# Nanoparticle Resonance Mechanism Behaviour in a Dye Environment

**Dr Vadiraj B Tangod***
Associate Professor
Head of Department of Physics
Government First Grade
College for Women’s
Dharwad-580008
Karnataka, India
vadirajtangod@gmail.com
*Corresponding author

**Dayanand Lalasangi**
Assistant Professor
Head of Department of Physics
Government First Grade
College, Dharwad-580008.
Karnataka, India
dayanandlalasangi@gmail.com

**Dr Sangeeta Kulkarni**
Assistant Professor
Head of Department of
Chemistry
Government First Grade
College, Dharwad-580008
Karnataka. India
sangeeta_bk1234@yahoo.com

## ABSTRACT

Nanoscience and nanotechnology are recent breakthrough scientific and technological advancements that have been advancing at a breakneck rate over the last decade. Because of the high surface-to-volume ratio, the quantum size effect, and electrodynamic interactions, materials in the nanoscale size domain exhibit behaviour that is transitional between that of a macroscopic solid and that of an atomic or molecular system.

Mie's Scattering theory was used to explore the optical characteristics of nano particles and their dependency on particle size. The surface plasmon resonance (SPR) is connected to the absorption spectra of gold nanoparticles with sizes ranging from 4 to 12nm. Our major aim is to use Mie's theory and available simulations to compute the extinction, absorption, and scattering coefficients of gold nanoparticles of various sizes. The observed results show that when the size of the nanoparticles rises from 4 to 50nm, the extinction efficiency at the resonant peak improves, as does the SPR shift from 520nm to 570nm.

The fluorescence and optical absorption intensities of the ADS680HO laser dyes in alcohol solvents with and without AuNP/AgNP bonding reveal quenching. This is related to the size, shape, energy transfer, and interaction of the AuNPs/AgNPs with the dye. Fluorescence quenching using AuNPs/AgNPs and ADS680HO laser dye has various uses, particularly in biomolecular labelling and fluorescence patterning.

Key words:, AuNP’s, AgNP’s, SPR, Quenching, Dye, Nanoparticles

## I INTRODUCTION

In the most recent technical discipline, nanoscience and nanotechnology are leading humanity into new realms of efficient and small tools and gadgetry. Every multidisciplinary subject, such as physics, chemistry, biology, or applied science, such as medicine or engineering, is erupting with enormous new nanoscale discoveries.

The typical field of physics or chemistry is the study of atoms and molecules. An atom is approximately 1-10 angstrom (1 = $10^{-10}$ metre). However, particles with sizes ranging from 1-100nm (1nm = $10^{-10}$ metre) are referred to as nanoparticles, regardless of whether they are distributed in gaseous, liquid, or solid environments. Studies conducted in the late nineteenth and early twentieth centuries revealed that the nanometre (nm) represents a collection of a few atoms or molecules. Materials at the 1-100nm scale have demonstrated that the physical, chemical, and optical characteristics of a material are affected by its size and form. Because of the absence of symmetry at the interface or electron confinement that does not scale linearly with size, new features emerge at the nanoscale. Because of the absence of symmetry at the interface or electron confinement that does not scale linearly with size, new features emerge at the nanoscale. As a result, the nanometre scale (1-100nm) includes groups of atoms or molecules with characteristics that are neither of the individual constituents nor of the bulk.

Metallic nanoparticles have optical, electrical, chemical, and magnetic characteristics that are distinct from those of individual atoms and their bulk equivalents. Nano-sized metal particles ($10^{-9}$m) display optical qualities of high aesthetic, technological, and intellectual significance. Colloidal solutions of the noble metals, silver and gold, exhibit distinct hues that have piqued the interest of researchers.

Silver and gold are the metals found in nature in pure forms. The nanoparticles of these metals are having an extensive usage in the treatment of various diseases viz., cancer, diseases caused by various bacteria's, as drug delivery tools. Synthesis of the gold and silver nanoparticles using plant extracts has good advantage over the use of synthetic chemicals. The method of synthesizing the nanoparticles by using plant extract is very simple, less time consuming, eco friendly and economical compared to other methods.

Gustav Mie (1869-1957), a German physicist, wrote an important essay on light scattering in matter in Annalen Der Physik in 1908 with the title *“Beitr¨age zur Optik tr¨uber Medien, speziell kolloidaler Metall¨osungen*" This theoretical study serves as the basis for the theory that describes the optical characteristics of tiny metal particles. Metal particles, such as nanogold, are tiny in relation to the visible wavelength and exhibit distinct absorption and scattering characteristics. Gustav Mie used classical electromagnetic theory and the bulk optical characteristics of metallic gold to calculate the absorbance of colloidal gold particles as a function of particle size. This paper includes extensive calculations for gold and silver nanoparticles.

In this direction our study concentrates on the absorption and emission maxima of the ADS680HO and is very sensitive to the solvent polarity. This behaviour is mainly because of large difference in the dipole moments of the dyes between their ground state and excited electronic states. This particular property and their wide applications have prompted us to study these molecules in detail. Also, we have studied the behaviour of these dyes with nanoparticles.

This chapter describes the various experimental techniques adopted to study the synthesis of gold and silver nanoparticles by chemical reduction method, absorption, fluorescence emission measurements are made using UV/VIS spectrophotometer and fluorescence spectrometer, Scanning Electron Microscope (SEM) to characterize the synthesized nanoparticles. Also to study the effect of nanoparticles on dye in aqueous media is also our main motto.

### A. Properties of noble metals

Bulk gold is well known for being inert; however, the nanoparticulate size of gold displays extensively high chemical reactivity. Consequently, the rich surface chemistry of AuNPs / AgNP's allows surface modification reactions with wide varieties of chemical and biochemical appliances to tailor the needs of biomedical applications including imaging and therapy of cancer. Properties of bulk substances of noble metals (Table 1) in larger or in micrometre sizes have been studied for years by solid state physicists and material scientists are currently well understood.

### B. Importance of noble metals at nano scale

In biological systems, the nanometre scale is also of interest. Many proteins are in the tens of nanometer range. Due to the comparable size scales, structures that can be correctly created on the nanometre scale may be included into biological systems. Biological systems are complicated, with biological fluid production, structure, and functions that are rarely fully understood. Nanostructures are utilised as medication delivery agents, labelling agents, sensors, and to increase electromagnetic fields, among many other uses in electronics and chemistry, to name a few: Gold nanoparticles are used to improve electroluminescence and quantum efficiency in organic light emitting diodes; palladium and platinum nanoparticles are used as efficient catalysts; silver nanoparticles are used to develop glucose sensors; and iron oxide nanoparticles are used as contrast agents in cancer diagnosis using Magnetic Resonance Imaging (MRI).

Table 1 Properties of Gold / Silver in bulk size

| Properties | Gold | Silver |
|---|---|---|
| Atomic Number | 79 | 47 |
| Electronic Configuration | [Xe] $5d^{10}$ , $6s^{1}$ | [Kr] $4d^{10}$ , $5s^{1}$ |
| Weight | 79-196.97 amu | 47-107.87 amu |
| Density | 19.28 $gcm^{-3}$ | 10.50 $gcm^{-3}$ |
| Atomic Density | $5.90x10^{28}$ $m^{-3}$-<br>59.0 x $10^{-9}$ $m^{-3}$ | $5.86x10^{28}$ $m^{-3}$-<br>$58.6x10^{-9}$ $m^{-3}$ |
| Volume for Atom | 0.017 n $m^{3}$ | 0.017 n $m^{3}$ |
| Wigner Seitz radius | 0.159nm | 0.160nm |
| Electronic Density | 5.90 x $10^{28}$ $m^{-3}$ | 5.86 x $10^{28}$ $m^{-3}$ |
| Fermi Speed | 1.40 x $10^{8}$ cm $s^{-1}$ | 1.39 x $10^{8}$cm $s^{-1}$ |
| Fermi Energy | 5.51eV | 5.48eV |
| Plasma frequency | 1.31 x $10^{16}$ rad $s^{-1}$ | 1.30 x $10^{16}$ rad $s^{-1}$ |

| | | |
|---|---|---|
| Relaxation Time | $2.94 \times 10^{-14}$s | $4.01 \times 10^{-14}$s |
| Ionization Energy | 9.22eV | 7.57 eV |
| Electric Resistivity | $2.20 \times 10^{-6}\ \Omega$cm | $1.61 \times 10^{-6}\ \Omega$cm |
| MeltingPoint (temperature) | 1338K | 1235K |
| Boiling Point (temperature) | 3243K | 2435K |
| Thermal Conductivity | 3.17W $cm^{-1}\ K^{-1}$ | 4.29W $cm^{-1}\ K^{-1}$ |
| Heat Capacity at 25 $^{0}$C | 25.42 $Jmol^{-1}\ K^{-1}$ | 25.35 $Jmol^{-1}\ K^{-1}$ |
| Standard Potential | +1.69V | +0.80V |
| Electronegativity | 2.4 | 1.9 |
| Lattice | f.c.c | f.c.c |
| Lattice parameter | 0.408nm | 0.409nm |

Nanotechnology in life sciences is an attempt to speed up medical diagnosis and analysis. Quantum dots, which have the capacity to discriminate many distinct parts of a cell with a single excitation source, have been employed in medical imaging. They have an advantage over standard fluorescent dyes in that they are more photostable, and chemistry may be utilised to alter various hues for entrance into biological samples. Nanoparticles exhibits interesting novel properties which include nonlinear optical behaviour, increased in mechanical strength, enhanced diffusivity, high specific heat, magnetic behaviour and electric resistivity etc.,. Researchers have proposed a huge range of potential scientific applications of metal nanoparticles such as in the field of biotechnology, sensors, bio-imaging, biosensors, medical diagnostics, catalysis, contrast agents, high performance engineering materials, magnetic material media etc,.

### C. Properties of noble metals at nano scale

Nanometre-sized materials exhibit behaviour that is midway between that of a macroscopic solid and that of atomic or molecular systems. These disparities can be attributed to three key factors:

1. Larger surface-to-volume ratio
2. Quantum size effect
3. Electromechanical interactions

Metallic nanoparticles have optical, electrical, chemical, and magnetic characteristics that are distinct from those of individual atoms and their bulk equivalents. Metal nanoparticles have optical qualities of high aesthetic, technological, and intellectual significance. Colloidal solutions of noble metals, such as copper, silver, and gold, exhibit distinct colours that have piqued the interest of scientists. The unusual hues found in gold solutions have prompted substantial research into their optical spectroscopic features in an attempt to link their behaviour under various microenvironmental settings. Small particles have increased thermal conductivity due to their larger surface to volume ratio.

Massive breakthroughs in nanoparticles in material science have been noticed during the previous fifteen years. This is due to the fact that quantistic effects and surface atoms with partial coordination greatly impact the physical and chemical behaviour of nanomaterials, resulting in features that differ from, and sometimes complement, molecules and bulk solids.

The rapid proliferation of nanotechnology in this decade is entirely attributable to advancements in nanometre-scale characterisation and production techniques. This results in an intrinsic desire for an area rich in new physical phenomena and synthetic prospects. In this sense, Feynman's prognosis of looking at nanotechnology "just for fun" has come true, but the vast amount of money drawn by nanotechnology has a more substantial foundation. Indeed, major advances in information science and health were moulded by microtechnology and molecular chemistry throughout the previous century. Nonmaterials, which lie between molecules and micromaterials in terms of size and characteristics, now promise to further revolutionise human existence.

The importance of nanoscience and nanotechnology is highly increased since past decade. Because of their unique properties, gold and silver nanoparticles played an important role in this process.

This study depicts a scene in which gold and silver nanoparticles (AuNP's and AgNP's, respectively) play a prominent role. The surface plasmon resonance (SPR) has a $10^5$ to $10^6$ bigger extinction cross section than regular molecular chromophores, which is why AuNPs and AgNPs exist. Additionally, AuNPs and AgNPs exhibit good chemical stability, photostability, and are nontoxic to biological creatures.

### D. Historical background

Gold has been prized in many cultures from ancient times for its beauty as well as its unique physical and chemical qualities. Gold was most likely one of the earliest metals discovered by humans. Gold extraction began in Bulgaria in the fifth millennium B.C., and "soluble" gold arrived in Egypt and China at the same time. Colloidal gold and silver were utilised in ancient times to colour glass in strong colours of yellow or red, depending on the concentration of the two metals. The renowned Lycurgus Cup, which was discovered in the British Museum in the fourth century A.D., is a prime example. During the Middle Ages, Au colloids and soluble gold were utilised to reveal fantastic healing properties for numerous maladies such as sexual issues, diarrhoea, epilepsy, and tumours, as well as for syphilis diagnosis. Swarna bhasma and swarna bindu prashana were used in ancient Indian ayurvedic remedies to boost the body's immunity. Thus, the extraordinary properties of colloidal gold have been used for ages.

The first systematic study of metal nanoparticles was started by Michael faraday around 1851. Faraday was the first to recognize that the red colour of gold was due to nano size of the Au particles and turn to the blue by adding salt to the solution. He obtained the gold colloids reducing gold salts by phosphorous.

Synthesises of colloidal nano metal particles have been developed in the early 20th century by different methods including physical, chemical and green techniques. Fundamental and concrete work was initiated by Turkevitch in 1951.

## II SYNTHESIS OF NANOPARTICLES

Metal nanoparticle synthesis techniques may be divided into the following types.

- ✓ Chemical Reduction Method
- ✓ Sputtering Deposition
- ✓ Electrolysis
- ✓ Thin film coating (Chemical Vapour Deposition)
- ✓ Pyrolysis
- ✓ Nano Green Technology
- ✓ Many other methods (Electric Arc, Molecular Beam Epitaxy, Sol-Gel)

The most common methods for producing colloidal nanoparticles are based on chemical reduction in solution (wet chemistry). To avoid coagulation and precipitation, wet chemical techniques necessitate the reduction of gold and silver salts, as well as the chemisorption or physisorption of ligands on the surface of metal nanoparticles.

The Turkevitch approach is the most widely used for producing aqueous solutions of gold nanoparticles that may be readily functionalized with following procedures. This process involves reducing HAuCl4 in a boiling aqueous sodium citrate solution. Citrate molecules have both reducing and stabilising properties. This process may also be used to shape nanoparticles into spheres, prisms, cubes, rods, or wires. To make nanoparticles stable for a longer amount of time, stabilising agents or capping for the molecule are required. The nanoparticles can be capped using citrate, sodium borohydride, or botanical materials such as gum arabic, turmeric, cinnamon, neem, and so on.

### A. Synthesis of nanoparticles: Chemical Reduction method

### B. Materials

Himedia Laboratories Pvt Ltd., Mumbai, India, supplies trisodium citrate, hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4$. $3H_2O$), sodium borohydride ($NaBH_4$), and silver nitrate. All solution preparations were done using ultra deionized water. Ultra deionised water was used for all solution preparations. All glass wares are cleaned with aquaregia solution.

### C. Synthesis of gold nanoparticles

Gold nanoparticles (AuNPs) are created by reducing a 20mL aqueous solution comprising $2.5x10^{-4}$ M of $HAuCl_4$ and $2.5x10^{-4}$ M of trisodium citrate in two conical flasks. Mix both the components and stir rigorously on a magnetic stirrer for 15min. Further add 0.6ml ice-cold, freshly prepared 0.1M of $NaBH_4$ drop by drop, the solution turns to deep reddish colour, it indicates the nanoparticle formation (Figure 1). Here trisodium citrate acts as a capping agent, because it cannot reduce the gold salt. We can generate spherical gold nanoparticles of varied sizes by varying the pace at which the reducing agent is added to the metal salt solution.

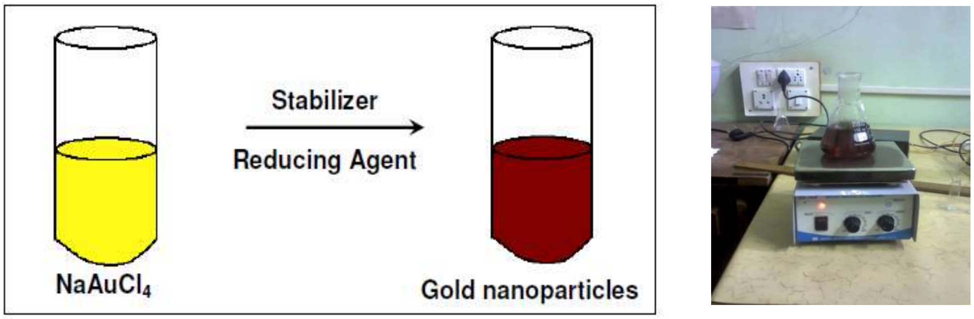


Figure 1 The chemical reduction approach was used to create gold nanoparticles.

A typical hydridic and carboxylate-based reduction method, on the other hand, results in nanoparticles with lesser stability and toxicity. To avoid the existing problems associated with the production of AuNPs, we chose a green nano technique that is non-toxic and uses trimeric alanine-based phosphine $P[CH_2NHCH(CH_3)\text{-}(COOH)_3]$ (Thpal) as a reducing agent, which provides an unprecedented pathway to produce AuNPs at acidic pH. Furthermore, AuNPs are capped with Gum arabic (glycoprotein) to avoid aggregation, and the synthesised AuNPs are stable for up to 6 months. Extensive research has demonstrated that Gum Arabic is an effective backbone for the stabilisation of AuNPs. SPR, SEM, and TEM images of AuNPs ranging in size from 4 to 12nm.

$$Au^{3+} + C_6H_5O_7^{-} + 3H_2O + 3e^{-} \longrightarrow Au + C_3H_8O + 3CO_2 + 3\,OH^{-}$$
$$2Au^{3+} + 6BH_4^{-} + 18H_2O \longrightarrow 2Au + 21H_2 + 6H_3BO_3$$

### D. Synthesis of silver nanoparticles

Chemical reduction was used to create silver nanoparticles. In 20ml of strongly deionised water, 1.0mM $AgNO_3$ was dissolved. The $AgNO_3$ solution was then mixed with 0.1mM trisodium citrate. Drop by drop, 0.6ml of 0.1mM $NaBH_4$ was added with continued swirling and mixing. The yellow-colored solution was created. There is no direct incident of light throughout the preparation procedure. Absorption spectroscopy of the yellow colour solution confirms the production of silver nanoparticles (Figure 2).

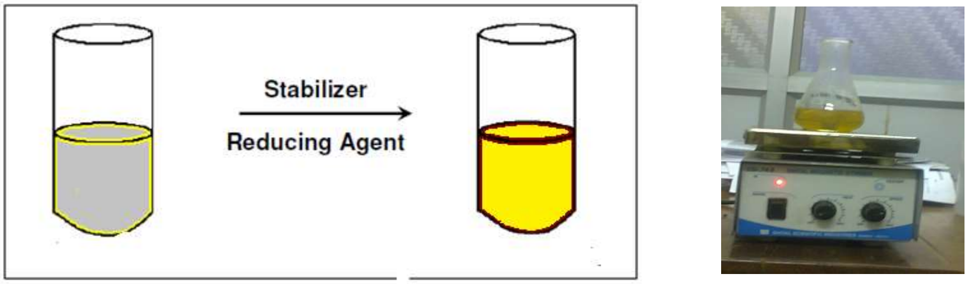


Figure 2 Synthesis of silver nanoparticles using chemical reduction method.

$$4\,Ag^{+} + C_6H_5O_7Na_3 + 2\,H_2O \longrightarrow 4Ag + C_6H_5O_7H_3 + 3\,Na^{+} + H^{+} + O_2\uparrow$$
$$AgNO_3 + NaBH_4 \longrightarrow Ag + \tfrac{1}{2}\,H_2 + \tfrac{1}{2}\,B_2H_6 + NaNO_3$$

## E. Spectra suite spectrometer: Ocean Optics

We have also adopted to measure the both absorption and fluorescence measurements using single beam Spectra Suite Ocean Optics Spectrophotometer (HR 400 high resolution model). This Spectra Suite spectrometer (Figure 3) allows us to perform the three basic spectroscopic experiments – absorbance, reflectance and emission.

Figure 3 UV/VIS/NIR Spectrophotometer, Ocean Optics.

## F. Fluorescence spectrophotometer

Fluorescence spectrophotometer (Hitachi, F7000) was used to record the fluorescence spectra of ADS680HO highly fluorescent laser dye.

## G. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) (Model: JEOL JSM-6360) is a form of electron microscopy that can provide high-resolution pictures of a sample's surface. SEM pictures have a three-dimensional look due to the way they are made and are useful for assessing the surface structure of the sample. The schematic diagram of SEM along with optical measurements is given in Figure.4.

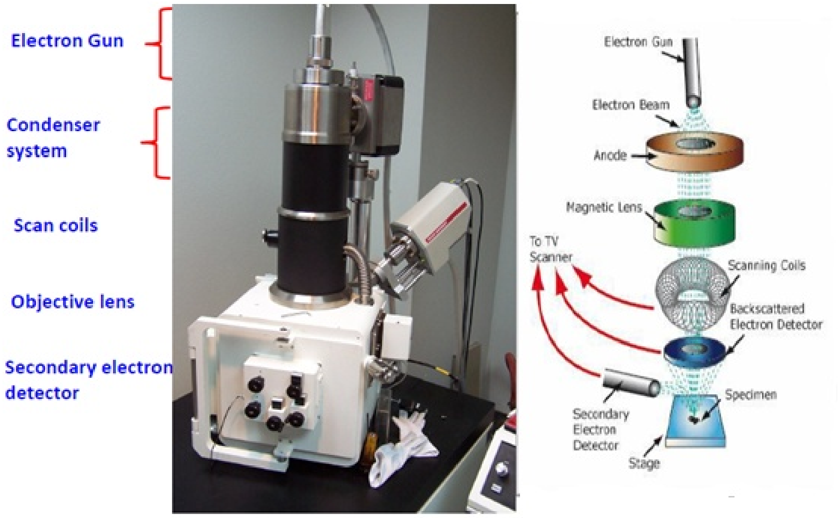


Figure.4 Schematic diagram Scanning Electron Microscope (SEM).

## III CHARACTERIZATION OF NANOPARTICLES

### A. Surface Plasmon Resonance (SPR)

Surface Plasmon Resonance of Au and Ag metal nanoparticles have attracted great attention due to their potential applications in medical diagnostics, therapeutics, biological and chemical imaging, and substrates for enhanced spectroscopy due to the unique optical property which is originating from the surface plasmon resonance.

Noble nanoparticles have a significant absorption band in the visible range, which is a tiny particle effect since they are missing in the individual atom as well as in the bulk. The coherent oscillation of conduction band electrons caused by an interacting electromagnetic field is the physical basis of light absorption by metal nanoparticles. Electromagnetic surface waves may travel over the interface between conducting materials and a dielectric at a wide range of frequencies, from dc and radio to visible. Surface plasmons are oscillation modes that consist of an electromagnetic field connected to the oscillations of conduction electrons.

An absorption band results when the incident photon frequency is resonant with the collective oscillation of the conduction band electrons is known as the surface plasmon resonance (SPR) ( Figure 5).

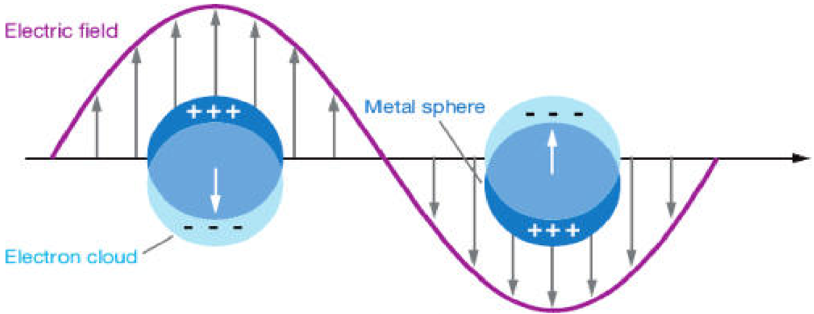


Figure 5 Surface Plasmon Resonance

The plasma frequency of several metals, such as Pb, In, Hg, Sn, and Cd, is in the UV portion of the spectrum. Hence, they do not exhibit SPR. While, noble metals such as Cu, Au and Ag exceptionally shows the SPR because of the following reasons.

1. They create colloids that are air-stable.
2. The plasma frequency is in the visible range due to d-d band transitions.
3. At the plasmon frequency the imaginary part of the dielectric constant is very small.

Hence, the surface plasmon experiments are very interesting. As a result, SPR investigations are most typically performed using Cu, Ag, and Au. The resonance frequency of this SPR is greatly influenced by the nanoparticles' size, shape, interparticle interactions, dielectric characteristics, and local surroundings.The following factors have a significant impact on the resonant frequency:

i. Electron density
ii. Effective electron mass
iii. Shape
iv. Charge distribution size

SPR (Figure 6 and 7) of metal nanoparticles using UV/Visible and Infrared absorption spectroscopy is very useful for obtaining basic information on the size, structure, and composition in a quick and affordable manner.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) investigations allow the accurate measurement of average size of particles and size distribution (Figure 8 and 9).

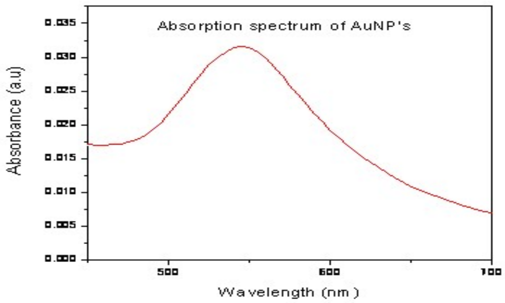


Figure 6 Absorption spectra of AuNPs in aqueous solution using Surface Plasmon Resonance.

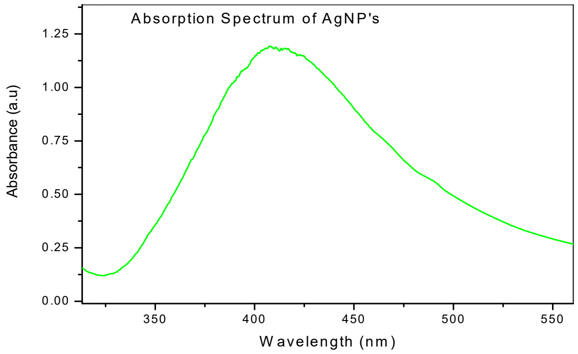
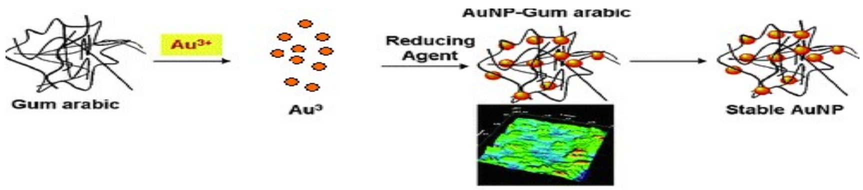
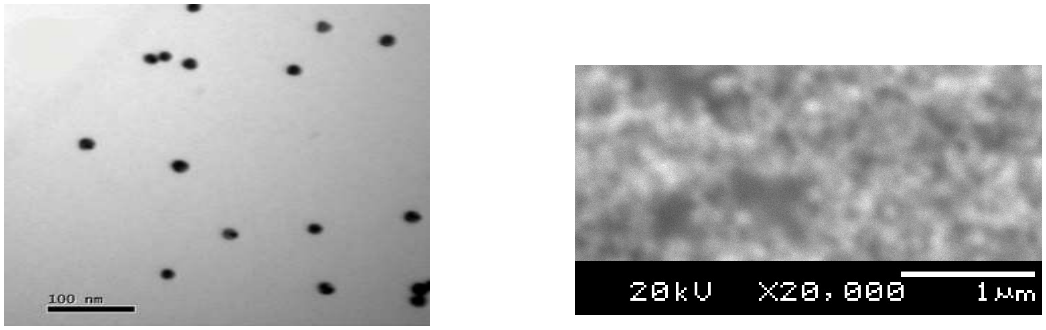


Figure 7 Absorption spectra of AgNPs in aqueous solution using Surface Plasmon Resonance.



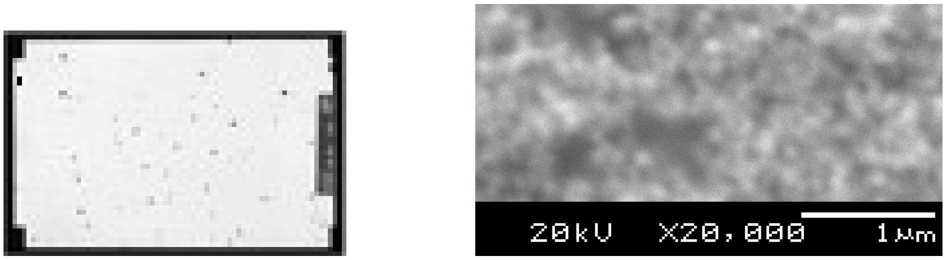
(a) Gum Arabic is used to cap AuNP’s



(b) Image of AuNP's TEM

(c) SEM image of AuNP’s

Figure 8 (a) Gum Arabic is used to cap AuNP’s , (b) TEM and (c)SEM images.



(a) TEM image (b) SEM image of AgNP's

Figure 9 Silver nanoparticles SEM and TEM images .

## IV OPTICAL PROPERTIES OF NANOPARTICLES – MIE'S THEORY

The optical properties of gold and silver have been intensively investigated in particular with respect to size dependence. An electromagnetic wave activates the electrical or vibrational states of a metal nanoparticle. This process generates dipole moments that oscillate at the incident wave's frequency. The surface plasmon resonance (SPR) is the collective oscillation of free conduction electrons.

Mie's theory may explain the extinction spectra of a dilute dispersion of colloidal gold and silver metal nanoparticles. Mie was inspired to apply the general theory of light extended to microscopic particles by the colour shift of colloidal gold/silver with particle size. He used Maxwell's equations in spherical coordinates with proper boundary conditions and numerous expansions of the incoming electric and magnetic fields to provide precise electrodynamic estimates of the interaction of light with spherical metallic nanoparticles. The theory addresses the extinction (absorption and scattering) of arbitrary-sized spherical particles.

### A. Mie's theory:

Mie's theory is based on the premise that the particle and its surrounding medium are both homogenous and can be described by their bulk optical dielectric functions. The electron density, which is supposed to have a sharp discontinuity at the particle's surface at radius R, defines the border. As input parameters, the particle size, optical material function of the particle, and surrounding medium were used. To connect the dipole plasmon frequency of metal nanoparticles to the dielectric constant, we examine light interaction with a spherical particle, which is significantly smaller than the wavelength of light ($2R << \lambda$), where R is the particle's radius. The electric field of light may be assumed to be constant in these situations, and the interaction is regulated by electrostatics rather than electrodynamics. This is commonly referred to as the quasistatic approximation. Mie's scattering theory has been used extensively to examine the optical characteristics of isolated colloidal particles, particularly their dependency on particle size effect. The Mie theory, in particular, is a mathematical scientific description of electromagnetic radiation scattering by spherical particles submerged in a continuous liquid.The Mie scattering solution starts with macroscopic Maxwell equations that use complex representations of the electric field, E, and the auxiliary magnetic field, H.

$$\nabla \cdot E = 0 \qquad 1$$

$$\nabla \cdot H = 0 \qquad 2$$

$$\nabla \times E = i\omega\mu H \qquad 3$$

$$\nabla \times H = -i\omega\varepsilon E \qquad 4$$

The Helmholtz relation describes the configuration of an incoming electromagnetic field with two components, the electric field E and the magnetic field H.

$$\nabla^2 E + k^2 E = 0 \qquad 5$$

$$\nabla^2 H + k^2 H = 0 \qquad 6$$

where k denotes the wave number specified by

$$k^2 = \omega^2 \varepsilon\mu \qquad 7$$

The series for E and H, which were used for the scattering amplitude functions, may be entered into the proper integrals, and by integrating term by term, we can obtain the extinction and scattering coefficients as follows.

$$\sigma_{ext} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)[\mathrm{Re}(a_n + b_n)] \qquad 8$$

$$\sigma_{sca} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\left(|a_n|^2 + |b_n|^2\right) \qquad 9$$

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca} \qquad 10$$

where x is the size parameter

$$x = \frac{2\pi R n_m}{\omega} \qquad 11$$

where R is the particle's radius, $n_m$ is the medium's refractive index, and $a_n$ and $b_n$ are the scattering coefficients, which may be stated in terms of the Ricatti-Bessel expressions:

$$a_n = \frac{m\Psi_n(mx)m\Psi_n^{'}(x) - \Psi_n(y)\Psi_n^{'}(mx)}{m\Psi_n(mx)\xi_n^{'}(x) - \xi_n(x)\Psi_n^{'}(mx)} \qquad 12$$

$$b_n = \frac{\Psi_n(mx)m\Psi_n^{'}(x) - m\Psi_n(y)\Psi_n^{'}(mx)}{\Psi_n(mx)\xi_n^{'}(x) - m\xi_n(x)\Psi_n^{'}(mx)} \qquad 13$$

in which $\Psi_n(x)$ and $\xi_n(x)$ are Ricatti-Bessel cylindrical functions and $m = n/n_m$, where $n$ is the complex refractive index of the particle and $n_m$ is the real refractive index of the surrounding medium. The prime denotes differentiation from the argument in the brackets. n is the summation index of the partial waves of the surrounding medium in these formulations. The dipole oscillation is represented by n = 1, the quadruple oscillation by n = 2, and so on. Depending on the particle size range, the influence of particle size on the peak resonant wavelength is caused by two separate methods. Only the electric dipole component contributes considerably to the extinction cross-section ($\sigma_{ext}$) in the limit of 2R << λ (R is the radius of the particle and is the wavelength of the light).

$$\sigma_{ext} = 9\frac{\omega}{c}\varepsilon_m^{3/2}V\,\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + [\varepsilon_2(\omega)]^2} \qquad 14$$

where $V = \left(\frac{4\pi}{3}\right)R^3$ is the volume of the spherical particle, is the exciting light's angular frequency, c is the velocity of light m, and ε (ω) [ε (ω) = $\varepsilon_1$ (ω) + i$\varepsilon_2$ (ω)] are the dielectric frictions of the surrounding medium and the material itself, respectively. When $\varepsilon_1$ (ω) = -2 $\varepsilon_m$ and $\varepsilon_2$ is small or weakly dependent on, the resonance requirement is satisfied.

## B. Determination of the extinction, absorption, and scattering coefficients of gold and silver nanoparticles

Mie's scattering theory has been used extensively to examine the optical characteristics of isolated colloidal particles, particularly their dependency on particle size effect. The absorption spectrum of gold nanoparticles of size 4-12nm shows a maximum in the region 540-550nm in the present example, which is connected to the plasmon resonance created by the nano sized (4-12nm) gold nanoparticles. This absorption band (surface plasmon resonance SPR) is caused by free electron interactions with incoming electromagnetic radiation in tiny metallic spherical objects. The plasmon resonance band detected indicates that the gold nanoparticles are spherical in form. Our major aim is to use Mie's theory and available simulations to compute the extinction, absorption, and scattering coefficients of gold nanoparticles of various sizes. The observed results show that when the size of the nanoparticles rises from 4 to 50nm, the extinction efficiency at the resonant peak improves, as does the SPR shift from 520nm to 570nm.

## C. Experimental setup

Ocean Optics HR4000 high resolution spectrometer was used to measure optical absorption and fluorescence. "nanohub.org" simulations were used to perform computational electrodynamics calculations such as absorption, scattering, and extinction efficiency. Origin 6.0 software was used to create graphical representations.

## D. Results and discussion

The absorption spectra of AuNPs in this case exhibits a maximum in the range 540-550nm with a peak at 545nm, which is connected to the surface plasmon resonance created by the nano-sized (4-12nm) gold particles. This absorption band is caused by free electrons confined to tiny metallic spherical objects interacting with incoming electromagnetic radiation. The plasmon resonance band detected indicates that the gold nanoparticles are spherical in form (Table 2).

The Extinction coefficient is the sum of the absorption and scattering coefficients. Scattering occurs when charged particles are accelerated and reradiate. Absorption happens when a particle absorbs energy from a beam and changes it to another form. Mie's extinction efficiency expression is given by Equation 14, and the extinction efficiency, absorption, and scattering spectrum for various nanoparticle radii may be shown in Figures 9 to 13. As the particle radius grows, the wavelength corresponding to maximum extinction moves to longer wavelengths (red shift). The 545nm peak corresponds to the resonance condition for tiny spheres, more especially when $(\omega) = -2\ \varepsilon_m$. When the particle radius is extended further, the dipole peak shifts significantly and the spectrum becomes considerably more complicated.

Mie theory was used to compute the extinction spectrum of a solid gold nanoparticle. This entails calculating extinction from Mie's equation at a variety of wavelengths. Figure 10 depicts the extinction spectrum for various nanoparticle radii. As the particle radius grows, the wavelength corresponding to maximum extinction moves to longer wavelengths (red shift).

Since the dielectric medium constant (ε) is related to the refractive index, $(n_{eff} + ik_{eff})^2 = \varepsilon_{eff}$ (($\varepsilon_{eff}$ is the effective dielectric constant of the nanocomposite, $n_{eff}$ is the real part of the nanocomposite's effective complex index of refraction, and $k_{eff}$ is the imaginary part of the effective complex index of refraction). We show that the evolution of the SPR band at longer wavelengths can be attributed to an increase in the effective refractive index of nanoparticles in the assembly, whereas the size of individual gold nanoparticles in the solution should remain largely constant, whereas the inter particle distance changes, resulting in changes in the inter particle dielectric medium constant or refractive index. The $n_{eff}$. will be represented by the refractive index 'n'. Surprisingly, the change in 'n' was discovered to have an almost linear relationship with max. Simulation findings for gold nanoparticles of various sizes (10-50nm) using Mie's theory, which fits the bands observed in terms of SPR wavelength. According to the established principle, the red shift of the plasmon band rises as the refractive index changes. The nanoparticles in the assembly environment have a greater refractive index than those in the aqueous environment, which is a key assumption for applying the Mie theory simulation to this system. The pattern of refractive index variations described in prior investigations for comparable assemblages of metal nanoparticles in diverse settings lends qualitative credence to this idea. The observed red shift in the plasmon resonance is caused by the impact of electromagnetic retardation in bigger sized nanoparticles.

Table 2 Extinction, absorption, and scattering effectiveness of gold nanoparticles of different sizes in aqueous medium.

| nanoparticle's radius (nm) | Position of $\lambda_{max}$ (nm) | Extinction efficiency | Absorption efficiency | Scattering efficiency |
|---|---|---|---|---|
| 10 | 521 | 1.349 | 1.339 | 0.019 |
| 15 | 527 | 2.121 | 2.066 | 0.055 |
| 20 | 527 | 3.041 | 2.681 | 0.368 |
| 25 | 527 | 4.004 | 2.842 | 1.162 |
| 30 | 533 | 5.010 | 3.263 | 1.847 |
| 35 | 539 | 5.856 | 3.523 | 2.331 |
| 40 | 551 | 6.459 | 3.782 | 2.777 |
| 45 | 556 | 6.825 | 3.976 | 3.921 |
| 50 | 568 | 6.949 | 4.048 | 4.719 |

Figure 9 to 13 and Figure 14 to 18 display the computed spectra of absorption, scattering, and extinction efficiency for gold and silver nanoparticles of radius 10-50nm. Dimensionless efficiencies may be translated to cross-sections with units of m2 because they represent an analogous cross-sectional area of the particle that contributes to the absorption, scattering, and extinction of incoming light. (Table 2 & 3).By altering the physical dimensions of spherical gold nanoparticles, the optical characteristics may be modified. The material's dielectric characteristics are critical, since they influence the intensity and location of the plasmon resonance. As the size of the spherical nanoparticles increases, the peaks expand and shift to longer (red shift) wavelengths. The change in dielectric medium and refractive index (RI) characteristics, which give a way to create optical signals for uptake or release of molecular species in the nanoparticles assembly, may be linked to the shift in SPR band location and intensity of the nanoparticles assembly. This type of interparticle property may also have applications in controlled drug delivery, electrical sensors, and the electrical response of nanoparticle assemblies to vaporsorption. Understanding the exact control of interparticle characteristics will be useful in nanostructured sensing applications.

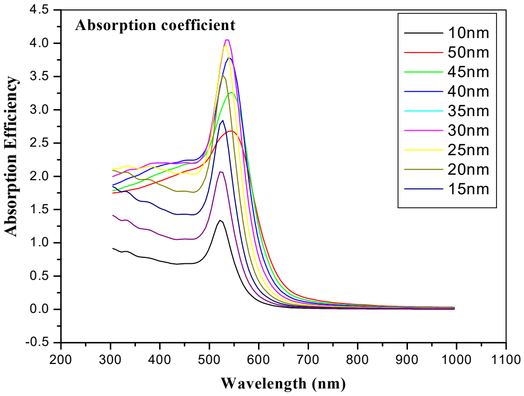


Figure 9 The absorption coefficient of gold nanoparticles ranging in size from 10 to 50nm.

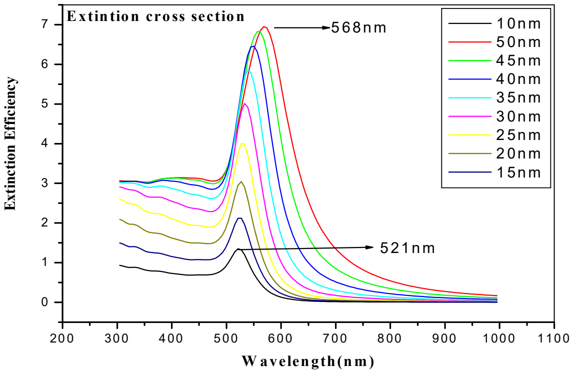


Figure 10 Extinction cross section of gold nanoparticles ranging in size from 10 to 50nm.

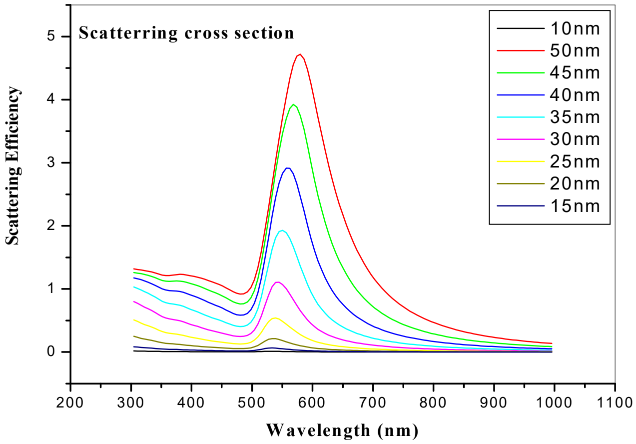


Figure 11 Scattering cross section of gold nanoparticles ranging in size from 10 to 50nm

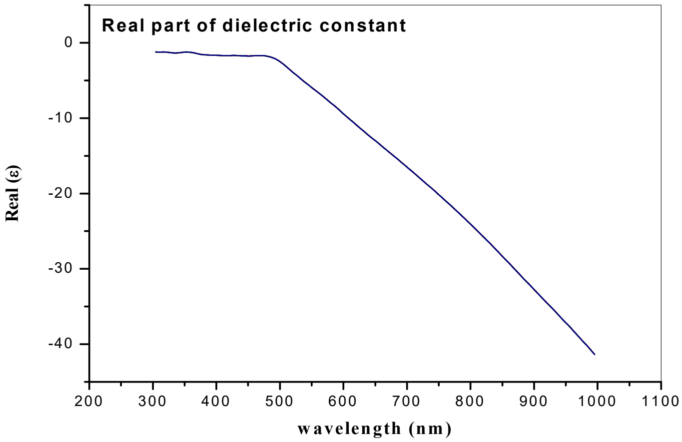


Figure 12 Real part of dielectric constant of gold nanoparticles.

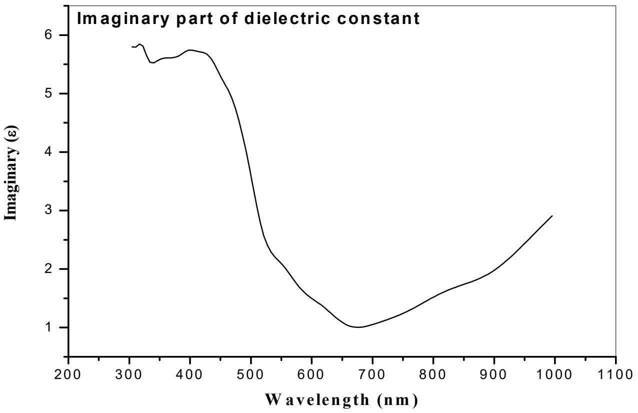


Figure 13 The imaginary component of gold nanoparticles' dielectric constant.

Table.3 Extinction, Absorption and Scattering efficiency of silver nanoparticles of various sizes in the surrounding aqueous medium.

| Radius of the nanoparticle (nm) | Position of $\lambda_{max}$ (nm) | Extinction efficiency | Absorption efficiency | Scattering efficiency |
|---|---|---|---|---|
| 10 | 386.8 | 21.885 | 18.153 | 3.732 |
| 15 | 392.6 | 23.362 | 13.819 | 9.542 |
| 20 | 398.5 | 20.945 | 8.080 | 12.864 |
| 25 | 404.3 | 16.774 | 4.136 | 12.637 |
| 30 | 416.0 | 14.040 | 2.111 | 11.928 |
| 35 | 427.7 | 11.712 | 1.020 | 10.691 |
| 40 | 445.3 | 9.886 | 0.560 | 9.325 |
| 45 | 457.0 | 8.404 | 0.392 | 8.011 |
| 50 | 480.4 | 7.314 | 0.301 | 7.012 |

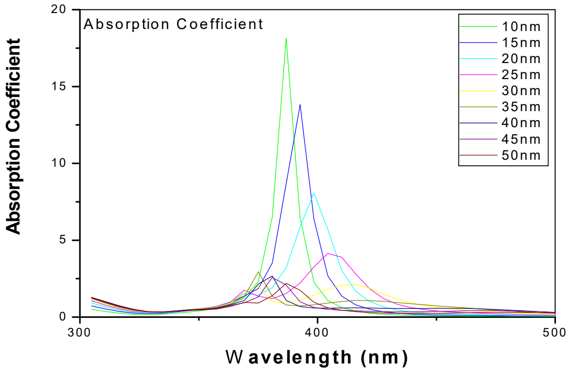


Figure 14 The absorption coefficient of silver nanoparticles ranging in size from 10 to 50nm.

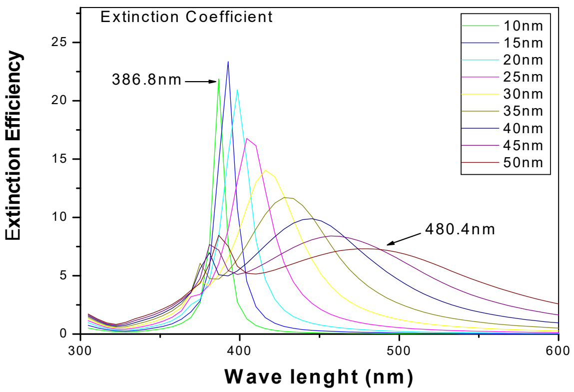


Figure 15 The cross section of extinction of silver nanoparticles ranging in size from 10 to 50nm.

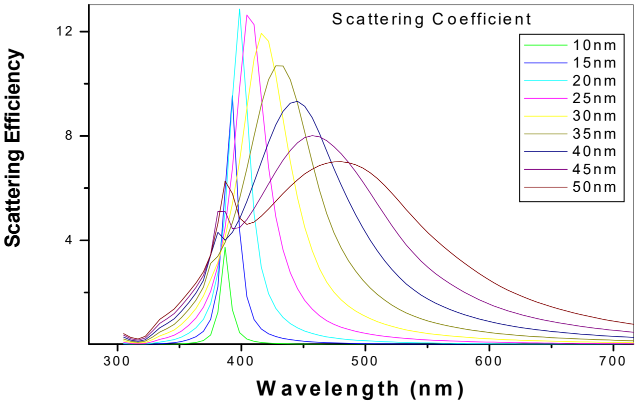


Figure 16 Scattering cross section of  silver nanoparticles of various sizes from 10-50nm.

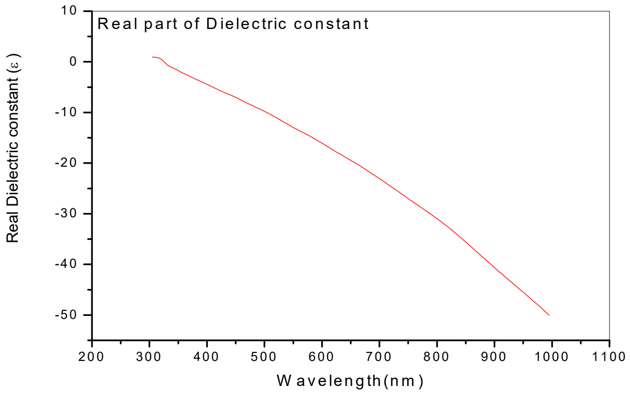


Figure 17 Real part of dielectric constant of silver nanoparticles.

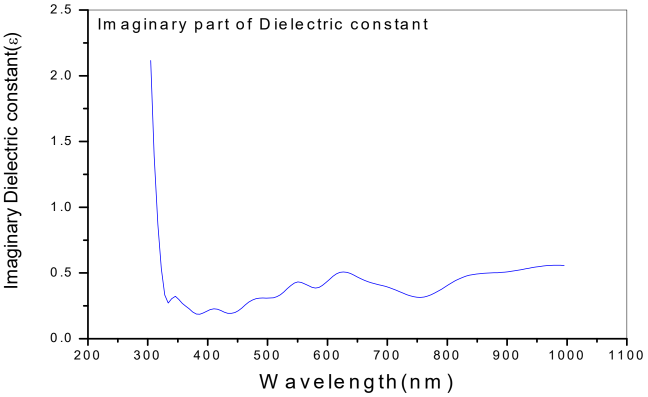


Figure18 Imaginary part of dielectric constant of silver nanoparticles.

## E. Absorption and fluorescence quenching of laser dyes with gold / silver nanoparticles

Fluorescence and absorption Any procedure that reduces the absorbance and fluorescence intensity of a sample is referred to as quenching. Quenching can be caused by a number of molecular interactions. Excited state processes, molecular rearrangements, energy transfer, ground-state complex creation, and dynamic (collissional) quenching are examples of these interactions. In this chapter, we will look into quenching caused by collisions between the fluorophore and the quencher, also known as collisional or dynamic quenching, caused by binding between the fluorescent sample and the quencher.

Fluorescence quenching has received a great deal of attention as both a fundamental phenomena and a source of knowledge about biological systems. These quenching biochemical applications are caused by molecular interactions that result in quenching. Static and dynamic quenching both need molecular interaction between the fluorophore and the quencher. The quencher must diffuse to the fluorophore during the excited state's lifetime in the case of collissional (dynamic) quenching. The fluorophore returns to its ground state upon touch, without emitting a photon. In general, quenching happens in the absence of any lasting change in the molecules, i.e., in the absence of a photochemical reaction. Static quenching results in the formation of a nonfluorescent compound between the fluorophore and the quencher The fluorophore and quencher must be in contact for this static or dynamic quenching to occur.

Fluorophores' interactions with metallic surfaces or nanoparticles have sparked significant interest in recent years. Because of their powerful interactions with light, gold and silver colloids exhibit brilliant hues. Fluorophores' intensity is frequently reduced near gold or silver nanoparticles.

There has been a lot of interest in the utilisation of gold / silver colloids on the surfaces of ADS680HO laser dye throughout this work. Many of the publications make advantage of gold and silver nanoparticles' high extinction coefficients and light scattering cross sections. The significant quenching of fluorophores near gold/silver surfaces can also be used to construct molecular beacons. ADS680HO included an alcoholic group that spontaneously attaches to the surface of gold/silver nanoparticles. The gold/silver nanoparticle surface was totally quenched when attached to the colloids ADS680HO. The process of gold quenching is most likely due to resonance energy transfer (RET) to the gold / silver absorption bands.

Fluorescence quenchers include a wide range of chemicals. Molecular oxygen (in alcohol, thiol, or ester group) and sulphur (in thiol group) are the most well-known colloidal quenchers, quenching practically all known fluorophores. The process by which oxygen quenches has long been debated. The most plausible mechanism is that the fluorophore undergoes inter system crossover to the triplet state due to paramagnetic oxygen and sulphur. The long-lived triplets are totally quenched in fluid solutions, therefore no phosphorescence is detected. These compounds presumably quench by donating an electron from the flurophore to the quencher.

AuNPs/AgNPs can outperform organic acceptor molecules as ultra-efficient quenchers of molecular excitation energy in chromophore-AuNP/AgNP composites. Theoretical modelling of quenching efficiency has been intensively studied during the last few decades. However, substantial studies were recently carried out in which critical factors such as the size of the AuNPs/AgNPs and the distance between the chromophores and the AuNPs were precisely regulated. Fluorescence quenching is found in investigations where conjugates of chromophores and metal nanoparticles are held in aqueous solution. Only when the chromophores and AuNPs are separated by bulky spacers, such as antibodies, is the fluorescence less quenched.

The absorption spectra of AuNPs in this example exhibits a maximum in the region 540-550nm, culminating at 545nm. Similarly, AgNPs have a maximum in the 405-410nm range, culminating at 408nm. Both are connected to the plasmon resonance caused by nanosized (4-12nm) gold / silver nanoparticles. This absorption band is caused by free electrons confined to tiny metallic spherical objects interacting with incoming electromagnetic radiation. The plasmon resonance band (Figures 6 and 7) demonstrates that the gold/silver nanoparticles are spherical in form.

## F. Absorption and fluorescence quenching of laser dye ADS680HO with gold nanoparticles

Figure 14 depicts the absorption spectra of ADS680HO in alcohols with and without AuNPs, revealing a wide band in the visible range 670-700nm. Figure 15 depicts a fluorescence spectrum with a wide band in the 700-750nm range.

The SPR of AuNPs (size 4-12nm) reaches a peak at 545nm. When AuNPs are introduced to ADS680HO, the absorbance band changes to higher wavelengths (red shift), peaking at 680nm (in methanol), 682nm (in ethanol), 684nm (in butanol), 686nm (in nonanol), 687nm (in decanol), and 689nm (in glycerol), and the intensity of the absorbance decreases. Similarly, the fluorescence band changes to a higher wavelength area with peaks at 716nm (in methanol), 721nm (in butanol), 711nm (in glycerol), and 718nm (in propanol), and the fluorescence intensity decreases. The band was dampened and broadened when these molecules complexed with the AuNPs. The dampening of the Au band suggests that the alcohol group's attachment to ADS680HO modifies the electron density of the AuNP's, directly impacting the absorption of the surface bound ADS680HO as well as the absorption band (Figure 16).

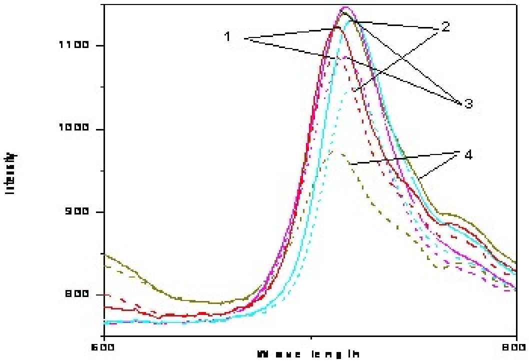


Figure 14 Absorption spectra of ADS680HO attached with (dotted)/without (lined) AuNP's in alcohol solvents (1- methanol, 2-butanol, 3-nonanol, 4-glycerol).

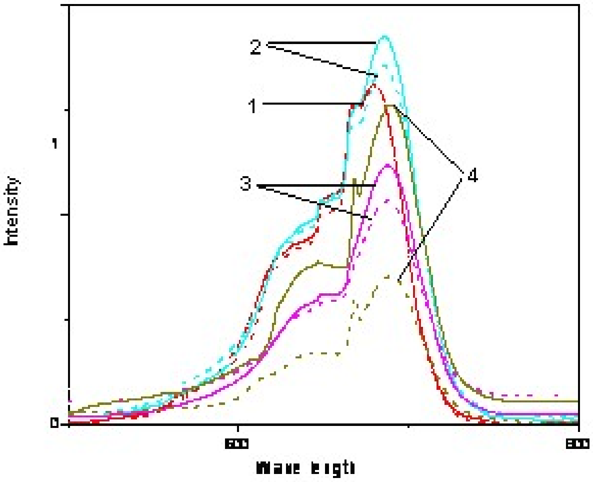


Figure 15 Fluorescence spectra of ADS680HO attached with (dotted)/without (lined) AuNP's in alcohol solvents (1- methanol, 2-butanol, 3-nonanol, 4-glycerol).

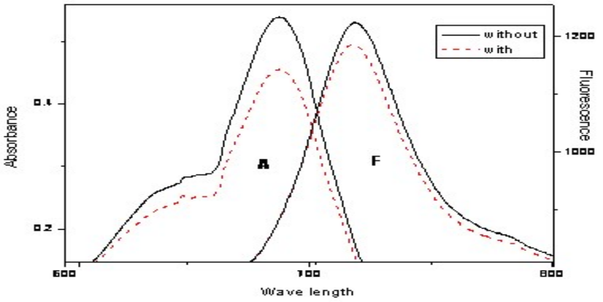
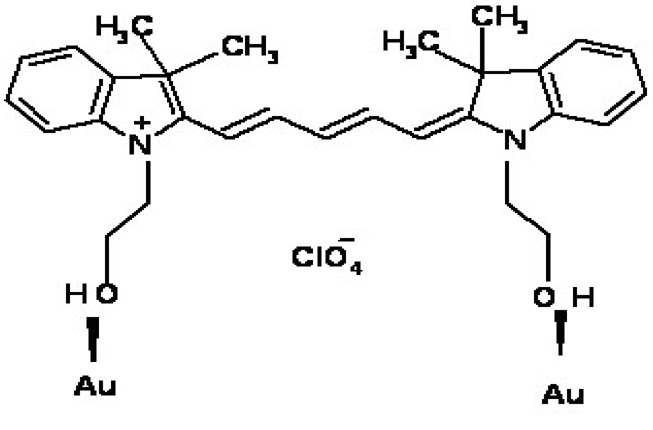


Figure 16 Absorption and emission spectra of ADS680HO in decanoll with (dotted)/without (lined) AuNP's (A-absorbance, F-fluorescence).



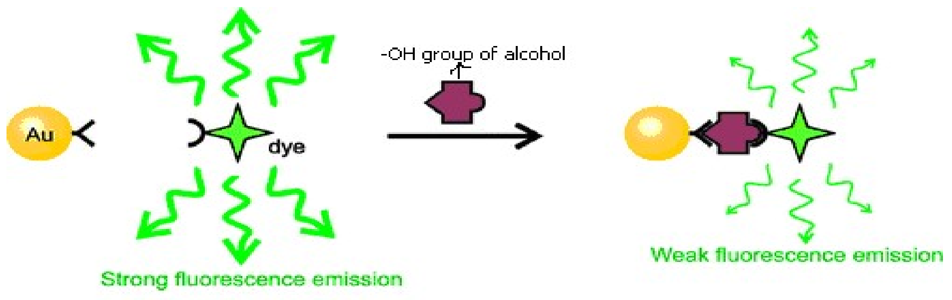


Figure 17 Attatchment of AuNP's with ADS680HO.

When AuNPs were introduced to the ADS680HO laser dye, the vibrational characteristics were clearly resolved and the intensity was suppressed because AuNPs were adsorbed on the OH- group and formed hydrogen bonds with the ADS680HO laser dye (Figure 17).

A fluorophore in its excited state behaves like an oscillating dipole. When these fluorophores are in close proximity to metal AuNPs (Figure 17), the rate of radiative energy emission changes. The interaction of the incident light with the neighbouring metal surface affects the electric field perceived by fluorophores. These interactions can increase/decrease the fluorophore's field and hence the radiative decay, resulting in a variety of favourable outcomes such as increased/decreased quantum yield and decreased/increased life duration.

### G. Absorption and fluorescence quenching of laser dyes with silver nanoparticles

The absorption spectra of AgNPs in this case exhibits a maximum in the range 405-410 nm with a peak at 408nm, which is connected to the surface plasmon resonance created by the nano sized (4-12nm) silver nanoparticles. This absorption band is caused by free electrons confined to tiny metallic spherical objects interacting with incoming electromagnetic radiation. We may deduce that the silver nanoparticles are spherical based on the observed SPR band and SEM picture.

### H. Absorption and fluorescence quenching of laser dye ADS680HO with silver nanoparticles

The absorption spectra of ADS680HO in alcohols with and without AgNPs is shown in Figure 19, which reveals a wide band in the visible range 670-700nm. Figure 20 depicts a fluorescence spectrum with a wide band in the 700-750nm range.

The SPR of AgNPs (size 4-12nm) is greatest at 408nm. When AgNPs are introduced to ADS680HO, the absorbance band changes towards higher wavelengths (red shift), peaking at 684nm (in methanol), 685nm (in ethanol), 683nm (in propanol), 686nm (in butanol), 685nm (in octanol), 686nm (in decanol), and 688nm (in nonanol). Similarly, the fluorescence band changes to longer wavelengths, peaking at 725nm in decanol, 724nm in nonanol, 730nm in octanol, 727nm in butanol, and 723nm in ethanol, and fluorescence intensity decreases. The band was dampened and broadened when these molecules complexed with the AgNPs. The dampening of the Ag absorbance band suggests that the alcoholic group's attachment to ADS680HO modifies the electron density of the AgNP's, directly impacting the absorption of the surface bound ADS680HO as well as the absorption band (Figure 19).

The vibrational characteristics of ADS680HO were clearly resolved when AgNPs were introduced to it, and the intensity was quenched because AgNPs were adsorbed on the OH- group and formed hydrogen bond with the ADS680HO laser dye (Figure 21).

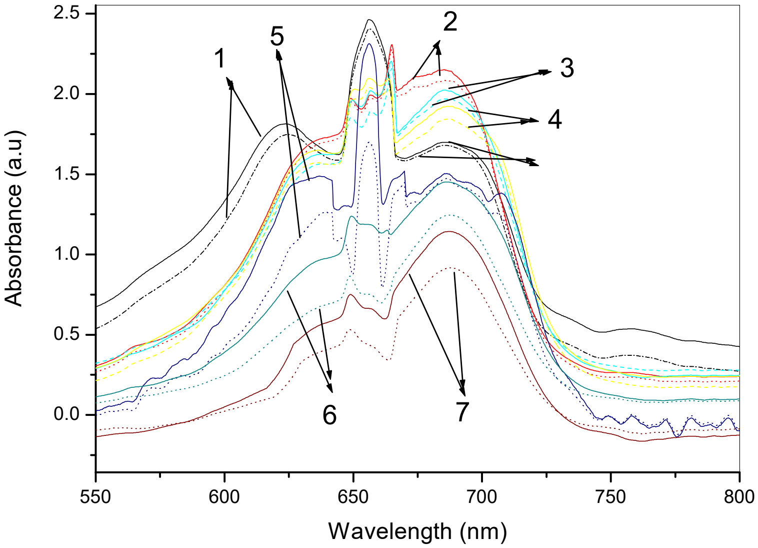


Figure 19 Absorption spectra of ADS680HO laser dye attached with (dotted)/ without (lined) AgNP's in alcohol solvents (1- methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol, 6-decanol, 7-nonanol).

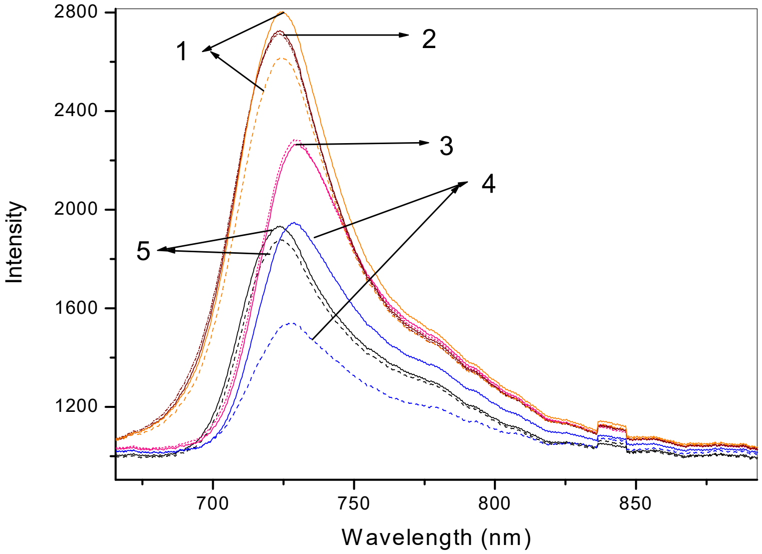


Figure 20 Fluorescence spectra of ADS680HO laser dye attached with (dotted)/ without (lined) AgNP's in alcohol solvents (1- decanol, 2-ethanol, 3-octanol, 4-butanol, 5-ethanol).

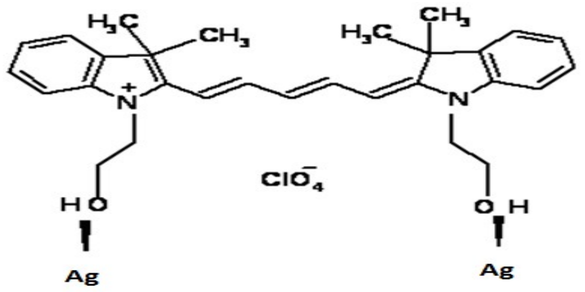


Figure 21 Attatchment of AgNP's with ADS680HO.

## I. Results and discussion on absorption and fluorescence quenching of laser dyes with gold and silver nanoparticles

In this scenario, quenching of absorption and fluorescence was observed for ADS680HO dye molecules in alcohols linked by hydrogen bonding to AuNPs and AgNPs. The energy transfer rate from dye to NP's is regulated by three parameters, which cause quenching.

1. Coulombic overlap integral.
2. Position (surface plasmon frequency)
3. Width (inverse surface plasmon life time) of the absorption spectrum of AuNP's/ AgNP's relative to the dye.

The influence of coulombic interactions on the energy transfer has been studied with two factors

1. Interaction between dye and AuNP's / AgNP's depends upon respective charge densities
2. The interaction within the dipole approximation

The charge densities of a dye, dipole moments of a dye and AuNP's/AgNP's are responsible for the energy transfer between dye to AuNP's / AgNP's which leads to quenching in optical absorption UV-Vis spectra, exhibits a band between 670-700nm (in ADS680HO) is due to π-π* transitions.

The attachment of AuNPs/AgNPs to a dye results in a substantial amplification / quenching of fluorescence, depending on the nature of the dye used. In our example, all three dyes exhibit quenching phenomena when tested with a nano probe.

The variations in molecular fluorescence near an AuNP's / AgNP's in close vicinity of a metal are explained by the widening of a plasmon, and the fluorescence rate of the molecules is a function of the distance between the probe molecule and the AuNP's /AgNP's metal surface. When a fluorescent dye comes into close touch with a nano metal, its fluorescence is entirely quenched. So, in our situation, AuNPs/AgNPs with a dye connection are somewhat longer.

By analysing the UV-Vis absorbance spectra in the range 450-800nm using a dye molecule, the size influence on the location of the surface plasmon band of alcoholic functionalized gold nanoparticles was examined. Alcohols were chosen as the solvent for particular interactions with the -OH group, thiol group, and ester group of the ADS680HO dye chain, which might have a significant impact on the optical characteristics of gold and silver nanoparticles.

When the dimensions of nanoparticles become smaller than the wavelength of the exciting light ($2R \ll \lambda$ ), energy can be confined in small spatial regions through the local excitation of surface plasmon resonance. The optical properties of metal nanoparticles are strongly influenced by their size, shape and surrounding environment, in addition to resonant energy transfer between closely spaced metal nanoparticles with the surrounding molecule also accounts.

A resonance energy transfer model based on non radiative decay provides a theoretical understanding of these observations of fluorescence quenching. The optical properties of molecules adsorbed on or enclosed in metallic and dielectric particles have been investigates both experimentally and theoretically in recent years. When a particle has been excited and is oscillating in the incident electromagnetic field, the exciting system may have a fluctuating electric dipole moment and causes the radiation. This light radiation from dipole moment provides the channel for radiative decay. On the other hand, the joule heating and plasmon absorption caused by these fields open the non-radiative decay channels. The competitions between radiative and nonradiative decay energy affects the fluorescence emission of the molecules located near the particles. Fluorescence quenching happens when nonradiative decay becomes dominant. Because the radiative and nonradiative rates behave differently at different distances, the apparent quantum yield always disappears at a small distance from a metallic nanoparticle.

The observed fluorescence quenching is due to the transfer of resonance energy from ADS680HO to gold / silver nanoparticles. The Forster resonance energy transfer (FRET) hypothesis can be used to study this nonradiative decay. When several gold/silver colloidal nanoparticles are put into an ADS680HO dye molecule solution in different alcohols, molecules prefer to cluster around the gold/silver particles due to physical adsorption. As the concentration of ADS680HO increases, more molecules adsorb on the gold particles. Gold nanoparticles have a high quantum efficiency.

$$Q=\frac{\Gamma^{R}}{\Gamma^{R}+\Gamma^{NR}} \tag*{15}$$

$\Gamma^{R}$ – radiative decay rate; $\Gamma^{NR}$– non radiative decay rate

Adsorption of AuNPs / AgNPs with the dye produces an increase in nonradiative decay rate, resulting in a loss in quantum efficiency or fluorescence quenching.Static quenching might also be attributed to dye interaction with gold / silver nanoparticles via complexes of the nano metal with -OH, thiol, and ester groups.

## CONCLUSIONS

The optical characteristics of spherical gold nanoparticles are critical in determining the strength and location of the plasmon resonance. As the size of the spherical nanoparticles increases, the peaks expand and shift to longer (red shift) wavelengths. The change in dielectric medium and RI characteristics can explain the shift in the SPR of the band location and intensity of the nanoparticle assembly.

The optical absorption and fluorescence intensities of ADS680HO laser dyes in alcohol solvents with and without AuNP/AgNP attachment reveal quenching. This is related to the size, shape, energy transfer, and interaction of the AuNPs/AgNPs with the dye. Fluorescence quenching using AuNPs/AgNPs and ADS680HO laser dye has various uses, particularly in biomolecular labelling and fluorescence patterning.

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