Nanoparticle Resonance Mechanism Behaviour in a Dye Environment

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Abstract

Nanoscience and nanotechnology are recent revolutionary developments of science and technology that are evolving at a very fast pace since a decade. Materials in the nanometer size regime show behavior which is intermediate between that of a macroscopic solid and an atomic or molecular system because of high surface to volume ratio, quantum size effect and electro dynamical interactions

Optical properties of nano particles and their dependence on particle size effect have been investigated through Mie's Scattering theory. The absorption spectrum of gold nanoparticles of size 4-12nm has a maximum peak in the range 540-550nm, which is related to the surface plasmon resonance(SPR). Our main task is to calculate the extinction, absorption and scattering coefficients of gold nanoparticle of various sizes using Mie's theory with available simulations. Observed results reveals as the size of the nanoparticles increases from 4 to 50nm, extinction efficiency at resonant peak is also increases, along with SPR shifts from 520nm to 570nm

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.

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

I INTRODUCTION

Nanoscience and nanotechnology are steering mankind into new realms of efficient and miniature tools and gadgetry in the latest technological field. Every interdisciplinary field, such as physics, chemistry, biology or applied science such as medicine or engineering is exploding with tremendous new discoveries at the nanoscale level.

The study of atoms and molecules is the conventional field of physics or chemistry. An atom measures about 1-10 angstrom, (1 Å = 10^{-10} metre). But, particles with sizes in the range of 1-100nm (1nm = 10^{-9} metre) are called nanoparticles, whether they are dispersed in gaseous, liquid or solid media. Studies in the late 19th and 20th century established that the nanometre (nm) represents a collection of a few atoms or molecules. Materials in the range 1-100nm scale have shown the physical, chemical and optical properties of a material become dependent on its size and shape. New properties develop on the nanoscale due to the lack of symmetry at the interface or to electron confinement that does not scale linearly with size. Thus, the nanometre scale (1-100nm) incorporates collections of atoms or molecules, whose properties are neither those of the individual constituents nor those of the bulk.

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. Nano (10^{-9}m) sized metal particles exhibit optical properties of great aesthetic, technological and intellectual values. Colloidal solutions of the noble metals namely, silver and gold show characteristic colours that have received considerable attention to researchers.

Gold and silver 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.

The German physicist Gustav Mie (1869-1957) in 1908 published an important article on light scattering in matter in Annalen Der Physik with the title *"Beitr¨age zur Optik tr¨uber Medien, speziell kolloidaler Metall¨osungen"*. This theoretical work is the foundation to the theory describing the optical properties of small metal particles. Metal particles like nanogold are small with respect to the visible wavelength and show characteristic absorbing and scattering properties. Gustav Mie calculated the absorbance of colloidal gold particles as a function of the particle size using classical electromagnetic theory with the bulk optical properties of metallic gold. These detailed calculations are done for gold and silver nanoparticles in this present work.

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

The nanometre scale is also interesting in biological systems. Many proteins are nearly 10's of nm in size. Since structures can be accurately designed on the nanometre scale they can be incorporated into biological systems, due to the similar size scales. Biological systems are complex, with biological fluid synthesis, structure and functions all are rarely understood in detail. Nanostructures are being used as drug delivery agents, labelling agents, sensors and to enhance electromagnetic fields, wide variety of applications in the fields of electronics, chemistry, just to mention few: gold nanoparticles are being used to enhance electroluminescence and quantum efficiency in organic light emitting diodes ; palladium and platinum nanoparticles are used as efficient catalysts; glucose sensors are developed based on silver nanoparticles; and iron oxide nanoparticles are used as contrast agents in diagnosing cancer 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	5.90×10^{28} m^{-3}- 59.0×10^{-9} m^{-3}	5.86×10^{28} m^{-3}- 58.6×10^{-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	5.90×10^{28} m^{-3}	5.86×10^{28} m^{-3}
Fermi Speed	1.40×10^8 $cm\ s^{-1}$	$1.39 \times 10^8 cm\ s^{-1}$
Fermi Energy	5.51eV	5.48eV
Plasma frequency	1.31×10^{16} $rad\ s^{-1}$	1.30×10^{16} $rad\ s^{-1}$

Relaxation Time	2.94×10^{-14}s	4.01×10^{-14}s
Ionization Energy	9.22eV	7.57 eV
Electric Resistivity	2.20×10^{-6} Ωcm	1.61×10^{-6} Ωcm
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 for life sciences represents an attempt to faster medical diagnosis and analysis. Quantum dots have been used in medical imaging with the ability to differentiate many different areas of a cell with single excitation source. They have advantages over traditional fluorescent dyes that they are more photostable than conventional dyes, and at the same time chemistry can be used to modify different colours for entry into the biological sample. 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

Materials in the nanometre size regime show behaviour that is intermediate between that of a macroscopic solid and that of atomic or molecular systems. There are three major factors that are responsible for these differences:
1. High surface-to-volume ratio
2. Quantum size effect
3. Electrodynamic 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. Nanometre-scale metal particles exhibit optical properties of great aesthetic, technological and intellectual value. Colloidal solutions of noble metals, viz., copper, silver and gold show characteristic colour that have received considerable attention from researchers. The interesting colours observed in gold solutions have led to extensive study of their optical spectroscopic properties in an effort to correlate their behaviour under different micro environmental conditions. The thermal conductivity is enhanced for small particles due to higher surface to volume ratio.

In the last fifteen years massive advances of nanomaterials in material science is observed. This is because of the reason quantistic effects and surface atoms with partial coordination strongly influence physical and chemical behaviour of the nanomaterials, originating properties different from both molecules and bulk solids, sometimes complementary with them.

The wide spread of nanotechnology in this decade is strictly due to the improvements in characterization and synthesis techniques of nanometre scale. This makes the innate curiosity towards a field generous of new physical phenomena and synthetic opportunities. From this point of view, Feynman's prophecy of looking at nanotechnology "just for fun" has been fulfilled, but the massive amount of money attracted by nanotechnology has also a more concrete basement. In fact, microtechnology and molecular chemistry shaped the last century by enormous advancements in information science and medicine. Now, nonmaterial's laying for size and properties in between molecules and micromaterials, promise to further revolutionize the human life.

The importance of nanoscience and nanotechnology is highly increased since past decade. Gold and Silver nanoparticles had a significant role in this process, due to their many peculiarities.

This research reveals panorama of gold and silver nanoparticles (AuNP's and AgNP's hereafter) are playing a protagonist role. The reason for the AuNP's and AgNP's are the surface plasmon resonance (SPR), which has 10^5 to 10^6 larger extinction cross section than ordinary molecular chromophores. Furthermore, AuNP's and AgNP's have high chemical stability, photostability and especially they are non toxic for living organisms.

D. Historical background

Since ancient times, gold has been valued in every culture for its beauty as well as for its unique physical and chemical properties. Gold is probably one of the first metals known to mankind. Extraction of gold started in the 5th millennium B.C. in Bulgaria, "Soluble" gold appeared around the 5th century B.C. in Egypt and China. Colloidal gold and silver have been used in ancient times to colour the glass of intense shades of yellow or red depending upon the concentration of the two metals. A best example is the famous Lycurgus Cup in the British Museum around 4th Century A.D. In the middle ages Au colloids and the soluble gold was used to disclose fabulous curative powers for various diseases, such as venereal problems, dysentery, epilepsy and tumours and for diagnosis of syphilis. Indian ancient ayurvedic medicines were using swarna bhasma, swarna bindu prashana to enhance the immunity power of the body. Thus, the remarkable features exhibited by colloidal gold have been utilized for centuries.

The first "scientific" 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

The approaches to metal nanoparticles synthesis can be classified in to following categories

- ✓ 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 widely used methods are based on chemical reduction in solution (wet chemistry) to yield colloidal nanoparticles. Wet chemical approaches require the reduction of gold and silver salts and the chemisorption or physisorption of ligands on the surface of metal nanoparticles to avoid their coagulation and precipitation.

The Turkevitch method is the most popular for obtaining Aqueous solutions of gold nanoparticles that are easily functionalizable with subsequent steps. This method consists of reduction of HAuCl$_4$ in a boiling aqueous solution of sodium citrate. Citrate molecules act both as reducing and stabilizing agent. This technique is also the basis to control nanoparticles shape and one can obtain spheres, prisms, cubes, rods or wires. Synthesized nanoparticles are extremely unstable to make stable for longer period and stabilizing agents or capping for the molecule is must. This capping of the nanoparticles can be done using citrate, sodium borohydride or some greenery materials like gum arabic, turmeric, cinnamon, neem etc., can be made.

A. Synthesis of nanoparticles: Chemical Reduction method

B. Materials

Trisodium citrate, Hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$. 3H$_2$O), Sodium borohydride (NaBH$_4$), Silver nitrate are procured from Himedia Laboratories Pvt Ltd. Mumbai, India. Ultra deionised water was used for all solution preparations. All glass wares are cleaned with aquaregia solution.

C. Synthesis of gold nanoparticles

Gold Nanoparticles (AuNP's) are synthesized via the reduction of 20mL aqueous solution containing 2.5x10^{-4} M of HAuCl$_4$ and 2.5x10^{-4} M of trisodium citrate was separately prepared 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. Depending upon the rate of addition of reducing agent to the metal salt solution we are able to prepare spherical gold nanoparticles of various sizes.
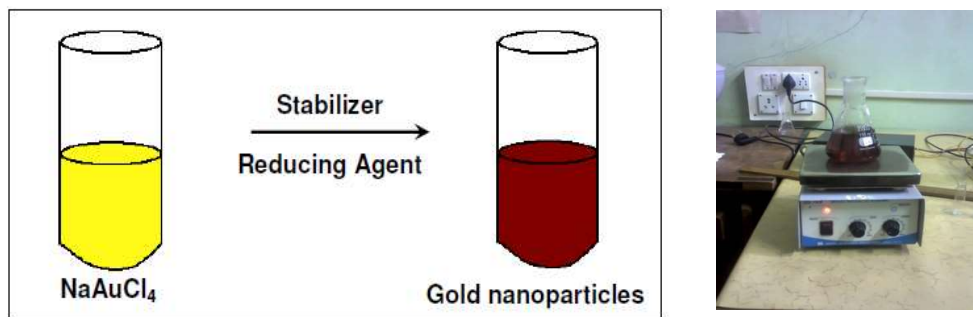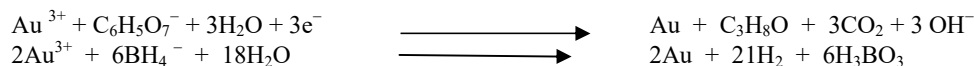
Figure 1 Synthesis of gold nanoparticles using chemical reduction method.

However, a traditional hydridic and carboxylate-based reduction strategy leads to nanoparticles of lower stability and toxicity. To circumvent existing problems associated with the production of AuNP's, we have chosen green nano technique towards the fabrication of biocompatible AuNP's and is non toxic, trimeric alanine-based phosphine $P[CH_2NHCH(CH_3)-(COOH)_3]$ (Thpal) as a reducing agent, that provides an unprecedented pathway to produce AuNP's at acidic pH. Further to prevent aggregations of AuNP's are capped with Gum arabic (glycoprotein) and the synthesized AuNP's are stable even up to 6 months. Indeed detailed investigations have confirmed that Gum Arabic serves as an excellent backbone for the stabilization of AuNP's. SPR, SEM, TEM pictures of AuNP's of size 4-12nm.

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

D. Synthesis of silver nanoparticles

Silver nanoparticles were synthesized by chemical reduction method. 1.0mM of $AgNO_3$ was dissolved in 20ml of highly deionised water. Solution of $AgNO_3$ was further added to 0.1mM trisodium citrate. With continues stirring and further mixing 0.6ml of 0.1mM $NaBH_4$ was added drop by drop. The yellow colour solution was formed. The preparation process is free from direct incident of light. The formation of silver nanoparticles is confirmed by absorption spectroscopy of the yellow colour solution (Figure 2).
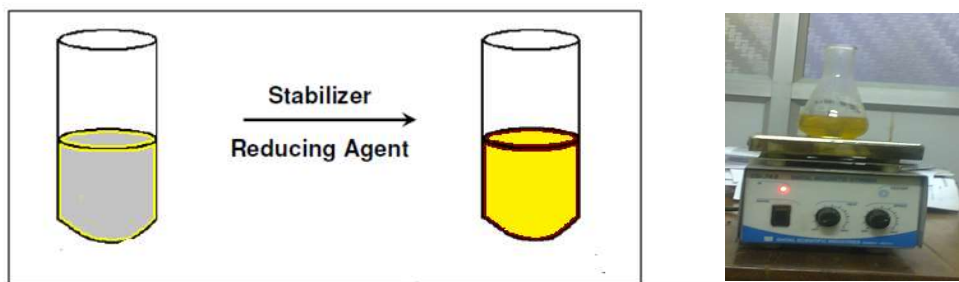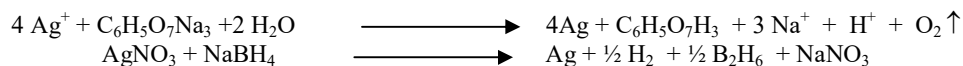

Figure 2 Synthesis of silver nanoparticles using chemical reduction method.

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

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.
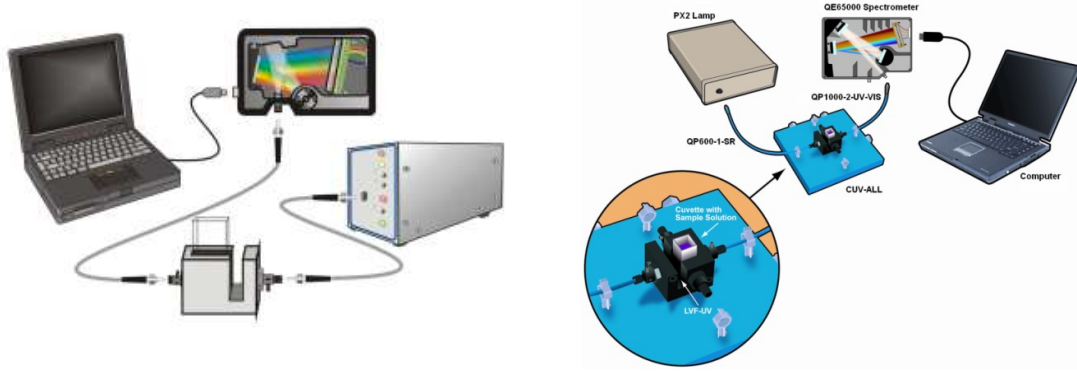

Figure 3 UV/VIS/NIR Spectrophotometer, Ocean Optics.

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) (Make: JEOL JSM-6360) is a type of electron microscopy capable of producing high resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. The schematic diagram of SEM along with optical measurements is given in Figure.4.
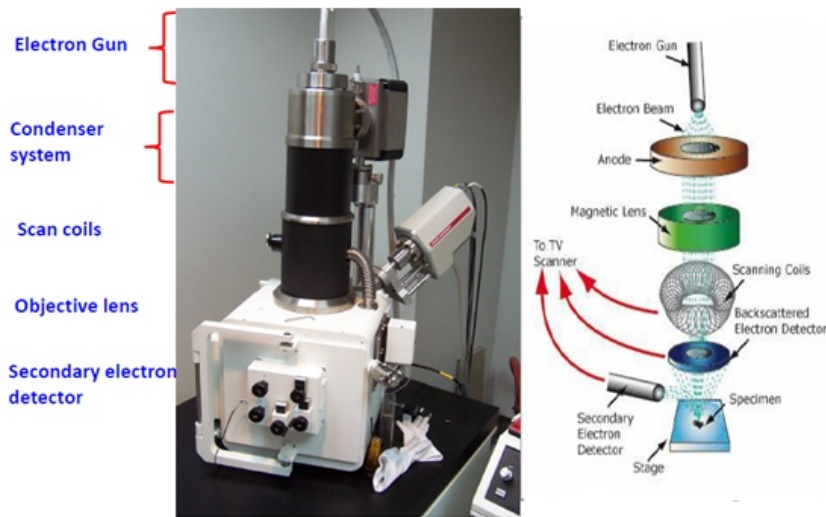
Figure.4 Schematic diagram Scanning Electron Microscope (SEM).

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.

Characteristically, noble nanoparticles exhibit a strong absorption band in the visible region and this is indeed a small particle effect, since they are absent in the individual atom as well as in the bulk. The physical origin of the light absorption by metal nanoparticles is the coherent oscillation of the conduction band electrons induced by the interacting with electromagnetic field. The electromagnetic surface waves can propagate along the interface between conducting materials and a dielectric over a broad range of frequencies ranging from dc and radio frequencies up to the visible. The oscillation modes comprise an electromagnetic field coupled to the oscillations of conduction electrons and are called surface plasmon.

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).
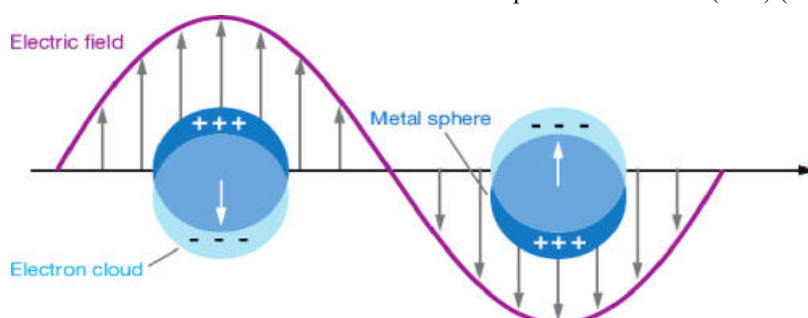

Figure 5 Surface Plasmon Resonance

For many metals, like Pb, In, Hg, Sn and Cd the plasma frequency lies in the UV region 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 form air-stable colloids.
2. Due to d-d band transitions, the plasma frequency lies in the visible region.
3. At the plasmon frequency the imaginary part of the dielectric constant is very small.

Hence, the surface plasmon experiments are very interesting.   So, SPR experiments are most commonly carried out with Cu, Ag and Au. The resonance frequency of this SPR is strongly dependent upon the size, shape, interparticle interactions, dielectric properties and local environment of the nanoparticles.

The resonant frequency is critically determined by the following factors:
  i. Density of electrons
  ii. Effective electron mass
  iii. Shape
  iv. Size of the charge distribution

Study SPR (Figure 6 and 7) of metal nanoparticles using UV/Visible and Infrared absorption spectroscopy is particularly helpful to obtain raw information about the size, structure and composition in a fast and inexpensive way.

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).
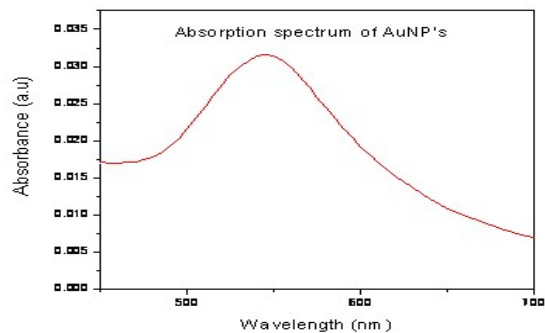
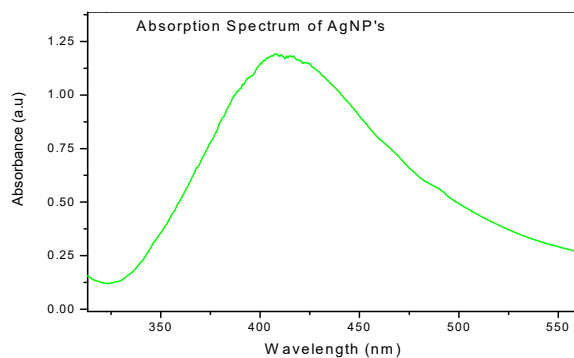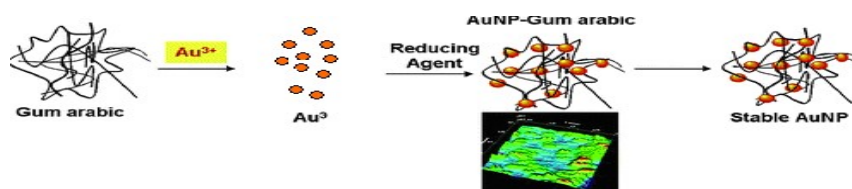Figure 6 Surface Plasmon Resonance absorption spectrum of AuNP's in aqueous solution.
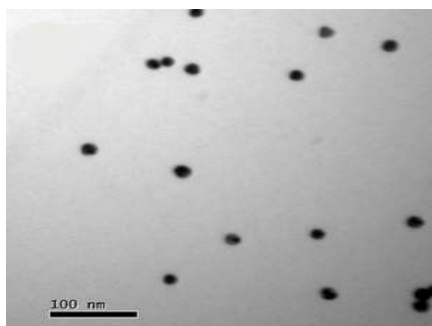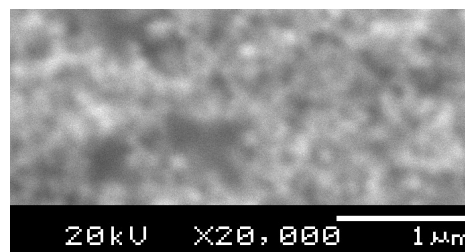

Figure 7 Surface Plasmon Resonance absorption spectrum of AgNP's in aqueous solution.

(a) AuNP's capping by gum Arabic.

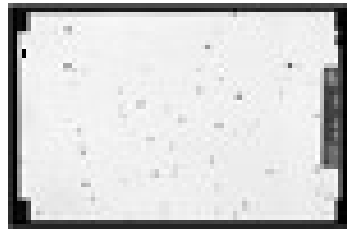(b) TEM image of AuNP's   (c) SEM image of AuNP
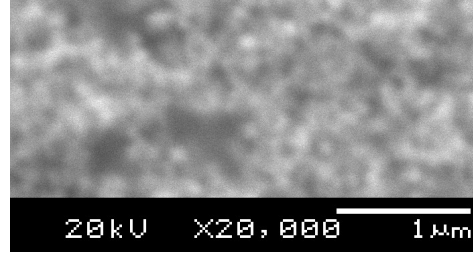
Figure 8 (a) AuNP's capping by gum Arabic,   (b) TEM and   (c)SEM images.

(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. When an electromagnetic wave passes through a metal nanoparticle, excites its electronic or vibrational states. This phenomenon induces dipole moments that oscillate at the respective frequency of the incident wave. This collective oscillation of the free conduction electrons is called the surface plasmon resonance (SPR).

The extinction spectra of a dilute dispersion of colloidal gold & silver metal nanoparticles can be explained using Mie's theory. It was the colour variation of colloidal gold/silver with particle size that motivated Mie to apply the general theory of light extended to small particles. He applied Maxwell's equations with appropriate boundary conditions in spherical coordinates using multiple expansions of the incoming electric and magnetic fields and offered exact electrodynamic calculations of the interaction of light with spherical metallic nanoparticles. The theory describes the extinction (absorption and scattering) of spherical particles of arbitrary sizes.

A.   **Mie's theory:**

The main assumption of Mie's theory is, the particle and its surrounding medium are each homogeneous and describable by their bulk optical dielectric functions. The boundary is defined by the electron density, which is assumed to have a sharp discontinuity at the surface of the particle at radius R. The particle size, optical material function of the particle and the surrounding medium were employed as the input parameters. To relate the dipole plasmon frequency of a metal nanoparticles to the dielectric constant, we consider the interaction of light with a spherical particle i.e., much smaller than the wavelength of light ($2R \ll \lambda$), where R is the radius of the particle. Under these circumstances, the electric field of light can be taken to be constant and the interaction is governed by electrostatics rather than electrodynamics. This is often called the quasistatic approximation. Optical properties of isolated colloidal particles and in particular, their dependence on particle size effect have been intensively investigated through Mie's scattering theory. In particular, the Mie theory is a mathematical physical description of the scattering of electromagnetic radiation by spherical particles immersed in a continuous medium. The Mie scattering solution begins with macroscopic Maxwell equations, using complex representation of the electric field, **E**, and auxiliary magnetic field, **H**.

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

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

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

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

The configuration of an incident electromagnetic field with two components, the electric field E and the magnetic field H can be described by the Helmholtz's relation as

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

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

in which k is the wave number defined by

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

The series for **E** and **H**, which were used for the scattering amplitude functions, may be inserted into the appropriate integrals and carrying out the integration term by term, we obtain the extinction and scattering coefficients as

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

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

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

in which the size parameter, x, is given by

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

where R is the radius of the particle, n_m is the refractive index of the medium, ω is the wavelength of the incident light in vacuum, a_n and b_n are the scattering coefficients, which may be expressed in terms of the Ricatti-Bessel expressions:

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

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

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 indicates differentiation with respect to the argument in the parentheses. In these expressions, n is the summation index of the partial waves of the surrounding medium. $n = 1$ corresponds to the dipole oscillation, while $n = 2$ is associated with the quadruple oscillation and so on. The effect of particle size on the peak resonant wavelength results from two different mechanisms depending on the particle size range. In the limit of $2R \ll \lambda$ (R is the radius of the particle and λ is the wavelength of the light), only the electric dipole term contributes significantly to the extinction cross-section (σ_{ext}) as;

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

where $V = \left(\frac{4\pi}{3}\right)R^3$ is volume of the spherical particle, ω is the angular frequency of the exciting light, c is the velocity of light ε_m and $\varepsilon(\omega)$ [$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$] are the dielectric frictions of the surrounding medium and the material itself respectively. The resonance condition is fulfilled when $\varepsilon_1(\omega) = -2\,\varepsilon_m$ provided ε_2 is small or weakly dependent on ω.

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

Optical properties of isolated colloidal particles and in particular their dependence on particle size effect have been intensively investigated through Mie's scattering theory. In the present case the absorption spectrum of gold nanoparticles of size 4-12nm has a maximum in the range 540-550nm, which is related to the plasmon resonance formed due to the nano sized (4-12nm) gold nanoparticles. This absorption band (surface plasmon resonance SPR) results from interactions of free electrons confined to small metallic spherical objects with incident electromagnetic radiation. The observed plasmon resonance band shows that the gold nanoparticles are spherical in shape. Our main task is to calculate the extinction, absorption and scattering coefficients of gold nanoparticles of various sizes using Mie's theory and available simulations. Observed results reveal that as the size of the nanoparticles is increases from 4 to 50nm, extinction efficiency at resonant peak is also increases, along with SPR shifts from 520nm to 570nm as the size of the nanoparticles increases.

C. **Experimental setup**

Optical absorption and fluorescence were recorded using Ocean Optics HR4000 high resolution spectrometer. Computational electrodynamics calculations like absorption, scattering and extinction efficiencies were calculated using "nanohub.org" simulations. Graphical representations were done through Origin 6.0 software.

D. **Results and discussion**

In the present case the absorption spectrum of AuNP's has a maximum in the range 540-550nm peaking at 545nm, which is related to the surface plasmon resonance formed due to the nano sized (4-12nm) gold particles. This absorption band results from interactions of free electrons confined to small metallic spherical objects with incident electromagnetic radiation. The observed plasmon resonance band shows that the gold nanoparticles are spherical in shape (Table 2).

Extinction coefficient is sum of absorption and scattering coefficients. Scattering arises when charged particles accelerated by a field and reradiate. Absorption occurs when the particle takes energy out of the beam and converts it to other forms. Mie's expression for extinction efficiency is given by Equation 14, the extinction efficiency, absorption and scattering spectrum for several nanoparticles radii can be seen in Figure 9 to 13. The wavelength corresponding to maximum extinction shifts to longer wavelengths (red shift) as the particle radius increases. The peak seen at 545nm corresponds to the resonance condition for small spheres specifically when ε_1 $(\omega) = -2\,\varepsilon_m$. A large shift of the dipole peak and a much more complex spectrum occur when the particle radius is increased further.

The extinction spectrum of a solid gold nanoparticle has been calculated using Mie theory. This consists of calculating extinction from Mie's equation at many different wavelengths. The extinction spectrum for several nanoparticle radii can be seen in Figure 10. The wavelength corresponding to maximum extinction shifts to longer wavelengths (red shift) as the particle radius increases.

Since the dielectric medium constant (ε) is related to refractive index i.e., $(n_{eff} + ik_{eff})^2 = \varepsilon_{eff}$ (ε_{eff} is the effective dielectric constant of the nanocomposite, n_{eff} is the real part of the effective complex index of refraction for the nanocomposite, k_{eff} is the imaginary part of the effective complex index of refraction). Here we show that, the evolution of the SPR band at the longer wavelength region can be considered as result due to the increase in effective refractive index of nanoparticles in the assembly, the size of individual gold nanoparticles in the solution should remain largely constant, where as the inter particle distance changes, which leads to changes in the inter particle dielectric medium constant or refractive index. Refractive index 'n' will be used to represent the n_{eff}. Interestingly, the change in 'n' was found to exhibit an approximate linear relationship with λ_{max}. Simulation results for gold nanoparticles for various sizes 10-50nm particles using Mie's theory, which matches with the bands in terms of the SPR wavelength as observed. On the basis of the documented principle, plasmon band red shift increases with refractive index changes. A basic assumption for applying the Mie theory simulation to this system is that the nanoparticles within the assembly environment have a refractive index higher than that in the water environment. This assumption is qualitatively supported by the trend of refractive index changes reported in previous studies for similar assemblies of metal nanoparticles in different systems. The effect of electromagnetic retardation in larger sized nanoparticles makes the observed red shift in the plasmon resonance.

Table 2 Extinction, Absorption and Scattering efficiency of gold nanoparticles of various sizes in the surrounding aqueous medium.

Radius of the nanoparticle (nm)	Position of λ_{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 show the calculated spectra of the efficiency of absorption, scattering and extinction for gold and silver nanoparticles of radius 10-50nm in size. The dimensionless efficiencies can be converted to the corresponding cross-sections σ_{abs}, σ_{ext} and σ_{sca} have units of m^2 because they represent an equivalent cross-sectional area of the particle that contributes to the absorption, scattering and extinction of the incident light (Table 2 & 3).

The optical properties of spherical gold nanoparticles can be tuned by adjusting the physical dimensions. The dielectric properties of the material are extremely important and play a large role in the intensity and position of the plasmon resonance. As spherical nanoparticles get larger the peaks broaden and shift to longer (red shift) wavelengths. This shift of the SPR band position and intensity of the nanoparticles assembly can be related to the change in dielectric medium and refractive index (RI) properties, which provide a means to produce optical signals for up taking or releasing of molecular species in the nanoparticles assembly. This type of interparticle property also has potential applications in controlled drug delivery, electrical sensors, the electrical response of nanoparticles assemblies to vaporsorption serve as an excellent example illustrating the correlation of the electrical with interparticle dielectric medium properties, The understanding of the precise control of the interparticle properties will benefit in the field of nanostructured sensing applications.
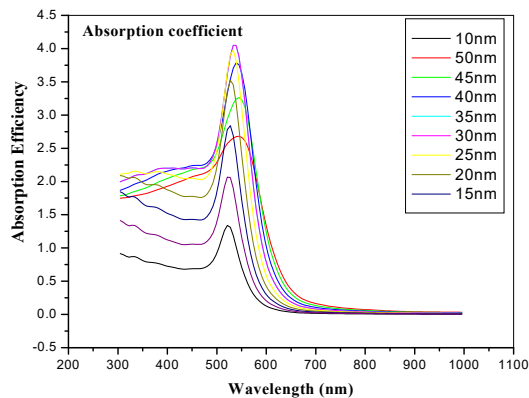

Figure 9 Absorption coefficient of gold nanoparticles of various sizes from 10-50nm.
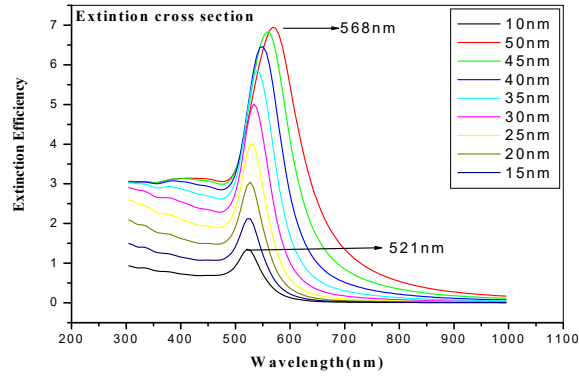
Figure 10 Extinction cross section of gold nanoparticles of various sizes from 10-50nm.
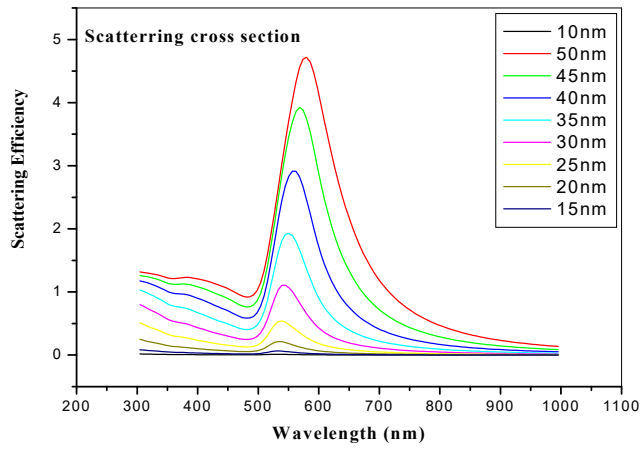

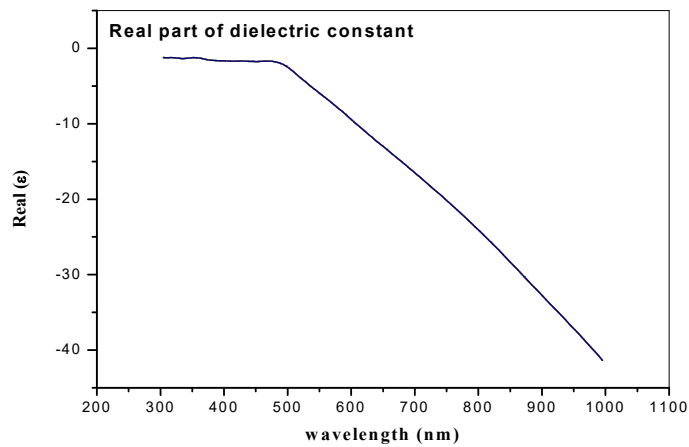Figure 11 Scattering cross section of   gold nanoparticles of various sizes from 10-50nm.

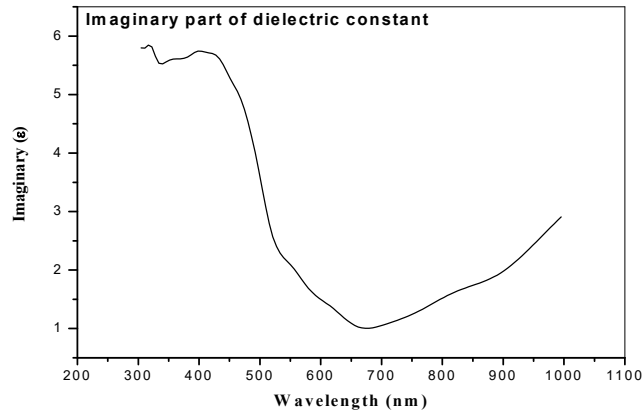Figure 12 Real part of dielectric constant of gold nanoparticles.

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Figure 13 Imaginary part of dielectric constant of gold nanoparticles.

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 λ_{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
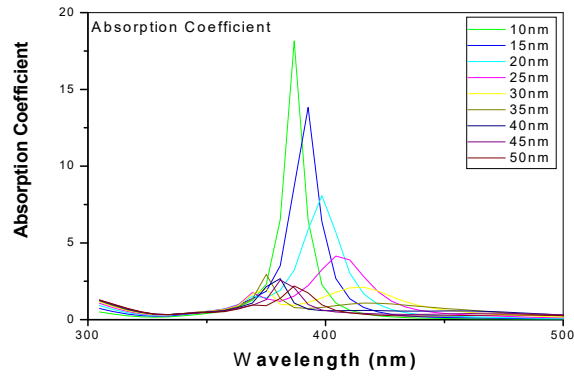
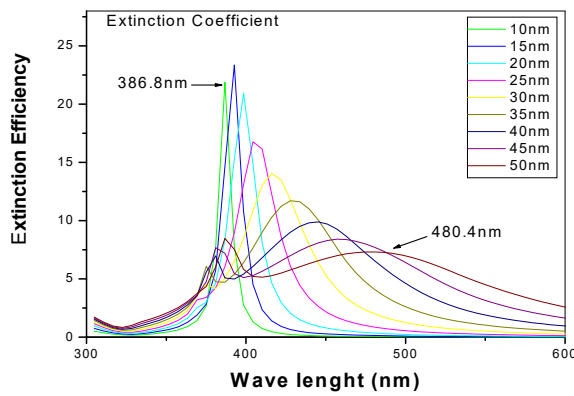Figure 14 Absorption coefficient of silver nanoparticles of various sizes from 10-50nm.

Figure 15 Extinction cross section of silver nanoparticles of various sizes from 10-50nm.
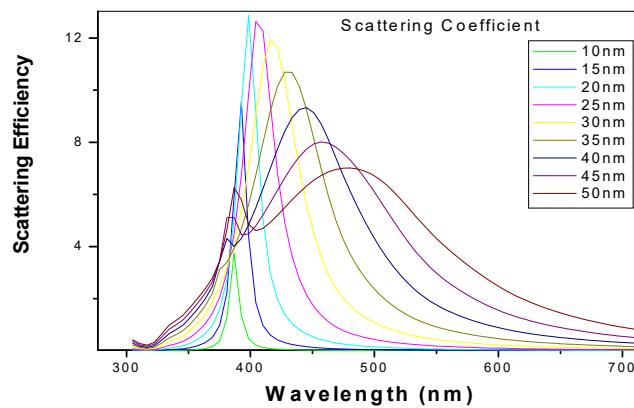

Figure 16 Scattering cross section of silver nanoparticles of various sizes from 10-50nm.
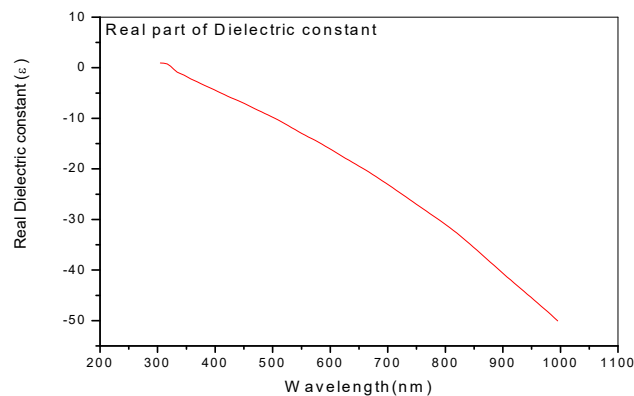
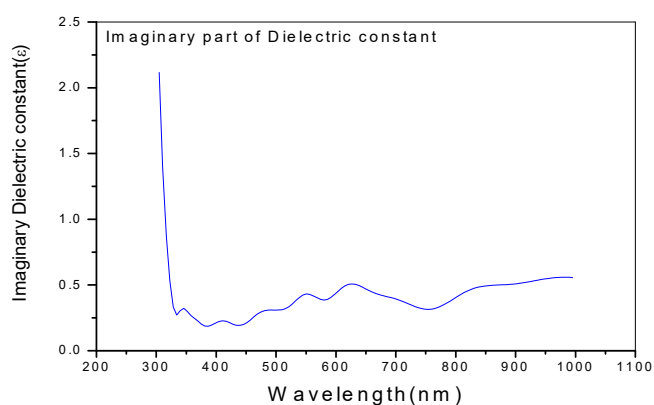Figure 17 Real part of dielectric constant of silver nanoparticles.

Figure18 Imaginary part of dielectric constant of silver nanoparticles.

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

Absorption and fluorescence quenching refers to any process that decreases the absorbance and fluorescence intensity of a sample. A variety of molecular interactions can result in quenching. These interactions include excited state reactions, molecular rearrangements, energy transfer, ground-state complex formation and dynamic (collissional) quenching. In this chapter we are considering quenching results from collissional encounters between the fluorophore and quencher, which is called collissional or dynamic quenching, due to binding between the fluorescent sample and the quencher.

Fluorescence quenching has been widely studied both as a fundamental phenomenon and as a source of information about biochemical systems. These biochemical applications of quenching are due to molecular interactions that result in quenching. Both static and dynamic quenching requires molecular contact between the fluorophore and quencher. In case of collissional (dynamic) quenching, the quencher must diffuse to the fluorophore during the life time of the excited state. Upon contact, the fluorophore returns to the ground state without emission of a photon. In general, quenching occurs without any permanent change in the molecules, i.e., without a photochemical reaction. In static quenching a complex is formed between the fluorophore and the quencher, this complex is non fluorescent. For this static or dynamic quenching to occur the fluorophore and quencher must be in contact.

During the past several years there has been increased interest in the interactions of fluorophores with metallic surfaces or nanoparticles. Gold and silver colloids display intense colours due to their strong interactions with light. The intensity of fluorophores near gold or silver nanoparticles is usually quenched.

During the present investigation, there has been great interest in the use of gold / silver colloids on the surfaces of ADS680HO laser dye. Many of the reports make use of the high extinction coefficients and light

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scattering cross sections of gold and silver nanoparticles. It is also possible to create molecular beacons based on the strong quenching of fluorophores near gold/silver surfaces. In case of ADS680HO contained alcoholic group that spontaneously binds to gold/silver nanoparticle surface. When bound to the colloids ADS680HO, adsorbed the gold/silver nanoparticle surface and were completely quenched. The mechanism of quenching by gold is probably due to resonance energy transfer (RET) to the absorption bands of gold / silver.

A wide variety of substances act as quenchers of fluorescence. The best-known colloidal quenchers is molecular oxygen (in alcohol, thiol or in ester group) and sulphur (in thiol group), which quenches almost all known fluorophores. The mechanism by which oxygen quenches has been a subject of debate. The most likely mechanism is the paramagnetic oxygen and sulphur causes the fluorophore to undergo inter system crossing to the triplet state. In fluid solutions the long lived triplets are completely quenched, so that phosphorescence is not observed. Quenching by these substances probably involves a donation of an electron from the flurophore to the quencher.

AuNP's/AgNP's can serve as ultra-efficient quenchers of molecular excitation energy in chromophore-AuNP/AgNP composites, outranging the quenching efficiency of organic acceptor molecules. The theoretical modelling of the quenching efficiency has been carried out extensively during the past decades. However, the meaningful experiments, where important parameters such as the size of the AuNP's/AgNP's and the distance between the chromophores and the AuNP's have been tightly controlled, were carried out recently. In those studies, where conjugates of chromophores and metal nanoparticles are kept in aqueous solution, a pronounced quenching of fluorescence is observed. Only in those cases where the chromophores and the AuNP's are separated by bulky spacers, such as antibodies, is the less quenched fluorescence.

In the present case the absorption spectrum of AuNP's has a maximum in the range 540-550nm peaking at 545nm. Similarly, AgNP's has a maximum in the range 405-410nm peaking at 408nm. Both are related to the plasmon resonance formed due to the nano sized (4-12nm) gold / silver nanoparticles. This absorption band results from interactions of free electrons confined to small metallic spherical objects with incident electromagnetic radiation. The observed plasmon resonance band (Figure 6 and 7) shows the gold/silver nanoparticles are spherical in shape.

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

Figure 14 is the absorption spectrum of ADS680HO in alcohols with and without AuNP's, shows the broad band in the visible region 670-700nm. While, Figure 15 shows the fluorescence spectrum with the broad band in the 700-750nm region.

The SPR of AuNP's (of size 4-12nm) shows a maximum at 545nm. When AuNP's was added to ADS680HO the absorbance band shifts towards higher wavelength (red shift) and peaking at 680nm (in methanol), 682nm (in ethanol), 684nm (in butanol), 686nm (in nonanol), 687nm (in decanol) & 689nm (in glycerol) and intensity of absorbance quenches. Similarly fluorescence band shifts to higher wavelength region peaking at 716nm (in methanol), 721nm (in butanol), 711nm (in glycerol) and 718nm (in propanol) and fluorescence intensity is also quenches. Dampening and broadening of the band was evident as these molecules complexes with the AuNP's. The dampening of the Au band indicates that due to attachment with ADS680HO via alcohol group alters the electron density of the AuNP's, thereby directly affecting the absorption of the surface bound ADS680HO as well as absorption band (Figure 16).
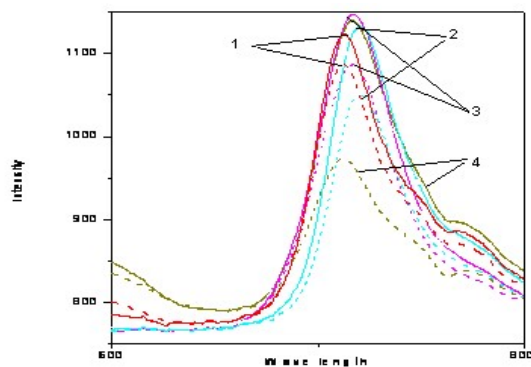

Figure 14 Absorption spectra of ADS680HO attached with (dotted)/without (lined) AuNP's in alcohol solvents (1- methanol, 2-butanol, 3-nonanol, 4-glycerol).
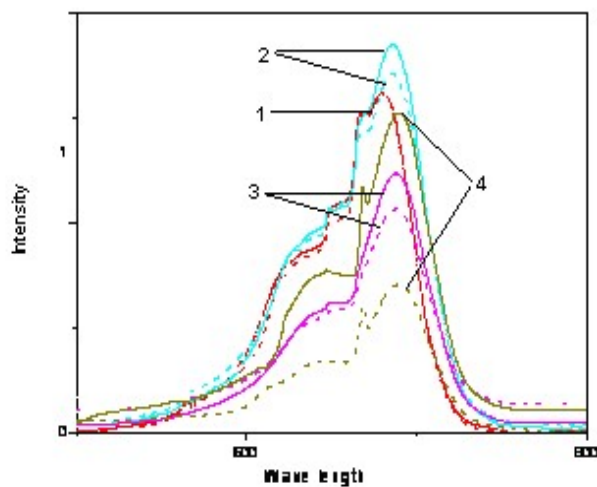
Figure 15 Fluorescence spectra of ADS680HO attached with (dotted)/without (lined) AuNP's in alcohol solvents (1- methanol, 2-butanol, 3-nonanol, 4-glycerol).
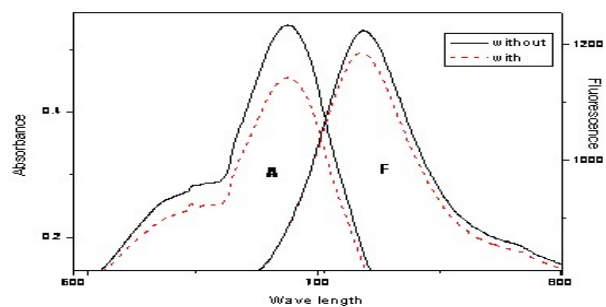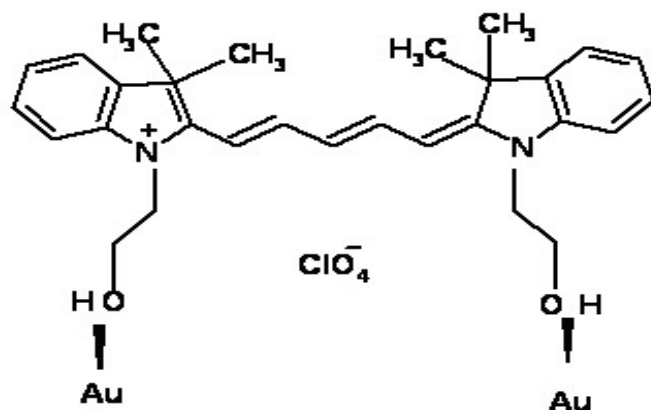

Figure 16 Absorption and emission spectra of ADS680HO in decanoll with (dotted)/without (lined) AuNP's (A-absorbance, F-fluorescence).
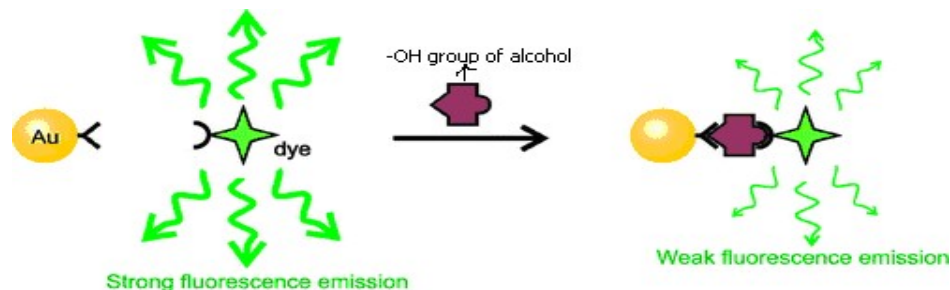
Figure 17 Attatchment of AuNP's with ADS680HO.

When AuNP's were added to the ADS680HO, the vibrational features are well resolved and the intensity was quenched due to AuNP's were adsorbed on the OH⁻ group and it forms hydrogen bonding with the ADS680HO laser dye (Figure 17).

Excited state fluorophore behaves as an oscillating dipole. When these fluorophores are in close proximity to the metal AuNP's (Figure 17), the rate of emission of radiative energy is modified. The electric field felt by the fluorophores are affected by the interaction of the incident light with the nearby metal surface. These interactions can increase/decrease the field felt by the fluorophore the increase/decrease the radiative decay resulting in many desirable effects such as increased/decreased quantum yield and decreased/increased life time.

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

In the present case the absorption spectrum of AgNP's has a maximum in the range 405-410 nm having peaking at 408nm, which is related to the surface plasmon resonance formed due to the nano sized (4-12nm) silver nanoparticles. This absorption band results from interactions of free electrons confined to small metallic spherical objects with incident electromagnetic radiation. From the observed SPR band and SEM image, we may conclude that the silver nanoparticles are spherical in shape.

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

Figure 19 is the absorption spectrum of ADS680HO in alcohols with and without AgNP's, shows the broad band in the visible region 670-700nm. While Figure 20 shows the fluorescence spectrum with the broad band in the 700-750nm region.

The SPR of AgNP's (of size 4-12nm) shows a maximum at 408nm. When AgNP's is added to ADS680HO the absorbance band shifts towards higher wavelength (red shift) and peaking at 684nm (in methanol), 685nm (in ethanol), 683nm (in propanol), 686nm (in butanol), 685nm (in octanol), 686nm (in decanol) and 688nm (in nonanol) and absorbance intensity quenches. Similarly fluorescence band shifts towards longer wavelength peaking at 725nm (in decanol), 724nm (in nonanol), 730nm (in octanol), 727nm (in butanol) and 723nm (in ethanol) and fluorescence intensity also quenches. Dampening and broadening of the band was evident as these molecules complexes with the AgNP's. The dampening of the Ag absorbance band indicates that due to attachment with ADS680HO via alcoholic group alters the electron density of the AgNP's, thereby directly affecting the absorption of the surface bound ADS680HO as well as absorption band (Figure 19).

When AgNP's were added to the ADS680HO, the vibrational features of ADS680HO were well resolved and the intensity was quenched due to AgNP's were adsorbed on the OH⁻ group and it forms hydrogen bonding with the ADS680HO laser dye (Figure 21).
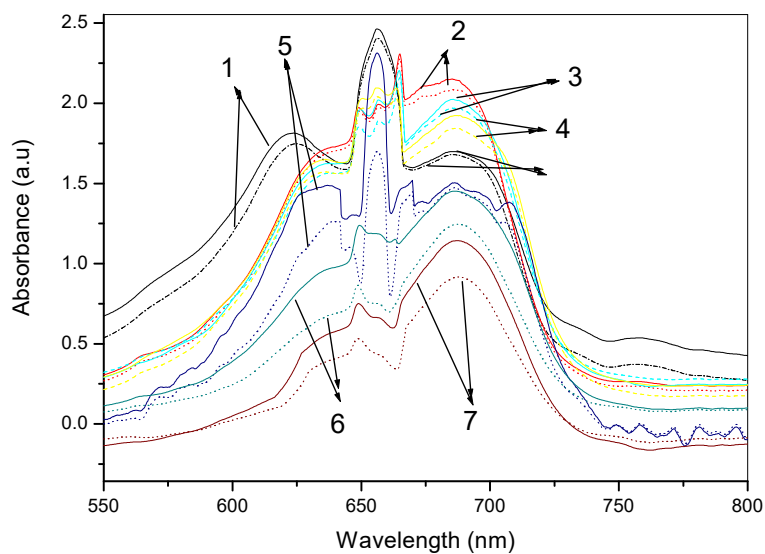
Figure 19 Absorption spectra of ADS680HO laser dye attached with (dotted)/ without (lined) AgNP's in alcohol solvents (1- methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol, 6-decanol, 7-nonanol).
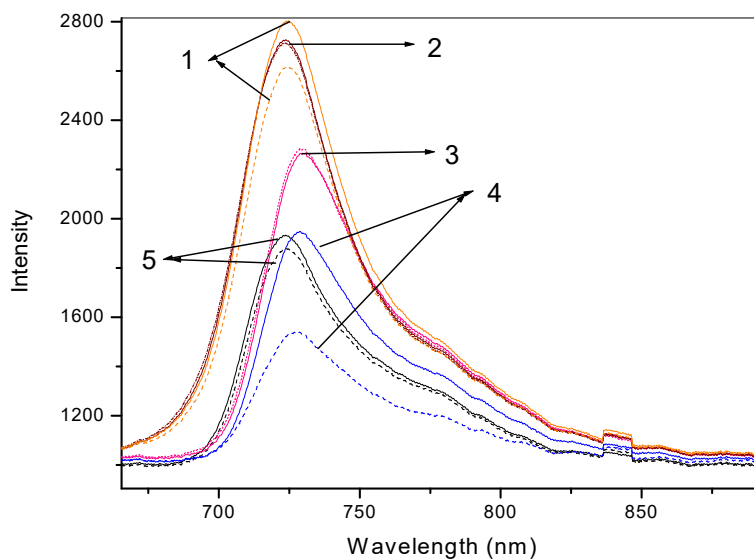

Figure 20 Fluorescence spectra of ADS680HO laser dye attached with (dotted)/ without (lined) AgNP's in alcohol solvents (1- decanol, 2-ethanol, 3-octanol, 4-butanol, 5-ethanol).
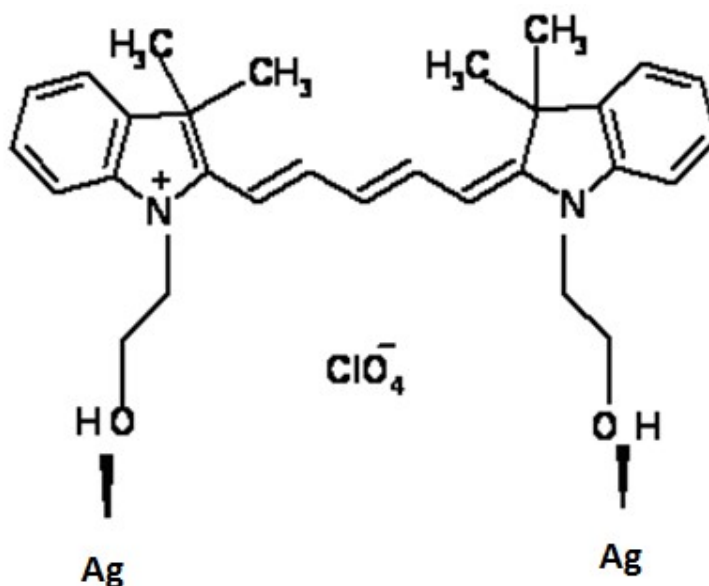
Figure 21 Attatchment of AgNP's with ADS680HO.

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

In the present case quenching of absorption and fluorescence was observed for ADS680HO dye molecules in alcohols attached with AuNP's and AgNP's via hydrogen bonding. Quenching is due to energy transfer rate from dye to the NP's is governed by three factors.
  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 AuNP's/AgNP's with a dye, induces a strong enhancement / quenching of fluorescence is observed depending on the nature of the chosen dye. In our case, all the three dyes showing quenching phenomena with nano probe.

Due to broadening of a plasmon explains the changes of molecular fluorescence near a AuNP's / AgNP's in the close proximity of a metal, 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 fluorescent dye is in direct contact with the nano metal, the fluorescence of a molecule is completely quenched. So, in our case AuNP's /AgNP's and a dye attachment is little longer.

The size effect on the position of the surface plasmon band of alcoholic functionalized gold nanoparticles was investigated by measuring the UV-Vis absorbance spectra in the range 450-800nm with dye molecule. Alcohols were chosen as solvent for specific interactions with the –OH group, thiol group and ester group of ADS680HO dye chain, could lead marked effects on the optical properties of gold and silver nanoparticles.

When the dimensions of nanoparticles become smaller than the wavelength of the exciting light (2R << λ), 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. If the nonradiative decay takes the dominating effect, fluorescence quenching occurs. The different distance behaviour of the radiative and nonradiative rates explains why the apparent quantum yield always vanishes at short distance from a metallic nanoparticle.

The observed fluorescence quenching is attributed to the resonance energy transfer from ADS680HO to gold / silver nanoparticles. This nonradiative decay can be theoretically studied using the Forster resonance energy transfer (FRET) theory. When some amounts of gold/silver colloidal nanoparticles are dropped in to the solution of ADS680HO dye molecule in various alcohols, molecules would tend to cluster around gold/silver particles due to physical adsorption. Increasing the concentration of ADS680HO leads to more and more molecules adsorb on the gold

particles. Quantum efficiency of gold nanoparticles is

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

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Γ^R – radiative decay rate; Γ^{NR} – non radiative decay rate

Here, adsorption of AuNP's / AgNP's with the dye causes more and more nonradiative decay rate, as a result quantum efficiency decrease or fluorescence quenching is observed.

Static quenching could also may ascribed to an association of the dye with the gold / silver nanoparticles through complexes of the nano metal with –OH group, thiol and ester group.

CONCLUSIONS

The optical properties of spherical gold nanoparticles are extremely important and play a vital role in the intensity and placement of the plasmon resonance. As spherical nanoparticles get larger the peaks broaden and shift to longer (red shift) wavelengths. This shift of the SPR of the band position and intensity of the nanoparticle assembly can be related to the change in dielectric medium and RI properties.

Optical absorption and fluorescence of ADS680HO laser dyes in alcohol solvents with and without attachment of AuNP's/ AgNP's shows quenching of absorption and fluorescence intensities. This is due to size, shape, energy transfer, coupling between the AuNP's / AgNP's and the dye. Quenching of fluorescence using AuNP's/ AgNP's with ADS680HO laser dye leads to many applications especially for advancement in biomolecular labelling and fluorescence patterning.

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