Chapter 1

Introduction

1.1 Nanotechnology

Nanotechnology can be understood as the production, design, characterization and application of structures and systems by controlling size and shape of the specimen at nanoscale\textsuperscript{[1-3]}. Changing the matter size and shape makes it possible to create novel materials with innovated mechanic, electric, magnetic or optical properties\textsuperscript{[1-3]}.

Nanoscience and nanotechnology are recent revolutionary developments of science and engineering that are evolving at a very fast pace. These are driven by the desire to fabricate materials with novel and improved properties that are likely to impact all areas of physical and chemical sciences, biological sciences, health sciences, and other interdisciplinary fields of science and engineering.

1.2 Nanoparticles

Nano refers to nanometer (nm). One nanometer is one billionth of a meter\textsuperscript{1}. A specimen is called nanoparticle in the diameter ranges from 1 nm to 100 nm. But, among these, the particles having size within 30 nm are called strongly confined nanoparticles, whereas the particle ranging from 30 nm to 100 nm are called loosely confined nanoparticle. The size of the nanoscopic particles compared to that of other "small" particles is shown in Figure 1.1, where the bacteria is huge in comparison\textsuperscript{4}.

![Figure 1.1. Size comparisons of small particles\textsuperscript{4}.](image)


To get an idea of about the size of the nanoparticles, some examples are presented in the following table 1.1.

**Table 1.1: Different system compare to nanoparticles**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>Red Blood Cell</strong></td>
<td><strong>5000 nm</strong></td>
</tr>
<tr>
<td><strong>Diameter of DNA</strong></td>
<td><strong>2.5 nm</strong></td>
</tr>
<tr>
<td><strong>Wavelength of Red light</strong></td>
<td><strong>680 nm</strong></td>
</tr>
<tr>
<td><strong>Nanoparticles</strong></td>
<td><strong>1-100 nm</strong></td>
</tr>
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</table>

Because the nanoparticles are larger than individual atoms but are smaller than the bulk solid, materials in the nanometer size regime show behavior that is intermediate between that of a macroscopic solid and that of an atomic or molecular system. There are three major factors that are responsible for these differences: high surface-to-volume ratio, quantum size effect, and electrodynamics interactions. Metallic nanoparticles possess unique optical, electronic, chemical, and magnetic properties that are strikingly different from those of the individual atoms as well as their bulk counterparts.

Nanoparticles can be broadly divided into two categories:

1) Semiconductor nanoparticles, and

2) Metal nanoparticles

Semiconductor nanoparticles such as II-VI III-V and IV-V compound semiconductor nanoparticles show different electronic and optical properties from their bulk counterpart due to decrease in size. These nanoparticles have tunable band gap and show blue shift in the optical absorption spectra due to band gap enhancement.

On the other hand, metal nanoparticles show surface plasmon resonance in the absorption spectra, which is a unique optical property of metal nanoparticles. Like semiconductor nanoparticles, optical property of metal nanoparticles is size dependent.
dependent. (e.g. width and absorption peak of the absorption spectra also depend on the size).

1.3 General Properties of metal nanoparticles

Metal nanoparticles show the following unique properties:\cite{1,2,9}:

1.3.1 Surface to volume ratio

The important property associated with nanoparticles is the existence of large surface to volume ratio due to its extreme small size \cite{1,2}. For example, consider a cube of iron of side 1 cm, the percentage of surface atoms would be only $10^5\%$. Dividing the same cube into smaller cubes with side 10 nm, results in a percentage of surface atoms of 10% and in a cube with side 1 nm every atom would be a surface atom\cite{10}. It illustrates why changes in the size range of a few nanometres lead to great changes in the physical and chemical properties of the nanoparticle. This large surface to volume ratio results in many unique properties of nanoparticles\cite{1,2,10}.

1.3.2 Melting points

Nanoparticle of metals is found to have lower melting temperature as compared with their bulk forms, when the particle size decreases below 100 nm\cite{1,2}. The lowering of the melting points is in general explained by the fact that the surface energy increases with a decreasing size. The decrease in the phase transition temperature can be attributed to the changes in the ratio of surface energy to volume energy as a function of particles size\cite{1}. Surface atoms are more easily rearranged than those in the center of the particle, and so the melting process, which depends on destroying the order of the crystal lattice, can get started at a lower temperature. The melting point of gold metal is 1064°C. For 11-12 nm gold particles it is about 1000°C, then begins to drop dramatically to 900°C for 5 to 6 nm particles and to 700°C for 2 to 3 nm particles\cite{4}.

1.3.3 Mechanical Properties

It is found that nanostructured metals have higher or lower strength and hardness compared to coarse grained materials depending on the methods used to vary
the grain size $^{1-3}$. Mechanical properties of various nanstructured element metals have been studied including silver, copper, palladium, gold, iron and nickel; the actual role of grain size or grain boundaries on mechanical properties is not clear and many factors can have significant influence on the measurement of mechanical properties of nanostructured materials such as residual strains and internal stresses $^1$.

1.3.4 Optical properties

The reduction of materials' dimension has significant effects on the optical properties. The size dependence can be generally classified into two groups. One is due to the increased energy level spacing as the system becomes more confined and the other is related to surface plasmon resonance $^{1-3}$.

(a) Surface plasmon resonance

Surface plasma resonance $^{[1,11,12]}$ is the coherent excitation of all the free electrons within the conduction bond, leading to an in-phase oscillation. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface plasma resonance is generated $^{[11]}$. For larger nanoparticles, the resonance sharpens as the scattering length increases $^{[11]}$. Noble metals have the resonance frequency in the visible light range $^{[1,11]}$.

(b) Quantum size effect

The unique optical property of nanomaterial may also arise from quantum size effect. When the size of a nanocrystal is smaller than the de-Broglie wavelength, electrons are specially confined and electric dipoles are formed and discrete electronic energy levels would be formed in all materials $^{[1,11]}$. Similar to particles in a box, the energy separation between adjacent levels increases with decreasing dimensions. However, in order to observe the localization of the energy levels in metal, the size must be well below 2 nm, that is, when the nanoparticle is made of approximately 100 atoms $^{[1,2]}$. 

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1.3.5 Electrical conductivity

The electrical conductivity decreases with a reduced dimension due to increased surface scattering. However electrical conductivity of nanomaterial also can be enhanced appreciably by ordering the microstructure \(^1\)\(^{-2}\).

1.3.6 Magnetic properties

The magnetic properties of nanostructured materials are distinctly different from that of bulk materials. Ferromagnetism of bulk materials disappears and transfers to superparamagnetism in the nanometer scale due to huge surface energy \(^1\).

All these properties are size dependent \(^1\), \(^{11}\). Due to these amazing properties, it is applicable to different branches of science.

1.4 Metal nanoparticles and Magic numbers

About 70% of the elements are metals \(^{13}\). Many of these have face-centered cubic (FCC) crystal structures. Each atom in this close-packed structure is surrounded by 12 other atoms. Figure 1.2 shows the 12 neighbors that surrounded an atom located in the center of a cube for a FCC lattice and Figure 1.3 presents another perspective of the 12 nearest neighbors.

![Figure 1.2 FCC unit cell](image)
These 13 atoms represent the smallest theoretical nanoparticle for a FCC lattice. Figure 1.2 shows the 14-sided polyhedron called cuboctahedron, which maintains the FCC geometry. This 14-sided polyhedron has six square faces and eight equilateral triangle faces. If another layer of 42 atoms is laid down around the 13-atom nanoparticle, a 55 atom nanoparticle with the same cuboctahedron shape is formed and so on. The smaller a particle becomes, the more the proportion of surface atoms increases. The total number of atoms in particles, 1, 13, 55, 147, ..., are called “structural magic numbers”.

For $n$ layers the number of atoms $N$ in this FCC nanoparticle is given by the formula:

$$N = \frac{1}{2} (10n^3 - 15n^2 + 11n - 3) \quad \text{..........(1.1)}$$

And the number of surface atoms is

$$N_{surf} = [10n^2 - 20n - 12] \quad \text{..........(1.2)}$$
The diameter of each nanoparticle is given by the expression \((2n-1)d\), where \(d\) is the distance between the centers of the nearest neighbor atoms, and \(c = \frac{\alpha}{\sqrt{2}}\), where \(\alpha\) is the lattice constant.

Nanomaterials can be produced by both top down or bottom up approaches. Lithography is an example of top down approaches whereas chemical route is a bottom up approaches. Many techniques, including chemical and physical means, have been developed to prepare metal nanoparticles. Physical ways usually need a high temperature (over 1000 °C), vacuum and expensive equipments. There are also easy and convenient chemical methods that use dilute aqueous solutions and simple equipment. In this work chemical reduction method have been used to prepare a few noble metal nanoparticles such as silver, gold and copper nanoparticles.

The distinctive colors of colloidal gold, silver and copper are due to a fact known as plasmon absorbance. Incident light creates oscillations in conduction electrons on the surface of the nanoparticles and electromagnetic radiation is absorbed. Silver, copper and gold nanoparticles show surface plasmon band or plasmon absorbance in the visible range. The position, the shape and intensity of the surface plasmon resonance strongly depend on various factors including the size, shape and monodispersity of the nanoparticles, as well as the composition of the surrounding media and interactions between stabilizing ligands and the nanoparticles. Due to this absorption in the visible range, these nanoparticles have great potential as a sensor, in biological imaging and thermal therapy tumor cell and in photonics and Surface Enhanced Raman Spectroscopy (SERS).

This Ph.D work is confined to a few noble metal nanoparticles only, such as silver, gold and copper nanoparticles.

1.5 Present work

In the present work, it has been attempted to synthesize silver, gold and copper nanoparticles by chemical reduction method. These prepared nanoparticles have been characterized by X-ray diffraction study (XRD), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), UV-Visible absorption spectroscopy (UV-Vis) and photoluminescence (PL). Size and shape of the
nanoparticles have been analyzed by XRD and TEM study whereas optical characterization have been done by FTIR, UV-Vis and PL study. These nanoparticles are attempted to test in optoelectronics as nano light emitting device and in biology as antibacterial agent.

1.6 Thesis outline

In this dissertation, the whole research work has been arranged in the following way.

Chapter 1: The Introduction (This chapter)

Chapter 2: In this chapter the synthesis of silver, copper and gold nanoparticles have been discussed.

Chapter 3: This chapter contains the characterisation techniques of prepared nanoparticles (samples).

Chapter 4: In this chapter applications of silver, copper and gold nanoparticles as nano light emitting (LED) device have been described.

Chapter 5: Applications of silver, copper and gold nanoparticles as antibacterials agents have been described in this chapter,

Chapter 6: This chapter concludes the work with future direction.
References


