiffrin and co-workers, where they used thiol based ligands for capping and obtaining the assembly of Au nanoparticles.\textsuperscript{225,226} Superlattices of Au, Ag and Pt were obtained by phase transferring the hyrosols to toluene solution containing thiol ligand.\textsuperscript{127,227} Assemblies of gold nanoparticles were obtained using different ligands like dodecanthiol, dodecylamine, octadecyl silane, trioctyl phosphine, dodecyl bromide, dodecyl iodide, dodecanol and decane. The superlattices formed with these different ligands are different in nature.\textsuperscript{228} Dodecylthiol capped nanoparticles formed better assemblies as compared to other ligands. 2-D and 3-D superlattices were synthesized in nonionic inverse micelle and capped with alkanethiol ligands by varying the alkanethiol chain length from C\textsubscript{6} to C\textsubscript{18}.\textsuperscript{229} It is possible to control the interparticle spacing of superlattices over a limited range by capping with organic thiols. Very small alkanethiols cause precipitation, and high alkanethiols restructure the nanoclusters, but intermediate alkanethiols, from C\textsubscript{6}SH to C\textsubscript{14}SH, result in the formation of uniform superlattices with controlled interparticle spacings. Polydispersity of the assembly increases with increase in chain length. Similar chain length dependent studies of superlattice formation were carried out by Prasad et al using thiols. Separate particles were formed when longer chain length (C\textsubscript{16}) thiols were used while for smaller chain length (C\textsubscript{8} and C\textsubscript{10}) 3D superlattices are formed.\textsuperscript{230}

Use of ligands that possess same functional groups at both the ends which can bind to two nanoparticles have also been used in formation of assemblies of nanoparticles. Brust and co-workers have used \(\alpha,\omega\)-dithols to assemble Au nanoparticles. Controlling such processes was seen to be difficult, never the less; it was achieved by varying the concentration of the ligand and optimizing it.\textsuperscript{216} Networks of nanoparticles which are photosensitive were prepared by using
azobenzene derivatives. The interparticle spacing could be controlled by the reversible trans–cis isomerization of the azobenzene moiety induced by UV and visible light, respectively.\textsuperscript{231} One of the examples where assemblies are formed in aqueous medium is reported by Kimura and co-workers.Mercaptosuccinic acid was used to achieve this. In the superlattices that have been obtained Au nanoparticles, arranged in hexagonal closed packed structures were interconnected by interparticle chemical binding due to mercaptosuccinic acid.\textsuperscript{232} Assemblies of nanoparticles are formed taking the advantage of specific interactions between the complimentary recognition units. Rotello and co-workers have used this method, where the ligands on surface of nanoparticles bind with complimentary recognition units leading to formation of assemblies.\textsuperscript{204,233}

Assemblies of magnetic nanoparticles are important for their application in recording media.\textsuperscript{144,234} Assembly of these magnetic nanoparticles largely depends on the composition and combination of dispersing solvent and the temperature during the deposition.\textsuperscript{78,235} Ordered array of Fe nanoparticles were obtained by coating these nanoparticles with Oleylamine.\textsuperscript{236} Assembly of cobalt nanoparticles were obtained using oleic acid and trioctylphosphine as ligand.\textsuperscript{156} Sidhaye et al. have obtained assembly of Ni and Co nanoparticles where the combination of sodium dodecyl sulphate (SDS) and oleic acid have been used to achieve the assembly of nanoparticles.\textsuperscript{141}
Efforts have been taken to assemble anisotropic nanoparticles like rods. Thomas and his group have been successful in achieving chains of gold nanorods using different ligands. Using $\alpha,\omega$-alkanedithiols nanorods were organized in end to end fashion where the alkanedithiols acts as linkers. Similar studies were carried out using other ligands/capping agents like carboxylic acid derivatives, namely, 3-
mercaptopropionic acid (MPA) and 11-mercaptoundecanoic acid (MUA), for assembling Au nanorods.\textsuperscript{238}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(A) Scheme shows DNA-based colloidal nanoparticles assembly method carried out step wise.\textsuperscript{92} (B) Illustrates TEM images of gold nanoparticles as prepared, (C) TEM images of DNA-linked gold nanoparticles show assembly formation.\textsuperscript{92}}
\end{figure}

Biological entities like DNA have also been employed to achieve assembly of nanoparticles. Mirkin’s group\textsuperscript{91} have shown DNA based assemblies obtained rationally and reversibly into macroscopic aggregates. This method involves attaching to the surface of two nanoparticles, a non-complimentary DNA-oligonucleotides attached with thiol group, which binds to gold. Addition of oligonucleotides duplex with sticky ends complimentary to two grafted sequences, leads to the formation of nanoparticle assembly.

Thus from above discussion, we observe that ligands/surfactants play a vital role in synthesis, shape control and assemblies of nanoparticles. They are also a key component in the preparation of organo nanoparticles, functional hybrids which find numerous applications like drug delivery and catalysis.
1.3 Objective of this thesis:

We have realized importance of metal and magnetic nanoparticles with their application point of view in different fields. Survey of various methods of synthesis has been described in earlier sections. Apart from this, we have also taken into account the role played by ligand in synthesis of nanoparticles as stabilizing agent, shape directing moiety and also as reducing entity.

In this thesis we concentrate on the effect of surfactant on shape and size of nanoparticles. We have also studied its effect on the crystal structure obtained. Subsequently effect on the properties has also been taken into consideration. We have also demonstrated the dual characteristics of ligand that as reducing agent and as capping moiety.

1.4 Outline of the thesis:

Brief background of the work carried out in the thesis has been described in above section.

Chapter 2 illuminates effects of two ligands, sophorolipid and a new carboxylic acid on the synthesis of cobalt nanoparticles. Synthesis protocol applied is simple reduction of metal salt with sodium borohydride. Different ligands lead to formation of different crystal structures of cobalt nanoparticles. Detailed magnetic measurements like FC-ZFC measurements, field dependent magnetization measurements and ferromagnetic resonance are found to vary depending on the crystal structure. Interaction of these ligands with nanoparticle surface is also studied.

Chapter 3 deals with exploring the dual nature of biosurfactant sophorolipid as reducing and capping moiety. Three different types of sophorolipids namely SA derived sophorolipid, OA derived sophorolipid and LA derived sophorolipid are considered. Synthesis of silver nanoparticles is carried out by two methods namely batch process and continuous flow method. Temperature dependent study is carried out for synthesis of silver nanoparticles using these three ligands as reducing/capping agent. The nanoparticles formed are characterized with UV-visible, FTIR, dynamic light scattering (DLS) and transmission electron
microscopy. Time dependent study is also carried out to optimize the reaction time for synthesis of Ag nanoparticles. Using the optimized reaction conditions the synthesis is carried out in continuous flow method using microreactors. Stainless steel tube was used as microreactor for this synthesis.

In Chapter 4 we have made use of commonly used ligands cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC). Au nanoparticles are synthesized using these ligands. Tryptophan is used as reducing agent for Au nanoparticles. Formation of triangular nanoparticles in case of CTAB and spherical nanoparticles in case of CTAC are seen. Both the species of nanoparticles were characterized by UV-visible, TEM, and XRD. Another interesting feature observed is the emission from triangular nanoparticles while it was absent in case of spherical nanoparticles. To support the observed result, detailed fluorescence and lifetime measurements are carried out.

Chapter 5 summaries the work carried out in this thesis by highlighting the prominent feature of the work. Here, we also give the possible future work that can be carried out using this work as the basis.
Chapter I

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