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Surface Plasmon Resonance of Gold and Silver Nanoparticles for Biomedical Physics Applications

A thesis

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وَفِي أَنْفُسِكُمْ أَفَلَا تُبْصِرُونَ

صدق الله العظيم

سورة الناريات

آية (٢١)



Dedication

To

Father and Mother

Brother and Sisters

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Published and Accepted Research Articles

- ❖ Rusul k. Ismail, Raad M. S. Al-Haddad and Tahseen H. Mubarak, "Time Effect on the Red Shift of Surface Plasmonic Resonance Core-Shell SiO₂: Gold Nanoparticles (AuNPs)", IP Conference Proceedings 2190, pp. 1-6, (2019).
- ❖ Rusul k. Ismail, Tahseen H. Mubarak and Raad M. S. Al-Haddad Surface Plasmon Resonance of Silver Nanoparticles: Synthesis, Characterization and Applications, J Biochem Tech, 10 (2), pp. 62-64, (2019).

Abstract

In this study, an identical surface plasmon resonance (SPR) within high surface energy of gold and silver nanoparticles spherical was chemically synthesized without and with coating by nano thin film layer of silica for treating the cell lines (MCF-7 and HBL-100).

Gold nanoparticles were chemically synthesized by Turkevich method from chloroauric acid and trisodium citrate dihydrate. The determination of the parameters effect such as temperature, trisodium citrate dihydrate content, deionized water volume, mixing speed, SiO₂ content, deionized water volume, gold nanoparticles solution volume and ethanol volume on the position of surface plasmon resonance (SPR), particle size, size distribution and shape gold nanoparticles in the blue and red shift regions were confirmed. While silver nanoparticles were chemically synthesized by reduction with gallic acid from silver nitrate and gallic acid, also the parameters effect such as time, gallic acid weight, temperature, SiO₂ content, silver nanoparticles solution volume and ethanol volume on position of surface plasmon resonance (SPR) of silver nanoparticles in blue and red shift regions were confirmed.

Optical measurements results showed peak band surface plasmon resonance (SPR) of gold nanoparticles (AuNPs) at 515nm and this peak shifted to 518nm after coating. In same time, the optical measurements of silver nanoparticles (AgNPs) adjusted by NaOH and NH₄OH showed that the peak band surface plasmon resonance (SPR) was shifted from 396nm to 398nm and from 405nm to 414nm respectively.

FTIR spectrum measurements results showed strong absorption peaks of the gold nanoparticles at 3431, 2341, 1627, 1506, 1388, 975, 962,632, 524 and 499 cm⁻¹, also strong absorption peaks showed at 3431, 2866, 2802, 2343, 2320 ,1622, 1616, 1494 1489 ,1384, 1379, 1072, 1062,

966, 655, 636 543, 484 and 426 cm^{-1} of silver nanoparticles adjusted by NaOH and NH_4OH , also it is observed that the gold and silver nanoparticles after coating almost have the same absorption peaks with a little shift for some absorption peaks this means that the coating method led to a little increase in the size with maintaining on nanoparticles shape and prevents it from deforming, the absorption bands 524 and 499 cm^{-1} of gold nanoparticles refer to harmony happening between inorganic elements (gold) and organic compounds (Trisodium Citrate Dihydrate), while refer the absorption bands 543, 484 and 426 cm^{-1} of silver nanoparticles to harmony happening between inorganic elements (silver) and organic compounds (Gallic acid).

Structure measurements results showed that the gold nanoparticles have a narrow size distribution and spherical shape with an average size 3-6nm. On another hand, there was a narrow size distribution and a little increase in the particles size 9-18nm that retaining its spherical shape with stability increase from (-25.02mV) to (-25.92mV) after coating by nano thin film layer of silica. In same time, the structure measurements of silver nanoparticles (AgNPs) adjusted by NaOH and NH_4OH showed have a narrow size distribution and spherical shape with an average 6-8nm and 3-6nm respectively. On another hand, there was a narrow size distribution and a little increase in the particles size 10-19nm and 12.9-16.7nm of coated AgNPs adjusted by NaOH and NH_4OH respectively that retaining its spherical shape with stability increase from (-58.17mV) and (-15.68mV) to (-62.86mV) and (-43.60mV) respectively after coating by nano thin film layer of silica.

Toxicity examination results showed of the surface plasmon resonance (SPR) of gold and silver nanoparticles without and with coating by nano thin film layer of silica have ability to destroy for MCF-7

cells at all concentrations. While, surface plasmon resonance (SPR) of gold and silver nanoparticles showed different effects on the normal HBL -100 cell line.

Therefore, the best optimization concentration of surface plasmon resonance (SPR) of gold nanoparticles (AuNPs) before and after coating by nano thin film layer of silica on MCF-7 and HBL-100 cell lines was 50 μ g/ml and 25 μ g/ml respectively showed the best rate of destroy MCF-7 cell line and on same time 50 μ g/ml and 25 μ g/ml was less the destroy rate of HBL-100 cell. While, the best optimization concentration of surface plasmon resonance (SPR) of silver nanoparticles (AgNPs) adjusted by NaOH and NH₄OH before and after coating by nano thin film layer of silica on MCF-7 and HBL-100 cell lines was 50 μ g/ml showed the best rate of destroy MCF-7 cell line and on same time 50 μ g/ml was increased the growth rate of HBL-100 cell.

Therefore, this study also provides the conclusive evidence of surface plasmon resonance (SPR) of gold and silver nanoparticles has toxic effect against breast cancer MCF-7 cell line at all concentrations compared with HBL-100 normal breast cell line. Further studies are required to elucidate the precise molecular mechanism involved in cell growth inhibition thereby permitting the synthesized chemically surface plasmon resonance (SPR) of gold and silver nanoparticles of cancer chemopreventive and/or therapeutic agents.

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List of Abbreviations

Symbol	Definition
SPR	Surface Plasmon Resonance
SPE	Surface Plasmon Extinction
SERS	Surface Enhanced Raman Scattering
LSPR	Localized Surface Plasmon Resonance
SP	Surface Plasmon
SPB	Surface Plasmon Band
CNT	Carbon Nanotubes
QDs	Quantum Dots
QD	Quantum Dot
QC	Quantum Confinement
NPs	Nanoparticles
AuNPs	Gold Nanoparticles
GNPs	Gold Nanoparticles
AgNPs	Silver Nanoparticles
SNPs	Silver Nanoparticles
TCD	Trisodium Citrate Dihydrate
GA	Gallic Acid
NTFL	Nano Thin Film Layer
SA:V	Surface Area per Unit Volume Ratio
AR	Aspect Ratio
NIR	Near-Infra Red
ROS	Reactive Oxygen Species
PDT	Photodynamic Therapy
PVs	Photovoltaics
BNCs	Bio-nanocomposites
UV-Vis	Ultraviolet-Visible
FTIR	Fourier Transform Infrared
AFM	Atomic Force Microscope
TEM	Transmission Electron Microscopy
FESEM	Field Emission Scanning Electron Microscope

AAS	Atomic Absorption Spectroscopy
SEM	Scanning Electron Microscope
SPM	Scanning Probe Microscope
STEM	Scanning Transmission Electron Microscopy
SAXS	Small Angle X-ray Scattering
DLS	Dynamic Light Scattering
MCF-7	Michigan Cancer Foundation-7
HBL-100	Human Breast Lactating, donor 100
SAR	Specific Absorption Rate
ROS	Reactive Oxygen Species
IC	Inhibitory Concentration
RPMI	Rosswell Park Memorial Institute
PBS	Phosphate Buffer Saline
MEM	Minimal Essential Medium
SFM	Serum Free Medium
FBS	Fetal Bovine Serum
DDW	Double Distilled Water
DDDW	Double Distilled Deionized Water
HEPES	(-hydroxyethyl)-1-piperazineethanesulfonic acid)-2)4
ICCMGR	Iraqi Center for Cancer and Medical Genetic Researches

List of Symbols

Symbol	Definition	Unit
A	Absorbance	-
λ	Wavelength	nm
I(z)	Intensity of the Incoming Beam After a Distance	$\text{eV/m}^2 \cdot \text{S}$
I_0	Incident Intensity	$\text{eV/m}^2 \cdot \text{S}$
I	Transmit Intensity	$\text{eV/m}^2 \cdot \text{S}$
n_0, N	Number of Particles Per Unit Volume	cm^{-3}
σ_{ext}	Extinction Cross-Section of a Single Particle	cm^{-2}
σ_{sca}	Scattering Cross Sections of a Single Particle	cm^{-2}
σ_{abs}	Absorption Cross Sections of a Single Particle	cm^{-2}
ω_d	Scattering Frequency	Hz
v_F	Electron Velocity at Fermi Level	m/s
r_∞	Mean Free Path of the Electron in the Bulk Metal	nm
G	Free Energy or Gibbs Free Energy	J
ΔG	Gibbs Free Energy Change	J m^{-3}
ΔG^*	Critical Free Energy Change	J
ΔH_f	Latent Heat of Fusion	J m^{-3}
H	Enthalpy	J mol^{-1}
S	Entropy	$\text{J mol}^{-1} \text{K}^{-1}$
γ	Surface Free Energy	J m^{-2}
T	Temperature	Kelvin
T_m	Melting Point	Kelvin
R''	Mean Free Path	nm
r, R	Particle Radius	nm
r^*	Critical Radius	nm
C	Concentration	$\mu\text{g/ml}$
Mo	Molar Concentration	mol/l
M.Wt	Molecular Weight	g/mol
V	Volume of Solution	ml
Wt	Weight	g



Chapter One

Concept of Nanoscience and Literature Review

1.1 Introduction

This chapter includes general introduction about the history of nanophysics, nanoparticles and their distinctive characteristics that made them enter in many different applications physical and biological. In addition to the literature review and aim of the work.

1.2 History of Nanophysics

The nanophysics is halfway between the size scales of quantum mechanics and macroscopic physics governed by the laws of Newton and Einstein. The correct definition of nanophysics is the physics of structures and artefacts with dimensions in the nanometer range or of phenomena occurring in nanoseconds. Modern physical methods whose fundamentals are developed in physics laboratories have become critically important in nanoscience. Nanophysics brings together multiple disciplines, using theoretical and experimental methods to determine the physical properties of materials in the nanoscale size range. Interesting properties include the structural, electronic, optical, and thermal behavior of nanomaterials; electrical and thermal conductivity; the forces between nanoscale objects; and the transition between classical and quantum behavior. Nanophysics has now become an independent branch of physics, simultaneously expanding into many new areas and playing a vital role in fields that were once the domain of engineering, chemical, or life sciences [1].

Nanoscience and nanotechnology are all about relating and exploiting phenomena for materials having one, two or three dimensions reduced to the nanoscale. Breakthroughs in nanotechnology require a firm grounding in the principles of nanophysics. It is intended to fulfill a crucial purpose. Nanophysics aims to connect scientists with disparate interests to begin interdisciplinary projects and incorporate the theory and

methodology of other fields into their work. Their evolution may be related to three exciting happenings that took place in a short span from the early to mid-1980s with the award of Nobel prizes to each of them. These were: (i) the discovery of quantum Hall effect in a two-dimensional electron gas; (ii) the invention of scanning tunnelling microscopy (STM); and (iii) the discovery of fullerene as the new form of carbon. The latter two, within a few years, further led to the remarkable invention of the atomic force microscope (AFM) and, in the early 1990s the extraordinary discovery of carbon nanotubes (CNT), which soon provided the launch pad for the present-day nanotechnology [2].

The STM and AFM have emerged as the most powerful tools to examine, control and manipulate matter at the atomic, molecular and macromolecular scales and these functionalities constitute the mainstay of nanotechnology. Interestingly, this exciting possibility of nanolevel tailoring of materials was envisioned way back in 1959 by Richard Feynman in his lecture, “There’s plenty of room at the bottom” [3].

1.3 Classification of Nanomaterials

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

According to the order of dimensionality, Nano materials can be classified as zero, one, two and three dimensional nanostructures [4].

1. Zero-dimensional (0-D) nanostructures

Zero-dimensional Nano materials are materials where all the dimensions are measured within the Nano scale. Also named as NPs with all possible morphologies, such as spheres, cubes and platelets these NPs include single crystal, polycrystalline and amorphous particles. If the NPs are single crystalline, they are often referred to as Nano crystals. When the NPs have dimension sufficiently small and quantum confinement effects are observed, the common term used to describe such NPs is quantum dots [4].

2. One-dimensional (1-D) nanostructures

The one-dimension Nano materials have one dimension that is outside the Nano scale. This type has been called by a change of names such as: whiskers, fibers or fibrils, nanowires and Nano rods. In many cases one-dimensional systems take into account carbon-based, metal-based or even oxide-based systems. Nanotubes and Nano cables are also considered one dimensional structures if the extension over one dimension is predominant over the other types [4-6].

3. Two-dimensional (2-D) nanostructures

Two-dimensional Nano materials are materials in which two of the dimensions are not confined to the Nano scale. They are one more important nanostructure, they include many shapes such as Nano films, Nano layers, Nano coatings and Nano discs, and thus they have been a subject of intensive study for almost a century [4-6].

4. Three dimensions (3-D) system

Three-dimensional Nano materials, as well known as bulk Nano materials, are relatively difficult to classify. However, it is true to say that bulk Nano materials are materials that are not confined to the Nano scale

in any dimension. These materials are thus characterized by having 3 randomly dimension above 100 nm [4].

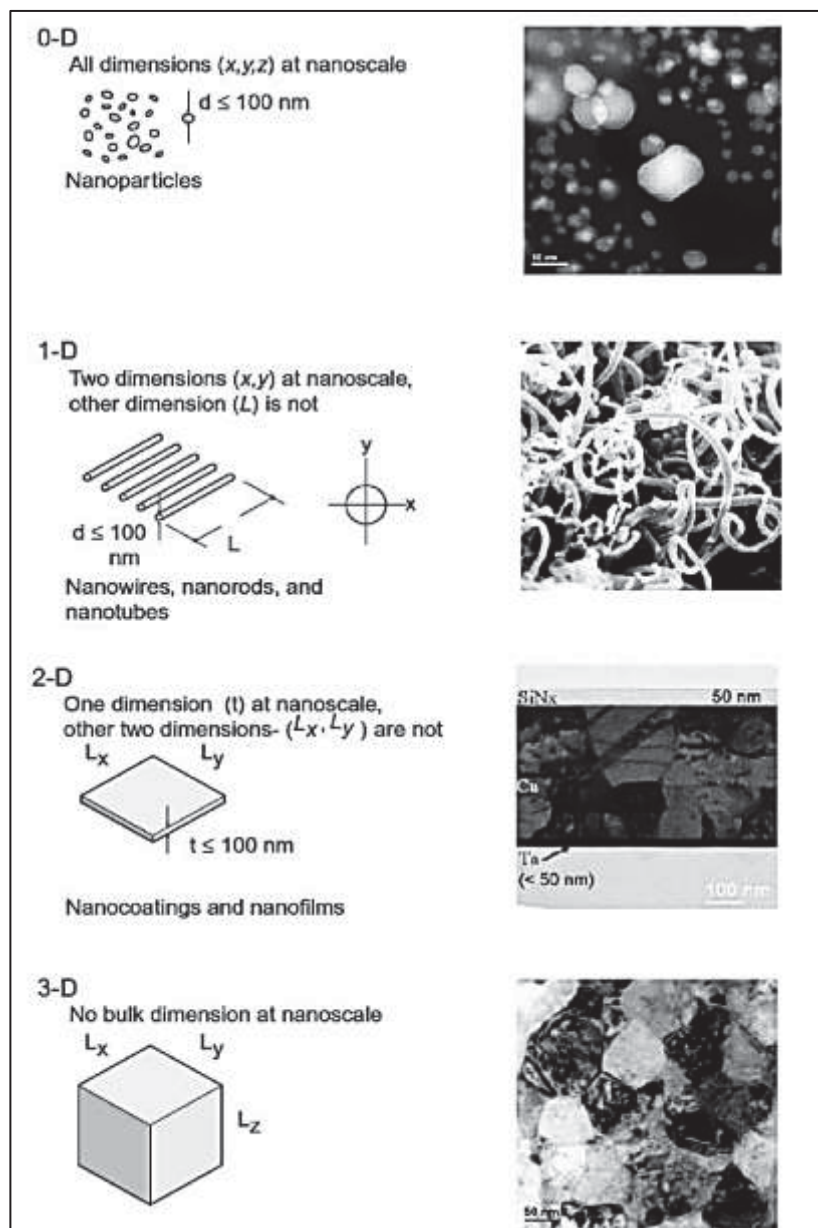


Fig 1.1: Classification of nanomaterial according to 0-D, 1-D, 2-D and 3-D [4].

1.4 Nanoparticles

The term “nanoparticles” is used to describe a particle with size in the range of 1-100nm, at least in one of the three possible dimensions. In this size range, the physical, chemical and biological properties of the nanoparticles changes in fundamental ways from the properties of both

individual atoms/molecules and of the corresponding bulk materials. Nanoparticles can be made of materials of diverse chemical nature, the most common being metals, metal oxides, silicates, non-oxide ceramics, polymers, organics, carbon and biomolecules. Nanoparticles exist in several different morphologies such as spheres, cylinders, platelets, tubes etc. Generally the nanoparticles are designed with surface modifications tailored to meet the needs of specific applications they are going to be used for [7].

1.5 Types of Nanoparticles

Nanoparticles can be broadly grouped into two, namely, organic nanoparticles which include carbon nanoparticles (fullerenes) while, some of the inorganic nanoparticles include magnetic nanoparticles, noble metal nanoparticles such as (gold and silver) and semi-conductor nanoparticles such as (titanium oxide and zinc oxide). There is a growing interest in inorganic nanoparticles i.e. of noble metal nanoparticles (gold and silver) as they provide superior material properties with functional versatility. Due to their size features and advantages over available chemical imaging drug agents and drugs, inorganic particles have been examined as potential tools for medical imaging as well as for treating diseases. Inorganic nonmaterial have been widely used for cellular delivery due to their versatile features like wide availability, rich functionality, good compatibility, and capability of targeted drug delivery and controlled release of drugs [7].

1.6 Noble Metal Nanoparticles

Noble metal nanoparticles such as Ag and Au NPs have been a source of great interest due to their novel electrical, optical, physical,

chemical and magnetic properties [8,9]. They were very attractive for biophysical, biochemical, and biotechnological applications due to their unusual physical properties, especially due to their sharp plasmon absorption peak at the visible region. Gold and silver nanoparticles are chemically stable and typically exhibit surface enhanced Raman scattering (SERS) in the visible wavelength range, where they may cause a tremendous increase in various optical cross-sections. The resonance frequencies strongly depend on particle shape and size as well as on the optical properties of the material within the near-field of the particle [10]. Silver, for example, has been for thousands of years, used as a disinfectant; from the other side nobody can neglect its value as a catalyst [11]. On the other hand, gold nanoparticles have gained considerable attention in recent years for potential applications in nanomedicine due to their interesting size dependent chemical, electronic and optical properties. Also, gold nanoparticles show promise in four enhancing the effectiveness of various targeted cancer treatments such as radiotherapy and photothermal therapy [12].

Metals nanoparticles exhibit improved properties such as plasmon resonance characteristics depending upon their size and morphologies [13]. An interesting thing about some metallic nanoparticles and especially silver and gold nanoparticles, is that these particles show strong plasmonic properties. When light photons interact with the surface of metal nanoparticles, the outer free electrons of the particles form localized plasmons [14]. Plasmons are density waves of the free outer electrons. Specific wavelengths of light cause the outer electrons to oscillate. This phenomenon is called the surface plasmon resonance (SPR). When these resonances occur, the intensities of absorption and scattering are much higher than those of the same particles without plasmonic properties. SPR are highly dependent on particle

characteristics [15]. A wide range of metal nanoparticles applications has emerged in consumer products ranging from disinfecting medical devices and home appliances to water treatments. Here we mainly discuss the applications of metal nanoparticles in biomedical.

1.6.1 Advantages of Metallic Nanoparticle

- ❖ Enhance Rayleigh scattering
- ❖ Surface enhanced Raman scattering
- ❖ Strong plasma absorption
- ❖ Biological system imaging
- ❖ Determine chemical information on metallic nanoscale substrate [16].

1.6.2 Disadvantages of Metallic Nanoparticles

- ❖ **Particles instability:** Nanomaterials can undergo transformation, as they are thermodynamically unstable and lie in the region of high energy local minima. This leads to deterioration of quality, poor corrosion resistance, and main concerned is retaining the structure becomes difficult.
- ❖ **Impurity:** While synthesising nanoparticles, nitrides, oxides, formation can aggravated from the impure environment. As nanoparticles are highly reactive, there can also be high chances of impurity as well. In solution form, nanoparticles should be synthesized in form of encapsulation. So, it becomes a challenge to overcome impurity in nanoparticles.
- ❖ **Biologically harmful:** nanomaterials has been reported toxic, carcinogenic and cause irritation as they become transparent to the cell dermis.

- ❖ **Explosion:** exothermic combustion can lead to explosion, as fine metal particles act as strong explosives.
- ❖ **Difficulty in synthesis:** while synthesizing nanoparticles, it should be encapsulated, because it is extremely challenging to retain the nanoparticles size in solution form [17].

1.6.3 Characteristics of Metallic Nanoparticles

- ❖ Large surface energies
- ❖ As compared to bulk they have large surface area to volume ratio
- ❖ Quantum confinement
- ❖ Plasmon excitation
- ❖ Increased number of kinks [18].

1.7 Literature Review

Castanon *et al.* (2008) prepared silver nanoparticles chemically from gallic acid, and studied antibacterial activity of silver nanoparticles with different sizes. UV–Vis spectrum show that the absorption spectrum of spherical silver nanoparticles present a maximum 420-450nm. TEM show that AgNPs are spherical and pseudospherical shape with the size ranges 7-89nm. It was found that the antibacterial activity of the nanoparticles varies when their size diminishes [19].

Tabrizi *et al.* (2009) prepared gold nanoparticle chemically by Turkevich method from chloroauric acid and trisodium citrate dehydrate, and also determined the effect of initial gold concentration, trisodium citrate concentration and mixing rate on particle size and size distribution were investigated the advantages for self-assembled monolayer formation and enhanced surface area [20].

Bahadur *et al.* (2011) prepared gold nanoparticles chemically from chloroauric acid and trisodium citrate dehydrate with a mean particle size 16nm. Au@SiO₂ nanoparticles prepared by microwave method the size uniformity and monodispersity were found to be better compared to the particles prepared by conventional methods. UV–Vis spectrum showed that the absorbance of SPR of AuNPs without coating at 522nm and this peak was shifted to longer wavelength after coating. Zeta potential of AuNPs before coating -52 mV and increase zeta potential of AuNPs after coating [21].

Amarnath *et al.* (2011) studied facile synthesis of biocompatible gold nanoparticles from vites vinefera and its cellular internalization against HBL-100 cells. Absorption measurements indicated that the Plasmon resonance wavelength of GAuNPs was 535 nm. TEM shows that AuNPs have spherical shape with the size ranges 20-45nm. Higher concentration of AuNPs conjugate, there was an asymmetric accumulation of AuNPs in the periphery of the cell nucleus of the HBL-100 cells which was confirmed by fluorescence microscopy [22].

Vivek *et al.* (2012) studied green biosynthesis of silver nanoparticles from Annona squamosa leaf extract and its in vitro cytotoxic effect on MCF-7 and normal HBL-100 cells. UV–Vis spectrum showed an absorption peak SPR of AgNPs at 444nm. TEM photography showed that AgNPs have spherical shape with the size ranges 20-100nm. The zeta potential value was -37mV. The cytotoxicity effect of AgNPs against MCF-7 increases with increasing concentration of AgNPs and did not affect the normal cells (HBL-100). However, increased concentration of AgNPs produced significant toxicity against the normal HBL 100 cells [23].

Jeyaraj *et al.* (2013) prepared biogenic silver nanoparticles from sesbania grandiflora leaf extract, and studied cytotoxicity effect of (AgNPs) against

MCF-7 cells. UV–Vis spectrum showed an absorption peak SPR 420nm. FT-IR spectrum shows the strong band at 1646cm^{-1} corresponds to the C=C stretches and broad peaks at 3394cm^{-1} clearly indicates the N-H stretches. The prominent bands at 1070cm^{-1} can be assigned as absorption bands of C-O-C. The band at 1397cm^{-1} in AgNPs may attribute to C-O stretching mode. FESEM micrograph, shows spherical shaped particles with the average size range 22 nm. AgNPs induce cytotoxicity on MCF-7 cell lines was found to be higher with increased concentration of AgNPs [24].

Britto and Química (2013) prepared silver nanoparticles using polyvinylpyrrolidone (PVP) as stabilizing agent, and capping AgNPs with mesoporous silica was obtained by sol-gel reaction using tetraethylorthosilicate (TEOS) in the presence of hexadecyltrimethyl ammonium bromide (CTAB). UV–Vis spectrum showed a single narrow band of AgNPs and AgNPs-SiO₂ at 419nm and 425nm respectively. Zeta potential analysis revealed stable AgNPs and AgNPs-SiO₂ -1.10mV and -28.9mV respectively. STEM shows silver-mesoporous silica nanoparticles, where nanoparticles with core-shell architecture and spherical shape are observed. SAXS shows AgNPs have 19 nm size whereas AgNPs- SiO₂ have 21 nm size [25].

Rejeeth et al. (2014) studied biosynthesis of silver nanoscale particles using spirulina platensis induce growth-inhibitory effect on MCF-7. UV–Vis spectrum showed an absorption peak SPR of AgNPs at 420nm. The zeta potential value of -36mV revealed the stability of AgNPs. SEM analysis, shows less aggregation with particles are spherical in shape and the size ranges 10-200nm. The in vitro screening of the AgNPs showed potential cytotoxic activity against MCF-7 and HBL-100 cells the inhibitory concentration (IC₅₀) were found to be 20, 40, 60 and 80 µg/ml

for AgNPs against MCF-7 and HBL-100 cells at 24 and 48h incubation respectively [26].

Sulthana *et al.* (2014) prepared silver nanoparticle chemically from gallic acid and studied antiphytopathogenic activity. The reduction of pure Ag⁺ ions was monitored by measuring in the UV-Vis Spectroscopy at 426nm. The plasma resonance of the gallic acid reduced silver particle is brownish yellow. TEM photography showed that AgNPs are spherical shape with the size range 14-60nm. Broth dilution method revealed antiphytopathogenic activity of the gallic acid reduced Terminalia chebula Retz. Silver nanoparticles against Xanthomonos axonopodis pv. malvacearum at a concentration of 70µg/ml [27].

Lakshmipathy and Nanda (2015) prepared silver nanoparticle chemically from gallic acid, and studied its biomedical application. UV-Vis spectrum showed narrow peak with λ_{\max} at 424nm. FESEM micrograph show the narrow size distribution of AgNPs with size <30nm and spherical to nearly spherical in shape. AgNPs showed potent antiproliferative activity on HEp-2 cells with IC₅₀<1mg/mL concentration accompanied by morphological disturbances and membrane damage. The strong affinity toward intracellular proteins and thiol formation accounts for its toxicity which may further be extended for varied biomedical applications as a broad spectrum therapeutic agent [28].

Loutfy *et al.* (2015) prepared gold nanoparticles and silver nanoparticle chemically from (chloroauric acid and trisodium citrate dehydrate) and (Silver nitrate, sodium citrate and polyvinyl pyrrolidone (PVP)) respectively, and studied the cytotoxic effects of metallic nanoparticles on MCF-7 cells. UV-Vis spectrum revealed a peak at 522nm and 405nm of AuNPs and AgNPs respectively. TEM photography showed that AuNPs and AgNPs are spherical shape. Zeta potential of AuNPs and AgNPs -33.6mV and -9.45mV respectively. Treatment of MCF-7 different with

different concentrations, with IC_{50} value at $14.48\mu\text{M}$ of AuNPs and IC_{50} value at $6.28\mu\text{M}$ of AgNPs [29].

Rahman (2016) prepared gold nanoparticles chemically by Turkevich method from chloroauric acid and trisodium citrate dehydrate. UV–Vis spectrum showed SPR Peaks occurs 517nm . SEM images showed that GNPs are spherical shape and different size GNPs exist in the solution which would cause some discrepancy between the actual and theoretical calculation [30].

Yahia and Al-Haddad. (2017) prepared gold nanoparticles chemically by Turkevich method from chloroauric acid and trisodium citrate dehydrate, then they were coated with sodium silicate stock solution and studied the effect of silica concentrations on the absorbance of AuNPs. UV-Vis spectrophotometer showed that the absorbance of SPR of AuNPs without coating at 521nm and 522nm with coating [31].

Acharya *et al.* (2017) studied comparative antibacterial properties of Ag and Ag@SiO₂ core-shell nanoparticles. UV–Vis spectrum showed the SPR peak of AgNPs at 425nm while for silica coated silver nanoparticles, the SPR peak shifts to 426nm . TEM photography showed that average size of AgNP $\sim 14\text{nm}$ and average size of silica coated silver nanoparticles $\sim 17\text{nm}$ [32].

Afrapoli *et al.* (2018) [35] prepared gold nanoparticles chemically by Inversed Turkevich from chloroauric acid and trisodium citrate dehydrate, and studied the effect of concentration and temperature on size. UV- Vis spectra show that absorbance curve of each samples had a single visible peak that was positioned in range of $519\text{-}531\text{nm}$ and it was related to spherical monodisperse gold nanoparticles. TEM photography showed that gold nanoparticles are spherical shape with the average size of $11.82\pm 1.77\text{nm}$ [33].

Yadav (2018) Prepared gold nanoparticles chemically by Turkevich method from chloroauric acid and trisodium citrate dehydrate. UV–Vis spectrum showed peak band at 520nm. FTIR spectrum shows peaks at 3129.94 and 3003 cm^{-1} are assigned to C-H ring stretching vibrations. The peaks at 1637 and 1474.79 cm^{-1} correspond to N-H bending (or C=C-bond) and the symmetric component of the C-C (or C-H) stretching modes. The bands at 1231 and 1059.30 cm^{-1} can be attributed to C-N bonding. Zeta potential of AuNPs -19 mV [34].

Thapliyal and Chandra (2018) Prepared silver nanoparticle chemically from gallic acid, and studied its antibacterial and anticancer potential of silver nanoparticles synthesized. UV–Vis spectrum showed narrow peak with λ_{max} at 412nm. SEM and DLS measurements showed spherical nanoparticles with a mean size of 68.06 \pm 0.2 nm. The negative surface zeta potential with -32 \pm 0.25 mV has indicated colloidal stability of nanoparticles. The synthesized AgNPs in bio-nanocomposites (BNCs) is a potential candidate for inhibiting the growth of pathogenic bacteria and showed significant cytotoxicity against MCF-7 cancer cell line with IC_{50} of 160 \pm 0.014 μg [35].

Dong *et al.* (2019) prepared gold nanoparticles chemically by Turkevich method from chloroauric acid and trisodium citrate dehydrate. The effect of the molar ratio of the reagent mixture (trisodium citrate to gold chloride), the scaled-up batch size, the initial gold chloride concentration, and the reaction temperature were studied. The AuNPs size was tuned from 15nm to 50nm by decreasing the molar ratio of NaCt to HAuCl₄ from 2.8 to 1.5. However, the AuNPs became more polydispersed and less spherical as the molar ratio de-creased. The batch synthesis was scaled up to 1.5L and the as-synthesized AuNPs exhibited identical optical property and morphology as the AuNPs synthesized in 50ml batches. At a constant molar ratio, the initial con-centration of HAuCl₄

had minimal effect on the final particle size and size distribution within the range tested. The particle size increased with decreasing reaction temperature at the molar ratio of 2.5. However, there was no significant effect of temperature on the particle size at the molar ratio of 7.6 [36].

1.8 Aim of the Work

- ❖ To synthesis the surface plasmon resonance (SPR) of gold and silver spherical nanoparticles.
- ❖ To determine the identical surface plasmon resonance (SPR) within high surface energy of gold and silver spherical nanoparticles in the blue and red shifts.
- ❖ To maintain and control on the shape and size of the nanoparticles and increasing its stability by coating nano thin film layer of silica.
- ❖ To evaluate the biological effect of gold and silver spherical nanoparticles without and with coating by nano thin film layer of silica on the treatment of the human breast cancer cell line (MCF-7) and normal cell (HBL-100).