Stimulus of Gold Nano particles on ADS560EI Highly Fluorescent Laser Dye

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Abstract - This paper describes the results of a new fluorescent laser dye ADS560EI is in attachment with gold nano particles of size 4-12nm.The main purpose of our research is to know the influence of gold nano particles on our chosen ADS560EI fluorescent dye. The attachment of AuNP's with ADS560EI possesses enhancement in optical absorption and fluorescence. Photo physical investigations reveal strongly that enhancement is due to size, shape, and the coupling between nano particles with adsorbed dye. It is also due to the energy transfer between gold nano particles to the dye. Enhancement in fluorescence using AuNP's with ADS560EI leads to advancement in printing, painting, lithographic industries and biomolecular labeling.

Key words: AuNP's, ADS560EI, absorption, fluorescence.

I. INTRODUCTION

Recently, metal nano particles have been intensively studied due to widely exploited use in catalysis [1], photonics [2], optoelectronics [3-4], surface enhanced Raman scattering(SERS) [1,5], drug delivery in a cancerous tumor [6], biosensors
[7-8], cosmetic and beauty applications [9], biological labeling, information storage, etc., this is because of the unique properties including high surface area and exceptional surface activity, especially gold and silver nano particles.

The free electrons in the metal (d-electrons in gold) are free to travel through the material [1]. The mean free path in gold is ~50nm; therefore, in particles smaller than this, no scattering is expected from the bulk. Thus, all interactions are expected to be with the surface. When the wavelength of light is much larger than the nanoparticle size it can set up standing resonance with the surface plasmon oscillation causes the free electrons in the metal to oscillate. As the wavefront of the light passes, the electron density in the particle is polarized to one surface and oscillates in resonance with the lights frequency causing standing oscillation. The resonance condition is determined from absorption and scattering spectroscopy and is found to depend on the shape, size and dielectric constants of both the metal and the surrounding medium. This is referred to as the surface plasmon resonance. As the shape, size and surrounding medium changes of the nanoparticle environment causing a shift in the electric field density on the surfaces. This causes a change in the oscillation frequency of the electrons, generating different cross-sections for the optical properties including absorption and scattering.

Researcher, have often used functional groups such as thiols [1, 10-15], amines or silanes to attach electro active or photoactive molecules to the gold surface. The ability of the gold surface to bind with the specific functional groups has made it suitable for optoelectronic applications such as fluorescence patterning. Colloidal gold particles adsorb strongly to some proteins, especially antibodies. Colloidal gold functionalized with specific binding groups can be used to label a wide variety of biologically active molecules, such as lipids, oligonucleotides and peptides. Since, fluorescence spectroscopy is a very sensitive technique. Fluorophore-bound AuNP's are useful probes for biomolecular labeling.

This communication reveals new and unique optical properties with respect to enhanced optical absorption and fluorescence of gold nano particles with ADS560EI (3-Ethyl-2-[3-[3-ethyl-3H-benzothiazol-2-ylidene]-1-propenyl]-benzothiazolium iodide) laser dye. Now, we examined the effect of AuNP's on a new compound ADS560EI, it has an important industrial application like security painting, Lithographic painting plates and many other printing applications. In spite of many industrial applications, however no systematic study related to effect of

optical absorption and fluorescence of AuNP's on ADS560EI in different solvents. This prompted us to carry out the present work. This communication reveals new and unique optical properties with respect to enhanced [16] optical absorption and fluorescence of AuNP's with ADS560EI laser dye.

II. EXPERIMENTAL

2.1. Solvents:

Spectroscopic grade, methanol, ethanol, propanol is obtained from Sigma Aldrich.

2.2. Dye:

ADS560EI (Fig 1) is purchased from American Dye Source, Inc. Canada and it is used as it received.

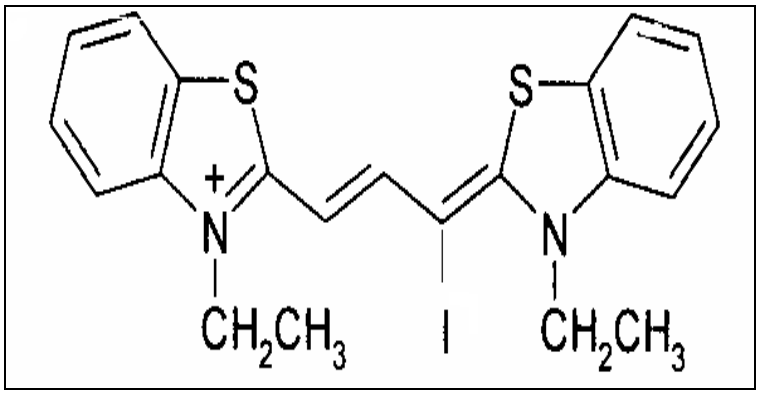


Figure 1. ADS560EI

2.3 Synthesis of Gold Nanoparticles:

Gold Nanoparticles (AuNP's) are traditionally [16-18], synthesized via the reduction of $AuClO_4^-$ with $NaBH_4$ or citratate. 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 (From Nanobio Chemicals India Pvt.Ltd), trimeric alanine-based phosphine $P[CH_2NHCH(CH_3)\text{-}(COOH)_3]$ (Thpal) as a reducing agent, provides an unprecedented pathway to produce AuNP's at acidic pH. Further to prevent aggregations of AuNP's Gum arabic (glycoprotein) is capped and it makes the AuNP's are stable even up to 6 months. Indeed, detailed investigations have confirmed that Gum Arabic [19] serves as an excellent backbone for the stabilization of GNPs. SEM, TEM pictures of AuNP's of size 4-12nm are shown in Fig 2.

2.4. Apparatus:

Optical absorption and fluorescence were recorded using Ocean Optics HR4000 high resolution spectrometer.

III. RESULTS AND DISCUSSION

3.1 Optical properties of gold nanopartiles:

The optical properties of spherical nanopartiles can be easily carried out by solving Maxwell's equation through Mie theory [20-24], through the expression for the extinction cross section C_{ext}. For very small particles compared with wavelength of incident light λ,

So that $[2\pi R/\lambda \leq 1]$

$$C_{ext} = \frac{24\pi R^3 \varepsilon_m^{\frac{3}{2}}}{\lambda} \frac{\varepsilon^{''}}{\left(\varepsilon^{'} + 2\varepsilon_m\right)^2 + \varepsilon^{''}} \qquad 1$$

Where ε′ and ε″are the real and imaginary parts of the complex dielectric function of the particle material and ε_m be the dielectric constant of the medium $\left(\varepsilon_m = \varepsilon^{'} + i\varepsilon^{''}\right)$

The origin of the strong color changes displayed by small particles lies in the denominator of the equation which predicts the existence of absorption peak when,

$$\varepsilon' = -2\ \varepsilon_m \qquad 2$$

In small metal particles, the dipole created by the electric field of light induces a surface polarization charge which effectively acts as a restoring force for the free electrons. The net result is that, when condition (2) is fulfilled, the long wavelength absorption by the bulk metal is condensed in to a small surface plasmon band.

In the present case the absorption spectrum has a maximum in the range 540-550nm peaking at 545nm, which is related to the 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.

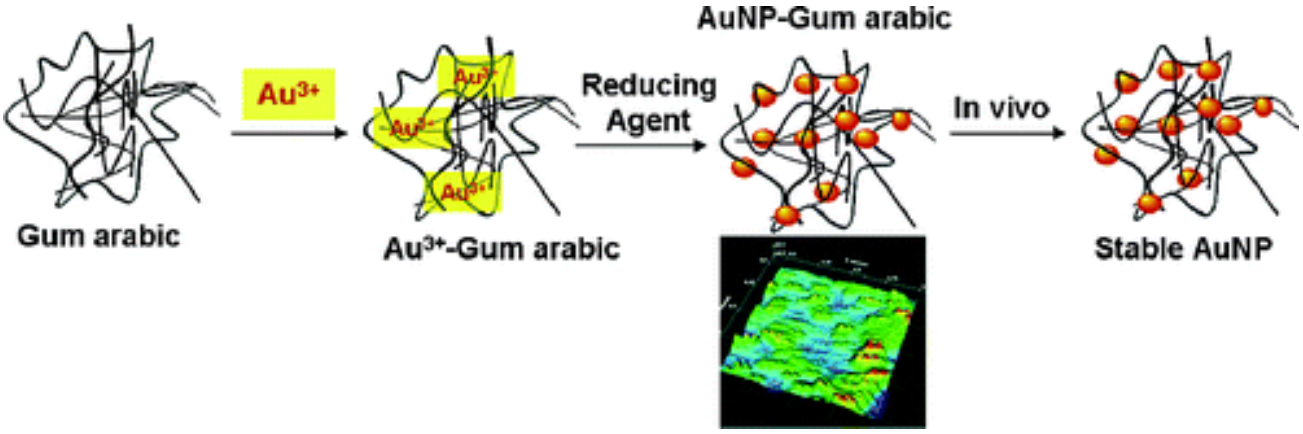
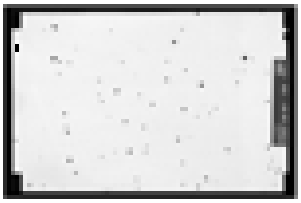
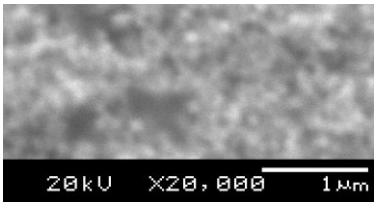


Fig 2.(a) AuNP's capping by gum Arabic,



2(b) TEM image of AuNP .



2(c) SEM image of AuNP

3.2 Optical Absorption and Fluorescence Emission effect:

The formation of AuNP's are confirmed by measuring the absorption of the solution containing gold nanoparticles at the wavelength ranging between 540-550nm. The maximum absorption was obtained at wavelength 545nm (Fig 3) showing the formation of AuNP's.

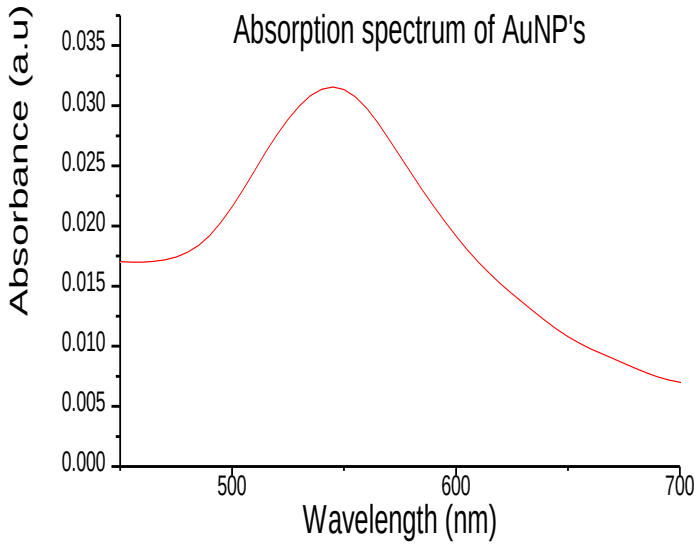


Fig 3. Plasmon resonance absorption spectrum of AuNP.

Fig4 shows the absorption spectrum of ADS560EI in alcohols with/without AuNP's. Absorption spectrum of ADS560EI in alcohol shows the broad band in the visible region 520-570nm.

The surface plasmon of AuNP's (of size 4-12nm) shows a maximum at 540-550nm. When ADS560EI is added to AuNP's the plasmon band shifts towards higher wavelength [23] (red shift) peaking at 556nm (in methanol), 557nm (in ethanol) & 559nm (in propanol)] and absorbance value enhances. Dampening and broadening of the surface plasmon band was evident as these molecules complexed with the AuNP's. The damping of the Au plasmon band indicates the attachment with ADS560EI alters the electron density of the AuNP's, thereby directly affecting the absorption of the surface bound ADS560EI as well as surface plasmon absorption band (Fig 5 & 6).

When AuNP's are added to the ADS560EI, the vibrational features of ADS560EI are well resolved and the intensity was enhanced due to 'S' of benzothiazol in ADS560EI is adsorbed [25-26] on the nano metal surface (Fig 7).

Excited state fluorophore behaves as an oscillating dipole. When these fluorophores are in close proximity to the metal AuNP's, the rate of emission of radiating 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 and the increase/decrease the radiative decay resulting in many desirable effects such as increased quantum yield and decreased life time.

In the present case enhancement of absorption and fluorescence was observed for ADS560EI molecule in alcohols attached with AuNP's via benzothiol groups, this is due to energy transfer rate from AuNP's to the dye is governed [27] 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 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 depends upon respective charge densities.2. The interaction within the dipole

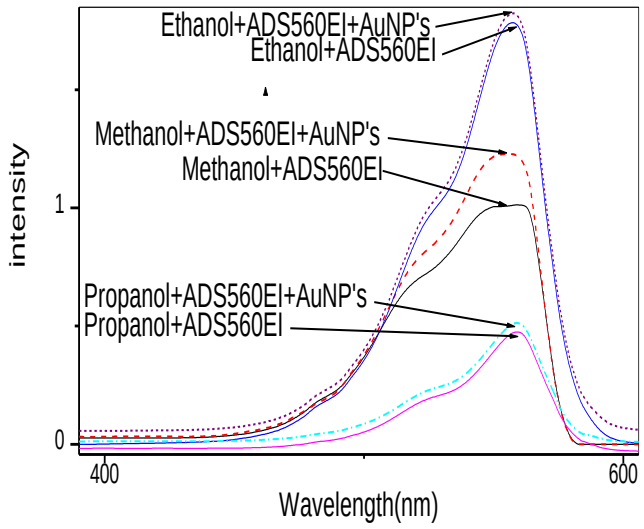


Fig 4. Absorption spectra of ADS560EI attached with (dashed)/without (straight) AuNP's in alcohol solvents.

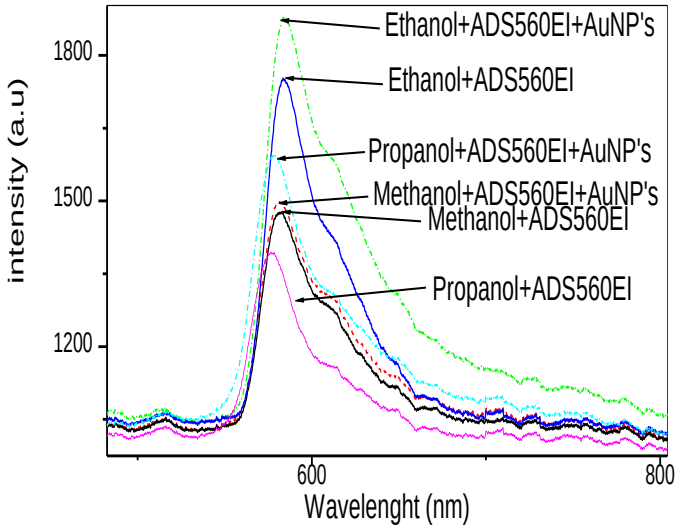


Fig 5. Fluorescence spectra of ADS560EI attached with (dashed)/without (straight) AuNP's in alcohol solvents.

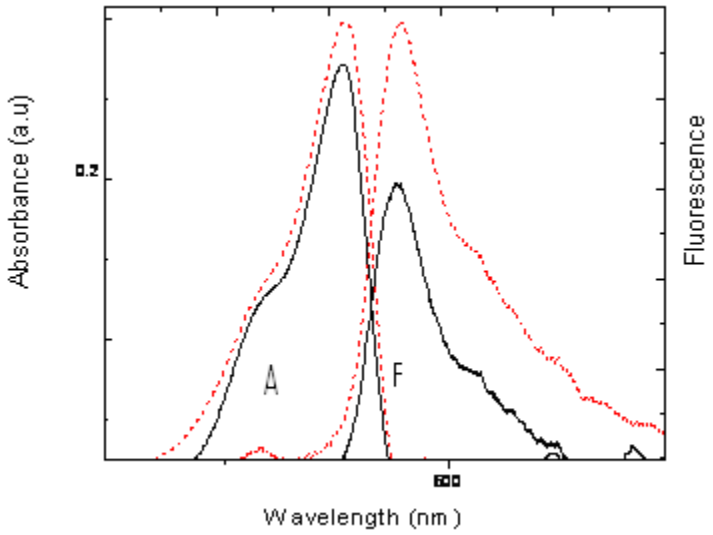


Fig.6 Absorption and emission spectra of ADS560EI in propanol with (straight) and without (dash) AuNP's (A-absorbance, F-fluorescence)

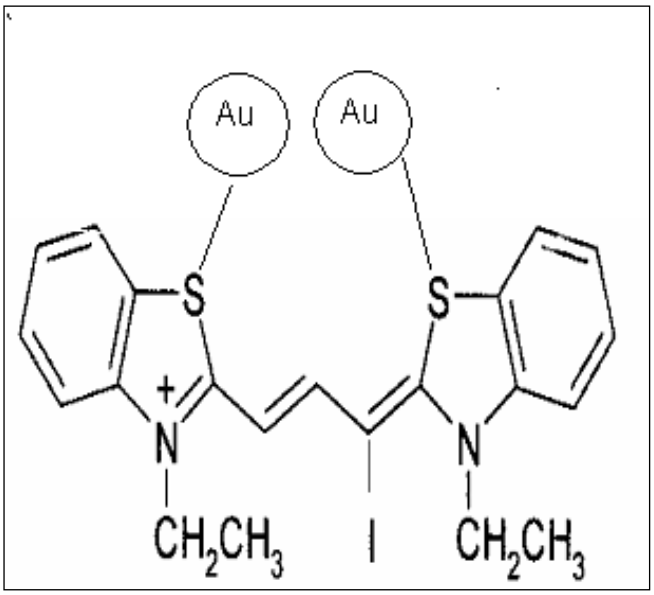


Fig 7. Attachment of AuNP's with ADS560EI

approximation, the charge densities of a dye, dipole moments of a dye and AuNP's are responsible for the energy transfer between dye to AuNP's which leads to enhancement. Fig5 for a typical set of UV-Vis spectra, exhibits a band between 520-570nm due to π-π* transitions.

Due to the attachment of AuNP's with a dye, induces a strong enhancement/quenching [16, 27] of fluorescence is observed. In our case enhancement is observed.

Due to broadening of a plasmon explains the changes of molecular fluorescence near a AuNP'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 metal surface. When in direct contact with the metal the fluorescence of a molecule is completely quenched. So, in our case AuNP and a dye attachment is little longer.

IV. CONCLUSION

Optical absorption and fluorescence of ADS560EI in alcohol solvents with/without attachment of AuNP's shows an approximately 2-fold increase in enhancement of absorption and fluorescence intensities. This is due to size, shape, coupling between the AuNP's with dye and energy transfer between AuNP's to dye. Enhancement of fluorescence using AuNP's with ADS560EI leads to advancement in printing, painting and lithographic industries, biomolecular labeling, fluorescence patterning.

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