INTRODUCTION

Chapter 1
This chapter is an introduction to the research work presented in this thesis. It begins with a bird’s eye view of the field of nanoscience and nanotechnology, covering from its history to the latest development. The chapter proceeds to describe surface functionalisation and its importance, different types of functionalisation and its applications in biology.
1.1. Introduction

Nanomaterials are built through the assembly of nanometer-scale units into ordered super lattices and they offer exciting perspectives as novel materials whose optical, electronic, magnetic, transport, mechanical and thermodynamic properties may be controlled by the selection of the composition and sizes of the building-block units and that can be made further use of.\(^1\) The work reported in this thesis is an endeavor towards that explained in the previous sentence. This chapter is a brief introduction to the research work presented. It begins with the definition of ‘nanotechnology’ and its birth, elaborating on why it is so important. The advent and ongoing development of technology has aided in studying these particles which though have been in existence since time immemorial, could be researched closely only in this generation of science. The properties of the nanomaterials are followed by an outline of the various synthesis procedures, its applications and the health risks involved in introducing them into the environment. The science of surface functionalisation of nanoparticles is explained with different types and their applications in various fields, with due emphasis in biology. The objective of the thesis and an outline of the thesis are provided at the end of this chapter.

1.1.1. Profile of nanoparticles

Nanomaterials have been in existence in nature for long; much before the famous address by Richard P. Feynman, Professor of Physics at the California Institute of Technology and Nobel Laureate, in 1959, at the American Physical Society, which is published in *Engineering and Science*, entitled “Plenty of Room at the Bottom”.\(^2\) For example, nano-sized gold and silver has been used in glass to tint them for ages and carbon black (10 to 400 nm sized carbon particles) has been in use as fillers for automotive tires for more than 100 years. However, the era of ‘nano’ began in the last century and the achievements of the challenges posed by Prof Feynman proved his prophecy true. In 1960, William McLellan constructed a small motor by hand using tweezers and a microscope and in 1985, Thomas Newman wrote the first page of Charles Dickens’ *A Tale of Two Cities* using a computer controlled finely focused pencil electron beam on an area of 5.9 micrometers square.\(^3\) Nanoscience and nanotechnology, ever since, has been an explosion of understanding, designing and fabricating new nanomaterials for applications of interest, in any field. With the
advancing technology that helped make breakthroughs in the field of microscopy, which made the burgeoning field feasible, scientists witnessed the dawn of a new era. TEM, SEM, STM and AFM are those tools with which the study at a scale of nanometers is carried out and every field on earth is influenced. A nanometer is the equivalent in size of ten hydrogen atoms and one-millionth the diameter of the head of a pin.\(^3\)

On the website of US National Science Foundation, nanotechnology is defined as research and technology development at the atomic, molecular or macromolecular level, in the length scale of \(~1-100\) nm range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.

**1.1.2 What are these nanoparticles and why are they so important?**

The word ‘Nano’ meaning dwarf in Greek is already in the market on the wide range of applications. As the definition above, systems in which the dimensions measure in the range of nanometers are covered under the large canopy of the nanoscience and nanotechnology. The nanoscience and nanotechnology has taken an upswing over the frontiers in scientific research. The nanoparticles can be of different types comprising of metal or metal oxide nanoparticles, organic/inorganic nanoparticles, quantum dots, polymeric nanoparticles, liposome, DNA machines, and carbon nanotubes (CNT), graphene, etc.

Nanoscience and nanotechnology thus encompass a range of techniques rather than a single discipline and stretch across the whole spectrum of science, touching medicine, physics, engineering and chemistry. The gap between the physics/chemistry of atoms/molecules and bulk materials/condensed matter is bridged by a broad slope (See Figure 1.1) and not a fall as shown in red; it reflects both the geometric and delocalized electronic shell structures of the clusters of atoms or molecules. Chemists may prefer to think of small nanoparticles as clusters of molecules.
The broad slope is characterized by the size-dependent variations in the matter, which determines the physical and chemical properties of the system involved. Quite often, the discontinuous behavior of quantum size effects is superimposed on a smoothly scaling slope which also reflects the size of a quantized system. The intense research in the field of nanoparticles by chemists, physicists and materials scientists is motivated by the fundamental question of how molecular electronic properties evolve with change in size in this intermediate region between molecular and solid-state physics. To elaborate, the size variations involved are in the range of a few hundreds to few nanometers, which is illustrated in the representation, Figure 1.2. The change in properties can be explained in the following section, size-dependent effects.

1.1.2.1 Size-dependent effects

It is important to understand the process of size quantization or quantum confinement before plunging into more about nanoparticles. The unusual properties of nanoparticles are primarily due to confinement of electrons within particles of dimensions smaller than the bulk electron delocalization length. This process is known as quantum confinement. In the size regime of a few nanometers, the boundaries of the crystallite are comparable in dimension to the wavelength of electrons in the extended solid. As a consequence, the optical and electrical properties of the nanocrystals are dominated by quantum effects. Size quantization refers to changes in the energy-level structures of materials as the material-unit (most
often a crystal) size drops below a certain size. This size, which can be identified with the Bohr diameter of the material, can vary from almost 100 nm to a single nanometer or even less.

Figure 1.2. Size comparison ranging from atomic nucleus to man. [Adapted from ref 7]
For metals, it is smaller than a few tens of nanometers. For gold clusters, it is approximately 1 nm (often less than 100 atoms). Size quantization is characterized by an increase in band gap (blue-shift in optical spectra) and increasing separation of energy levels with decrease in crystal size. (see Figure 1.3) As the energy-level structure changes continuously with change in crystal size (in the size-quantization regime), a material of a particular fixed chemical composition can be made with varying and tunable physical properties.\(^8\)

**Figure 1.3.** Evolution of the band gap and the density of states as the number of atoms in a system increases (from right to left). \(d\) is the so-called Kubo gap. (Adapted from ref \(^4\))

Thus, the basic material properties are determined by both the physics of the material and its chemistry. In addition to the quantum size effects, the surface effects also affect the physical & chemical properties of the materials, which is discussed in the following section.
1.1.3 Properties of nanoparticles

Colloidal nanocrystals are sometimes referred to as ‘artificial atoms’ because the density of their electronic states — which controls many physical properties — can be widely and easily tuned by adjusting the crystal’s composition, size and shape. The physical and chemical properties of nanoparticles can be tuned over a range by variation of the particle size. Depending upon which new properties arise such as quantum confinement, plasmon excitation, superparamagnetism, the Coulomb blocking effect, etc. The optical properties of nanoparticles, especially metal nanoparticles, have been of great interest. The strong color of the colloid of the noble metal nanoparticles is caused by the surface plasmon absorption. Surface Plasmon Spectroscopy is a versatile technique for studying chemisorptions, redox reactions, (bio) sensing, alloying, and electrochemical processes such as under potential deposition involving small metal nanocrystals that exhibit well-defined surface plasmon modes. This includes Au, Ag, Cu, Sn, Pb, Hg, Cd, In and the alkali metals. Many metals such as Sn, Pb, Hg, Cd and In have plasma frequency in the UV part of the electromagnetic spectrum and thus the nanoparticles do not display strong color effects. Moreover, such small metal particles also get readily oxidized making surface plasmon experiments difficult. However, the coinage elements like Au, Ag and Cu are exceptional: (1) they are noble and form air-stable colloids and (2) due to d-d band transitions, the plasma frequency is pushed into the visible part of the spectrum. For ages, the ‘soluble’ Au and Ag have been in use for the exhibition of their unique colors. For example, the first optical metamaterial is the ruby glass, which contained tiny gold droplets, typically 5-60 nm in size. As demonstrated by the exquisite Lycurgus Cup (see Figure 1.4) these gold particles color the glass in an extraordinary way. In daylight the cup appears a greenish color, but illuminates it from the inside and it glows ruby.
It appears green when viewed in reflected light, but looks red when a light is shone from inside and is transmitted through the glass. Analysis of the glass reveals that it contains a very small amount of tiny (~70 nm) metal crystals containing Ag and Au in an approximate molar ratio of 14:1. Bulk Au looks yellowish in reflected light, but thin Au films look blue in transmission. This characteristic blue color steadily changes to orange, through several tones of purple and red, as the particle size is reduced down to ~3 nm. The surface plasmon resonance and its effects are explained in Chapter 4.

Small crystals require lower melting temperature and the scaling laws in the nanometer regime is driven by the fact that in this regime, the liquid phase has lower surface energy than a solid with facets, edges and corners. The effect can be quite significant, leading to a halving of the melting temperature for a solid particle of 2–3 nm diameter relative to that of the corresponding bulk solid. Melting is a cooperative phenomenon which is not well defined for a small number of members of the ensemble like nanoparticles. A sharp melting point is only obtained in the thermodynamic limit of an infinite number of particles as is the case in a bulk material. For the nano regime, melting points are broad and size-dependent. Thus we find changes in the melting point as we go from bulk to nano. It is known that the
atoms or molecules at the surface layers suffer lower stabilization due to less coordination as compared to the interior. The extrapolation of this fact to the nanoparticles, explains the size-dependence of the melting point of the same material. The Gibbs-Thomson equation describes how the melting point scales inversely with the radius of the particle:

\[
\frac{T_m - T_m^*}{T_m^*} = \frac{\Delta T_m}{\Delta T_m^*} = \frac{2 V_m(l)Y_{sl}}{\Delta H_m r}
\]

where, \(T_m\) is the melting point of the cluster with radius \(r\), \(T_m^*\) is the melting point of the bulk, \(V_m(l)\) the molar volume of the liquid, \(Y_{sl}\), the interfacial tension between the solid and the liquid surface layer, and \(\Delta H_m\) is the bulk latent heat of melting.

Also, the catalytic activity of the nanoparticles is well established, for example, the excellent catalytic activity of small gold particles, which is an inert metal in the bulk state, is known. The selectivity, however, is most sensitive to the packing of atoms on the surface or the exposed facets of a nanocrystal. The weak intrinsic fluorescence of noble bulk metals (quantum yield \(\sim 10^{-10}\)) results from the electronic inter-band transition. Nanorods also have enhanced emission over bulk metal and nanospheres, due to the large enhancement of the longitudinal plasmon resonance.

Elements that are non-magnetic at bulk state become magnetic at nano-size. Nanoparticles comprising several hundred atoms of Au, Pd and Pt embedded in a polymer revealed magnetic moments corresponding to several unpaired electron spins per entire particle. The magnetic properties of iron oxide nanoparticles is discussed in Chapter 3 (Part II).

### 1.1.4. Synthesis of nanoparticles and its applications

The most challenging part of research in the field of nanoscience & nanotechnology is the cost effective and environmentally safe procedures for synthesizing the desired nanomaterials. Of the two distinct synthesis procedures, (1) top-down approach and (2) bottom-up approach, the latter is more effective and hence commonly used. (see Figure 1.5) The top-down approach has been developed from ancient methods like lithography, writing or stamping. Now the top-down approach is capable of creating...
features down to the sub-100 nm range, using sophisticated tools like electron-beam writing, advanced lithographic techniques using UV or hard X-ray radiation \(^{25}\) and techniques like microcontact printing. \(^{26}\) In contrast, bottom-up methods aim to guide the assembly of atomic and molecular constituents into organized surface structures through processes inherent in the manipulated system. The bottom-up approach is inherently non-equilibrium phenomenon and the growth scenario is governed by the competition between kinetics and thermodynamics of the reaction.

![Figure 1.5](image.png)

*Figure 1.5. Two different approaches to control matter at the nanoscale. [Adapted from ref\(^ {27}\)]*

In this thesis, we have used bottom-up approach to synthesis nanoparticles from metal-ions in solution phase. The synthesis system consists of the typical three components: precursors, organic surfactants and solvents. Upon crossing the threshold of the activation energy (by means of temperature, catalyst or active chemical like a reducing agent), the precursors chemically transform into active atomic or molecular species (monomers); these then form nanocrystals whose subsequent growth is greatly affected by the presence of surfactant molecules. The formation of the nanocrystals involves two steps: nucleation of an initial ‘seed’ and growth. During nucleation, precursors form a supersaturation of monomers followed by a burst of nucleation of nanocrystals.\(^ {9}\) These nuclei then grow by incorporating additional monomers still present in the reaction medium, until all of it is exhausted.
In our work, the metal ions are reduced by a reducing reagent in solution; they nucleate to form clusters and grow into nanoparticles while in the presence of protective ligands. Either the stoichiometry of the available metal ion supply or the passivation of further growth by the protective ligands, in combination with numerous other parameters like the temperature, osmotic potential, dilution factor, stirring rate, etc. can determine the eventual nanoparticles size. Reduction of \( \text{HAuCl}_4 \) by boiling sodium citrate solution to obtain spherical gold nanocrystals is one of the most popular methods of synthesizing gold nanoparticles.\(^{28, 29}\) There are numerous methods in wet-chemistry to synthesize gold, silver, platinum nanoparticles, etc. In fact, the synthesis procedures have reached the stage of controlling various parameters (such as size, shape, crystallinity, composition) to achieve control\(^9\) and to fine-tune the properties of the nanoparticles.\(^{30}\) To obtain well-defined structures, tailored syntheses of colloidal nanocrystals are available, such as co-precipitation in aqueous phase, using reverse micelles as templates, hydrothermal/solvothermal synthesis and surfactant-controlled growth in a hot organic solvent.\(^{31, 32}\) Depending on the ratio of the salt and capping agent, the particle size can be tuned. Xiaogang Peng et al\(^{33}\) in his paper conclude suggesting that the continuous monitoring and adjustment of the monomer concentration provides an optimal growth sequence, so that the average size present is always just slightly larger than the critical size, for reproducibly and reliably large amounts of uniform size. Figure 1.6 in the following page shows the narrow distribution achieved in their work.

Phase transfer\(^{34, 35}\) and ligand exchange reactions\(^{36, 37}\) are other methods of synthesis. Complex morphologies such as dendritic heterostructures have been produced in colloidal nanocrystals synthesis (CdSe on CdTe).\(^{38}\) To name a few breakthroughs in the synthetic procedures, read the following. The ‘Nano-filling method’ is a unique way of synthesizing stable nanowires. Confinement of electrons in one or more dimensions to show unique quantum properties is essential for nanoelectronics devices. However, nanowires of few atoms thick are structurally and chemically unstable. Ryo Kitaura and co-workers have shown that ultrathin metal nanowires can remain stable for long periods if they are grown inside carbon nanotubes.\(^{39, 40}\)
Multi-walled Carbon Nano-Tubes (CNT) are found to penetrate tomato seeds and accelerate sprouting process. The seeds treated with CNTs grew faster, with larger biomass and longer stems\textsuperscript{41}. This opens up new approaches for delivery agents in agriculture and horticulture and new avenues in bio-fuel research.

Optomechanical crystals have been created that can act as both photonic and phononic crystals, allowing light and sound to be confined within a small region.\textsuperscript{42, 43} This kind of research is a combination of art permeating science. (Figure 1.7.)

The advent of quantum dots has revolutionized the imaging and analysis field of biological samples, by overtaking the organic fluorophores. The quantum dots do not photo-bleach; they give better results with high resolution and also provide a readily accessible range of colors. The quantum dots and rods are also used as alternatives to semiconductor polymers in light emitting diodes\textsuperscript{44}, lasers\textsuperscript{45} and solar cells.\textsuperscript{46}
Chromophores within ~5 nm of the surface of the metal nanoparticle have their fluorescence quenched while chromophores at distances of ~10 nm or greater have their fluorescence enhanced up to 100-fold. The electric field of the metal nanoparticle is still near enough to influence the fluorescence and enhance it, but cannot interact directly with the chromophores electrons and quench it. Working to improve the performance of lithium-ion batteries, it is shown that energy storage can be improved by building the battery anode from silicon nanotubes. Likewise, the applications of nanoparticles in various fields is innumerable and still increasing magnanimously.

### 1.1.5. Nanoscience, nanotechnology and risks

Concerns arise in this cross-disciplinary area about toxicological aspects and ethical implications. One can find nanoparticles in day-to-day uses, such as sunscreens, toothpastes, sanitary ware coatings and even medicines and food products. According to Dan M. Kahan, there exists a reciprocal link between the development of nanotechnology and research into public perceptions of risk. Also, an increase in knowledge does not result in reduced aversion to risks. Hence addressing the health risks and environmental effects is an important part of ‘nano’ research. This section gives a brief summary of the risks and effects mentioned. The actual health risk will depend not only on the intrinsic hazard of the agent but also on the likely exposure. With the rise in wide interests and faceted applications, the nanoparticles production has increased tremendously from multi-ton carbon-black and fumed silica for applications in plastic fillers and car tires to microgram quantities of fluorescent quantum dots used for markers in biological imaging.
The nanoparticles could affect at the molecular, cellular, physiological levels and attack the organs as well. For example, the schematic below shows the possible routes a nanoparticle can take within the lung aided by the fluid present in the pleural space, which lubricates the movement of lungs. (Figure 1.8.)

![Figure 1.8. Movement of particles through the lungs. [Adapted from ref51]](image)

Small particles and short nanotubes move rapidly and drain easily through the pores, whereas long and fibrous nanotubes get lodged at the drainage points and block. This causes to inflammation leading to pathological changes over time.51 Strong immune and inflammatory responses are already detected when using nanoparticles in different mammalian systems.52-56

Evidences suggest that the key factors contributing to nanomaterials related cytotoxicity are size/mass (size distribution), shape, surface area, chemical composition (purity, crystallinity, electronic properties, etc.), solubility and stability, bio-persistence, surface charge and surface functionalisation. The paucity of sound data renders it premature to formulate any definitive risk assessment about engineered nanomaterials; therefore, several other important issues require close attention.50
1.2. Surface functionalisation of nanoparticles
Surface functionalisation of nanomaterials holds the potential for creation of new materials and new applications. After the synthesis of the colloidal particles, further modifications are necessary to stabilize the particles against aggregation\(^57\), \(^58\); the modifications enable easy use, depending upon the requirement of the application. Different interactions may be then controlled through the process of surface ‘functionalisation’ (or ‘derivatization’) as explained below.

1.2.1. Science of surface functionalisation
The inorganic cores possess useful properties that are controlled by their composition, size and shape, and the surfactant coating ensures that these structures are easy to fabricate and process further into more complex structures.\(^9\) Synthesis of the nanomaterials requires passivation of the surfaces to protect against modifications of their properties by their environment and to inhibit their propensity to agglomerate or sinter. Through its chemical interaction with a metal surface, the presence of a capping agent can change the order of free energies for different crystallographic planes, and thus their relative growth rates. The plane with a slower addition rate will be exposed more on the nanocrystal surface.\(^59\) Organic surfactant molecules in the growth medium are chosen for their obsolete nature to adhere to a growing crystal. More than half the atoms of the nanocrystals may be present on the surface and this makes growth strategy at the inorganic-organic interface pivotal.\(^9\) That is how in nature, the biomineralisation, where the complex patterns of biologically organized organic functionalities control the temporal and the spatial arrangement of some inorganic solids.

One of the most elegant passivation routes is through self-assembly, that is spontaneous formation of passivating monolayers.\(^1\) It is well known that immersion of coinage metals such as gold, silver and copper in organic solutions of alkanethiols results in the spontaneous assembly of densely packed monolayers, termed the ‘self-assembled monolayers’ or SAMs, of the alkanethiols on the substrate surface.\(^60\) The surface functionalisation involves in the control of the interactions between the particles and a host medium, a substrate or other individual species like molecules, other particles or biological systems. This control is usually achieved through the process of functionalisation of the nanoparticles, which consists of grafting
molecules onto their surfaces with specific chemical functions. These functions may be chosen either

(i) to just ensure the stabilization of the particles by playing on dispersion forces, or

(ii) to allow their binding to more or less specific sites of the target substrate.\(^6\)

1.2.2. Different types of surface functionalisation

Inorganic nanoparticles such as gold, silver, CdS etc. can be stabilized with ionizable groups such as carboxylic acids and amine groups. \(\omega\)-functionalized thiol derivatives are normally used to modify the surface of noble metal and metal sulfide quantum dots. The thiol groups are known to chemisorb on such nanoparticle surface while the terminal ionizable or long chain functional groups enable stabilization of the particles via Coulomb and steric interactions. Depending upon the chemical nature of the surface of the nanoparticle, a different number of variants of the technique is used for the assembly of inorganic ions, biomacromolecules (proteins and DNA), and inorganic nanoparticles at the air-water interface.\(^6\) A few examples of organic surfactants are alkyl phosphine oxides, alkyl phosphonic acids, alkyl phosphines, fatty acids and amines, and some nitrogen-containing aromatics. These molecules all contain metal coordinating groups as well as solvophilic groups. The former group is typically electron-donating to allow coordination to the electron-poor metal atoms at the nanocrystals surface. This prevents further growth and aggregation.\(^9\)

Hydrophobic nanoparticles may simply float on the surface of the water, compressed into a close-packed monolayer and transferred onto suitable solid supports by the versatile Langmuir-Blodgett methods, using the Coulomb or electrostatic interactions in the nanoparticle (such as silver, gold, semiconductor quantum dots such as CdS and CdTe, oxides such as SiO\(_2\), TiO\(_2\), Fe\(_3\)O\(_4\), and \(\gamma\)-Fe\(_2\)O\(_3\) and latex spheres) assembly at the air-water interface.\(^6\)

To further derivatize the nanocrystal surface, introduction of other competing ligands is also possible, through surfactant exchange; allowing the introduction of a wide range of possible chemical functionalities. This strategy has the additional advantage for chemical manipulation of the nanocrystals properties which is sensitive to the
nature of the functionalized surface coating. One of the most popular soft lithographic techniques applications for creating patterned structured in SAMs is based on micro-contact printing (μCP). For sub-micron ranges silicon chips, photolithographic techniques are used; the pattern in the photo-resist is generated by light exposure through a mask followed by chemical development, transferred into thin films of immobilized molecules. The process of immobilization or functionalisation is in itself a large science which in turn is determined by the applicability. Thus, functionalisation of various nanosystems provides various means to link them to other surfaces and biomolecules.

1.2.3. Applications in biology

Functionalizing biomolecules on surfaces have applications that range from medical diagnostics, analytical chemistry, and culturing and studying cells on surfaces, to synthesizing or engineering useful biomolecules. A Lab-on-a-Chip device is a combination and integration of fluidic elements, sensor components and detection elements to perform the complete sequence of a chemical reaction or analysis, including sample preparation, reactions, separation and detection. Modifications of the surface of this device are essential for the designed functionality. These include modifications of wetting characteristics (hydrophobic/hydrophilic), increased biocompatibility, reducing or eliminating solute interactions, changing the electro-osmotic flow, immobilizing the reagents, enzymes, antibodies, proteins, DNA, etc. to carry out chemical reactions or detection mechanism, or to provide a proper surface for immobilization, increasing the surface area for catalytic reactions, and tethering sieving matrices or stationary phases for separation devices. The enhanced scattering cross section of metal nanoparticles due to surface field effects can be used as a powerful technique to image biological systems. Functionalizing gold particles with antibodies, such as anti-EGFR antibody, El-sayed et al., are able to distinguish between cancer and non-cancerous cells.

Of all the applications of nanoscience in biology, medicine forms the major thrust, in terms of impact and utilization. The design of multilevel molecular aggregates at nano- and meso- levels that have novel functional and dynamic properties (size-dependent and site-specific) are desirable for applications in medicine. Moreover,
nanomedicine forms the stepping of a highly modernized form of personalized medicine. Miniaturation, parallelization, integration, as well as automation, along with speed, convenience, accuracy and low cost are mandatory and this can be consummated in nanomedicine. Kristina Riehemann et al. discuss the diagnosis, analysis methods, therapy, research and development using nanomedicine. In addition to the developments in medical science and technology, progress in materials science definitely helps progress in medical device technology. The implants used in medicine interact with a highly sophisticated manner through its surface; hence biocompatibility is an important parameter to be considered seriously while designing an implant. The following two examples exemplify the importance of surface functionalisation as well as the application of nanobiotechnology.

The technology used in developing an implantation stent (used in combating vascular diseases and myocardial infarction) with the anti-proliferative drug, using nanoporous alumina membrane has saved millions of lives to date. The surface of the stent has to be functionalized accordingly using biocompatible material and drug storage-release capacity. Similarly, implantation of seeds containing radioactive nuclides (such as $^{125}$I and $^{103}$Pd) to irradiate tissues locally in cancers or to irradiate the restenotic area, uses nanostructure implant surfaces, that are safe, with the system acting as a nano test tube producing homogeneous activity.

1.3. Outline of the thesis

The thesis consists of 5 chapters.

• The second chapter describes the experimental procedures used in the research work for characterization and analysis, presented in this thesis. The principle, theory and working specifications are outlined with suitable diagrams wherever necessary.

• The third chapter describes the study of (i) gold nanoparticles synthesized by antibiotics like cephallexin, cefaclor and ampicillin and (ii) iron oxide nanoparticles capped by enzyme Penicillin G acylase. The synthesis, characterization and biological activity of these nanoparticles are discussed here.

• The fourth chapter describes the capturing of gold nanoparticles during its synthesis by the antibiotic cephallexin using optical methods like Dynamic Light Scattering (DLS) and Surface Plasmon Resonance using UV-Vis light spectroscopy.
These methods are elaborated for a better understanding. The data is supported by TEM micrographs and SAED pattern. Unique bimodal distribution is observed at different temperatures (15 °C, 25 °C & 35 °C) using DLS. This study also provides a good comparison between the different techniques used.

- The fifth chapter describes the functionalisation of gold nanoparticles in aqueous media using curcumin, the wonder drug obtained from turmeric, acting both as reducing and stabilizing agent. The study begins with the spectroscopic evidences of solubilising curcumin in water in a temperature-dependent manner. An attempt to explain the mechanism involved is elaborated. The as-synthesized gold nanoparticles are characterized using different techniques and these nanoparticles are shown to possess good anti-oxidant activity.
1.4. References
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Ramya Jagannathan University of Pune