

Fluorescence Enhancement of C 314 Laser Dye Based on ICT between C 314 Laser Dye and Green Synthesized Gold Nanoparticles

B.M.Mastiholi¹, P.U.Raikar², V.B.Tangod¹, S.G.Kulkarni¹ and U.S.Raikar^{1*}

¹Department of Physics, Karnatak University, Dharwad-580003, India.

²Visvesvaraya Technological University, Machhe-590018, Belgaum, Karnataka, India

Abstract: This paper describes synthesis of gold nanoparticles (AuNP's) using green tea leaves and the effect of Coumarin 314 (C314) laser dye is in attachment with the gold and silver nano particles. The main purpose of our research is to study the green synthesis of nanoparticles and to know the influence of green synthesized gold nano particles on C314 laser dye. The attachment of AuNP's with C314 laser dye possesses enhancement in optical absorption and fluorescence. Photo physical investigations reveal strongly the enhancement is due to Plasmon resonance effect over the ICT excited state promoting an increase of its radiative rate constant (metal Plasmon-coupled emission effect) and also due to the energy transfer between gold nano particles to the dye. Enhancement in fluorescence using AuNP's with C314 laser dye leads to advancement in important industrial applications like optical brighteners, fluorescence indicators, laser dyes, enzymology, blood thinners, treating the cancer affected cells, and even as sunburn preventives.

Keywords: AuNP's, C314, absorption, fluorescence, enhancement.

I. Introduction

Nanotechnology concerns with the development of experimental processes for the synthesis of nanoparticles of different sizes, shapes and controlled dispersity [1] Recently, metal nano particles have been intensively studied due to widely exploited use in catalysis[2], photonics[3], optoelectronics[4-5], surface enhanced Raman scattering(SERS) [6], drug delivery in a cancerous tumour [7], biosensors [8-9], cosmetic and beauty applications [10], biological labeling, information storage, etc., this is because of the unique properties due to high surface area and exceptional surface activity.

The free electrons in the metal (d-electrons in gold) are free to travel through the material [2]. 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, which causes the free electrons in the metal to oscillate is called surface plasmon resonance(SPR). 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. 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.

To date, biomedically important metallic nanoparticles are mostly synthesized by noble metals, Among the noble metals, gold is the metal of choice in the field of biological system, living organisms and medicine [11]. Green synthesis of nanoparticles is an emerging branch of nanotechnology [12]. The use of environmentally caring materials like plant leaf extract, bacteria and fungi for the synthesis of gold nanoparticles offers numerous benefits of eco-friendly and compatibility for pharmaceutical and biomedical applications as it does not involve the toxic chemicals in the synthesis process. Green synthesis of nanoparticles provides advancement over the chemical and physical methods as it is cost effective and eco friendly[13].

This communication reveals new and unique optical properties with respect to enhanced optical absorption and fluorescence of gold nanoparticles with C314 laser dye. In present study we examined the effect of AuNP's on a C314 laser dye and it has important industrial applications like optical brighteners, fluorescence indicators, laser dyes, enzymology, blood thinners, treating the cancer affected cells, and even as sunburn preventives. In spite of many industrial applications, however so far no systematic study has been done related to the effect of optical absorption and fluorescence of AuNP's on C314 laser dye in different solvents. This prompted us to carry out the present work. Present communication reveals new and unique optical properties with respect to enhanced [14] optical absorption and fluorescence of C314 laser dye with AuNP's.

II. Materials And Methods

2.1. Solvents:

Spectroscopic grade methanol, ethanol, propanol solvent are procured from Sigma Aldrich.

2.2. Dye:

Coumarin 314 Laser Dyes was obtained from Sigma Aldrich and is used without further purification. The molecular structure and IUPAC name is given in Figure 1. Gold salt is procured from Hi media.

Molecular formula – C₁₈H₁₉NO₄

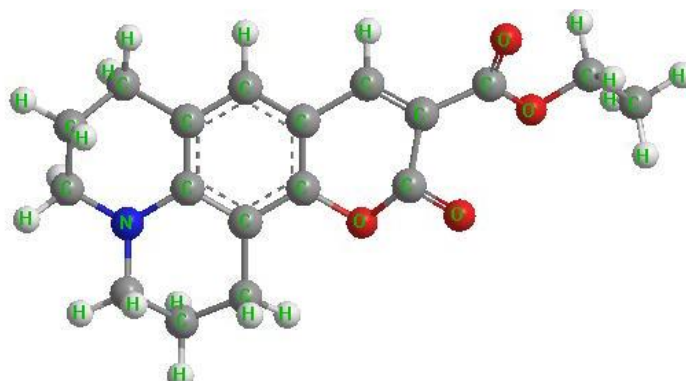


Figure 1. Molecular Structure and IUPAC name of C314

2.3 Synthesis of Gold Nanoparticles:

Green tea leaves were collected locally and shade dried. 2gm of dried green tea leaves were washed using deionised water and boiled with 150ml of deionised water for 10 min and the extract was filtered and used for further experiments.

In a conical flask 0.5ml of 0.01M HAuCl₄ is dissolved in 20ml of deionised water, then drop wise green tea extract is added with stirring on a magnetic stirrer until the colour changes to wine red which indicates the formation of gold nanoparticles.

2.4. Instrumentation:

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

III. Theory

3.1 Optical properties of gold nanoparticles:

The optical properties of spherical nanoparticles can be easily studied by solving Maxwell's equation through Mie's theory [15-19], using the expression for the extinction cross section C_{ext} . For very small particles compared with wavelength of incident light λ ,

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

$$C_{ext} = \frac{24\pi R^3 \epsilon_m^{\frac{3}{2}} \epsilon''}{\lambda (\epsilon' + 2\epsilon_m)^2 + \epsilon''} \quad 1$$

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 ($\epsilon_m = \epsilon' + i\epsilon''$)

The origin of the SPR displayed by small particles is due to the condition in equation 1 is,

$$\epsilon = -2 \epsilon_m \quad 2$$

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

IV. Results And Discussion

4.1 SPR of Green synthesized nanoparticles:

UV-Vis absorption spectroscopy is an important technique to monitor the formation and stability of metal NP's in aqueous solution because of SPR phenomenon. The absorption spectrum of metal NP's is sensitive to several factors, including particle size, shape, and particle-particle interaction with medium. The absorption

spectrum of green synthesised nanoparticle has a maximum in the range 535-545nm peaking at 540nm, which is related to the plasmon resonance formed due to the nano sized 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.

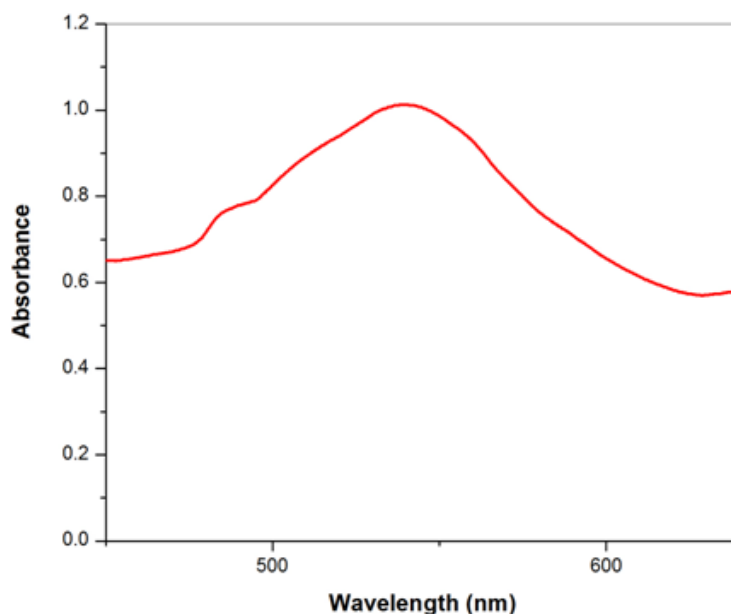


Figure 2. Plasmon resonance absorption spectrum of AuNP

4.2 Optical Absorption and Fluorescence Emission effect:

Absorption and fluorescence emission spectra of a Coumarin 343 molecule is recorded in various solvents of different solvent parameters of dielectric constant (ϵ) and refractive index (n). The absorption is peaking at 437nm (in methanol), 435nm (in ethanol) & 438nm (in propanol) an emission is peaking at 488nm (in methanol), 486nm (in ethanol) & 485nm (in propanol).

The formation of AuNP's is confirmed by measuring the absorption spectrum of the solution containing gold nanoparticles at the wavelength ranging between 535-545nm. The maximum absorption was obtained at wavelength 540nm (Fig 3) showing the formation of AuNP's.

Fig 3 shows the absorption spectra of C314 in alcohol solvents with/without AuNP's. Absorption spectra of C314 in various alcohol shows the broad band in the visible region 430-440nm and the emission spectra of C314 in alcohol solvents with/without AuNP's. Emission spectra of C314 in different alcohol solvents shows the broad band in the visible region 480-490nm.

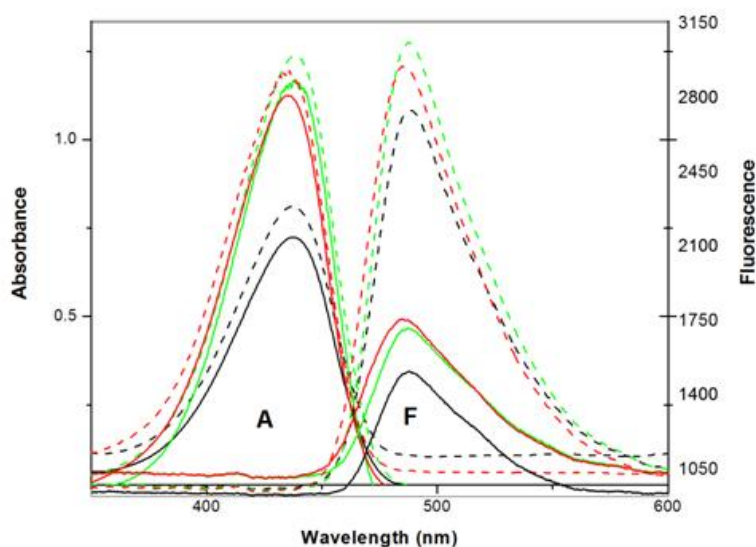


Figure 3. Absorption and Fluorescence spectra of C314 attached with (dashed) / without (straight) AuNP's in alcohol solvents

When AuNP's is added to C314 the absorbance intensity value enhances. Dampening and broadening of the absorbance band was evident as C314 molecules complexed with the AuNP's. The damping of the band indicates the attachment of AuNP's with C314 alters the electron density, thereby directly affecting the absorption of the surface bound C314 with surface plasmon absorption band (Fig 3).

When AuNP's are added to the C314, the vibrational features of C314 are well resolved and the intensity was enhanced due to gold nanoparticles are attached to alkane group in C314 (Fig 4).

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.

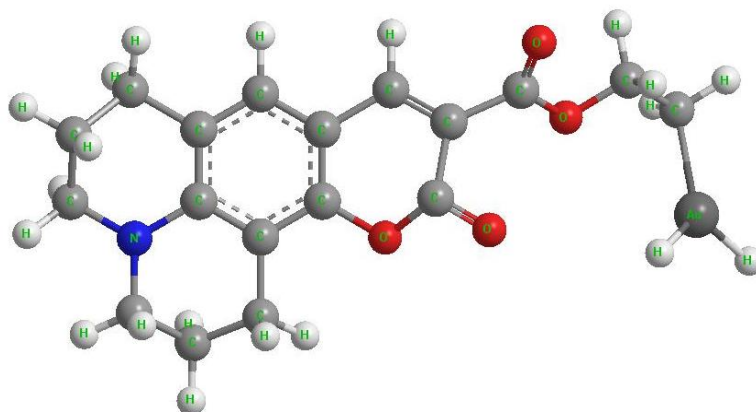


Figure 4. Attachment of AuNP's with C314

In the present case enhancement of absorption and fluorescence was observed for C314 laser dye molecule in alcohols attached with AuNP's via alkane group, 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, the charge densities of a dye, dipole moments of a dye and AuNP's are responsible for the energy transfer between AuNP's to dye which leads to enhancement.

Due to the attachment of AuNP's with a dye, induces a strong enhancement/quenching [20, 21] of fluorescence is observed. In our case enhancement is observed.

Broadening of plasmon explains the changes of molecular fluorescence near a AuNP's, in the close proximity of a dye molecule, 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 enhanced.

V. Conclusion

Green syntheses of gold nanoparticles is carried out using green tea leaves. The absorption spectra (SPR) of colloidal gold nano particle solution confirms the formation of spherical gold nanoparticles. Optical absorption and fluorescence spectra of C314 laser dye in alcohol solvents with attachment of AuNP's shows an approximately 2-fold increase in enhancement of absorption and fluorescence intensities. This is due to plasmon resonance effect over the ICT excited state promoting an increase of its radiative rate constant (metal plasmon-coupled emission effect) and it also due to size, shape, coupling between the NP's with dye and energy transfer between NP's to dye. Enhancement of fluorescence using AuNP's with C314 leads to advancement in important industrial application like optical brighteners, fluorescence indicators, laser dyes, enzymology, blood thinners, treating the cancer affected cells, and even as sunburn preventives.

Acknowledgements:

The authors are sincerely thankful to Vision Group On Science and Technology (VGST), Govt. of Karnataka, India for the award of K-FIST Level-II Project and UGC for the award of RFSMS.

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