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Absorption and Fluorescence Mechanisms of Red Mega 480 Laser Dye Coupled with Silver Nanoparticles

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ABSTRACT

Herein, we used the chemical reduction method to synthesize silver nanoparticles. The characterization of synthesized particles is done using UV-Vis, SEM, and TEM techniques, which reveal sizes in the range of 4–12 nm. In this particular instance, the optical absorption spectra of synthesized silver nanoparticles produced a maximal spike in the 400–410 nm region. This spike is attributed to surface plasmon resonance. The spectra of emission and absorption intensities of the exceptionally brilliant laser Red Mega 480 dye in alcohol solvents with the addition of silver nanoparticles indicate quenching. This is related to the size, shape, and transfer of energy between silver nanoparticles and dye. The quenching of fluorescence intensity in the presence of nanoparticles with Red Mega 480 dye leads to advancements in biomolecular labeling, printing technology, 3D graphics, glossy painting, fluorescence patterning, and cancer treatment.

Keywords: *Nanoparticle, Fluorescence, Absorption, Silver, Red Mega 480*

1. Introduction

In the most recent technical discipline, nanoscience and nanotechnology are leading civilization into new realms of efficient technology. Every interdisciplinary subject, such as physics, chemistry, biology, or applied science: such as medicine or engineering, is bursting with incredible new nanoscale discoveries. Between isolated atoms and aggregates large enough to be referred to as bulk material, nanoparticles are particles with diameters ranging from 1 to 100 nm. Since nanoparticles are bigger than individual atoms but smaller than bulk solids, materials in the nanoscale size range behave in a way that is halfway between that of macroscopic solids and an atomic or molecular system. These discrepancies can be explained by three primary reasons [1–5]:

1. Large ratio of surface to volume.
2. The effect of being bigger than an atom and smaller than a macroparticle
3. Maxwellian interactions.

Metal nanoparticles, specifically silver nanoparticles, are currently attracting a lot of interest due to their many fascinating features [6], plus several applications in medicine and technology. The optical properties of various nanomaterials have sparked a lot of interest. The radius-to-wavelength proportion becomes critical when silver is broken into increasingly tiny fragments and when the particle is smaller than the wavelength, the Rayleigh approximation (i.e., no retardation) holds and the mathematics becomes easy to understand. Mie's theory [7] established that plasmonic stimulation takes place when the radius is greater than the wavelengths of light and the plasmon retarding effect must be included to produce accurate results.

Silver particles (AgNPs) exhibit a yellow tint when they are tiny enough, owing to their substantial ability to absorb the green wavelength at 408nm that matches the frequency at which a plasmon resonance phenomenon happens when interacting with silver [8]. When the conductor's measurements are reduced, borders and contact with surfaces become more apparent. As a result, the collectively oscillating motion of conduction electrons dominates the optical characteristics [9] of tiny metal nanoparticles. Surface plasmon resonance (SPR) occurs when the incoming photon frequency is resonant with the collective oscillation of conduction band electrons. When laser dye comes into touch with a nanoparticle, the surface Plasmon resonance peaks are quenched, which inspires us to do research that will have more sophisticated industrial and medical applications. Quenching of optical fluorescence and absorbance of Red Mega 480 [1-(5-carboxypentyl)-6-2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl] ethenyl pyridinium-3-sulfonate] is reported in this communication [10,11].

The effect of AgNPs on the compound Red Mega 480 in laser dye has essential industrial applications such as security printing, lithographic printing plates and many more printing applications. Despite various industrial applications, no systematic investigation on the impact of the optical absorption and fluorescence of Red Mega 480 on various solvents in an environment of silver nanoparticles has been undertaken to date. In terms of optical absorption and fluorescence quenching with AgNPs, this study explains the novel and different spectroscopic characteristics of Red Mega 480 fluorescent dye [10, 11].

2. Experimentation

2.1 Chemicals and Dye

Sigma Aldrich's AR-grade methanol, propanol, ethanol, nanonol, decanol, and laser dye RedMega480 are used in this work. The chemical structure of Red Mega 480 is given in Fig. 1.

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Chemical composition of Red Mega 480 Laser dye: $C_{26}H_{30}N_2O_7S$

Nomeniclature:1-(5-carboxypentyl)-6-2-[7(diethylamino) -2-oxo2-chromen-3-yl] ethenylpyridiniumm -3-sulfonate

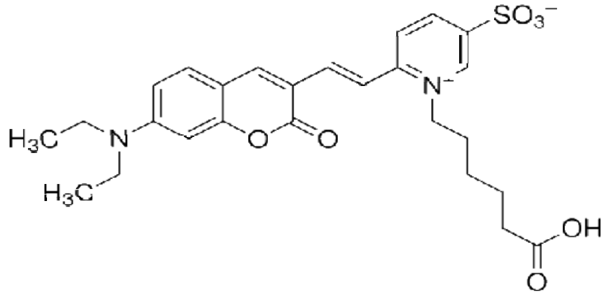

Fig. 1: Red Mega 480's molecular structure and IUPAC name

2.2 *Synthesis of silver nanoparticles (AgNPs)*

Silver nanoparticles can be synthesized by chemically reducing silver ions in an aqueous solution with sodium borohydride. The chemical reduction approach is used to create silver nanoparticles [12, 13]. Silver nitrate drops to 1.0 mM in 20 milliliters of substantially hydrogenated water. The colloidal yellow color solution was created after adding 0.1 ml of trisodium citrate to $AgNO_3$ solution drop by drop with continued and constant agitation and additional admixing of 0.6 milliliters of 0.1 mM sodium borohydrate dropwise, indicating the synthesis of silver nanoparticles. There was no direct incident light during the preparation process. Absorption spectroscopy of the yellow solution revealed the production of silver nanoparticles. The chemical equations are presented below [4]:

$4Ag + C_6H_5O_7Na_3 + 2\,H_2O \longrightarrow 4Ag + C_6H_5O_7H_3 + 3\,Na^+ + H^+ + O^2\uparrow$

$AgNO_3 + NaBH_4 \longrightarrow Ag + \frac{1}{2}H_2 + \frac{1}{2}B_2H_6 + NaNO_3$

2.3 Experimental Arrangements

Spectra suite HR4000 highly resolving powered spectrometer was used to measure optical absorption and fluorescence measurements.

3. Theory

Mie's scattering theory has been extensively used to examine the spectroscopic characteristics of silver nanoparticles, specifically the size of the particle, dependency on surroundings, and impact on targeted dye molecules in the presence of alcoholic solvents. Specifically, Mie's theory [14–16] is a quantum mechanical explanation for the scattering of electromagnetic radiation by spherically shaped nanoparticles that are in the surrounding medium. Mie's mathematical scattering equations start with the electric field vector E and the magnetic field vector H:

$$\nabla \cdot E = 0 \tag{1}$$

$$\nabla \cdot H = 0 \tag{2}$$

$$\nabla \times E = \iota\omega\mu H \tag{3}$$

$$\nabla \times H = -\iota\omega\varepsilon E \tag{4}$$

The Helmholtz relation [17, 18] explains the arrangement of an occurrence electromagnetic field with two parts.

$$\nabla^2 E + K^2 E = 0 \tag{5}$$

$$\nabla^2 H + K^2 H = 0 \tag{6}$$

Here, the wavenumber is k, which is assigned to

$$k^2 = \omega^2 \varepsilon\mu \tag{7}$$

Depending on the particle size range, the influence of particulate size resonance peak wavelength is induced by two distinct processes. In the limit of $2R \ll \lambda$ (R is the average radius of particles and λ is the wavelength of the light in the medium), mainly the dipole electrical components contribute considerably [5, 7, 15, 19] to the extinction cross-section (σ_{ext})

$$\sigma_{ext} = 9\,\frac{\omega}{c}\,\varepsilon_m^{3/2} V \,\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_m]^2+[\varepsilon_2(\omega)]} \tag{8}$$

Here, $V = (4/3)\,R^3$ represents the volume of a spherical particulate, c represents exciting light's angular frequency, m, $\varepsilon_{m,}$ and $\varepsilon(\omega)$ represent dielectric frictions of the enveloping medium and its material, where $[\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)]$. The condition for resonance is $\varepsilon_1(\omega) = -2\varepsilon_m$ is called SPR.

4. Discussion and Results

The optical absorption spectrum of Red Mega 480 laser dye in alcohol solvents with AgNPs is shown in Fig. 3 which shows a wide band in the wavelength range of 470–510 nm. Fig. 4 depicts a fluorescence spectrum with a wide band in the range 590–650 nm.

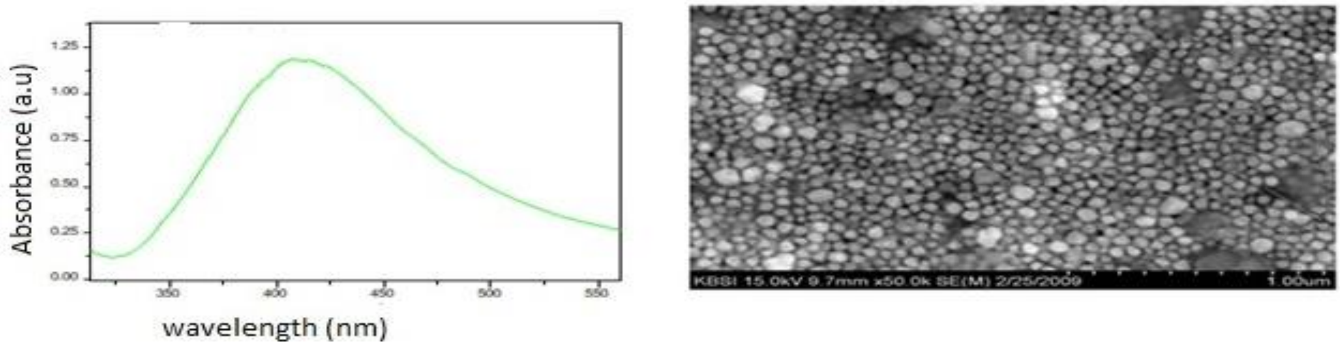

Fig. 2. (a): Surface plasmon resonance of AgNP; (b) SEM image

When AgNP’s are injected into Red Mega 480 laser dye, the absorption spectrum peak swings to the longer wavelength side (redshift), peaking at 498nm (methanol), 501nm (ethanol), 502nm (propanol), 497nm (nonanol), 503nm (butanol) and 491nm (decanol), along with absorbance intensity values quenching. Similarly, fluorescence band shifts in the higher region peaked at 637 nm (methanol), 629nm (ethanol), 620nm (propanol), 623nm (butanol), 606nm (nonanol) and 603 nm (decanol) and fluorescence intensity quenched (Figure 3 shows absorbance quenching and Figure 4 shows fluorescence quenching) specifically when molecules complexed with the AgNPs, the band was quenched and widened. The quenching of the Ag peak demonstrates the binding of the AgNPs to the Red Mega 480 laser dye via alcoholic, ester, and thiol groups, which changes the density of electrons in the AgNPs; as a result, the surface-bound Red Mega 480 laser dye absorption is immediately affected in addition to the SPR silver nanoparticles are closely bonding with the negative group element like sulphonyl and alcoholic group as a result sudden intensity in the absorption or fluoresce will fall down (Fig. 5.)

When AgNPs were added to the probe molecule of Red Mega 480 laser dye, the vibrational features of the probe molecule were well determined and the intensity had been quenched because AgNP’s were adsorbed on the OH$^-$ group, SO $^-$ group, ester group, and formed hydrogen bonds with the Red Mega 480 molecule as shown in Fig. 5.

In this scenario, suppression of absorption and fluorescence for Red Mega 480 dye molecules in alcohols connected with AgNPs via hydrogen bonding was possible. Three factors influence the rate of the transfer of energy between the dye and the nanoparticles [15, 21, 22].

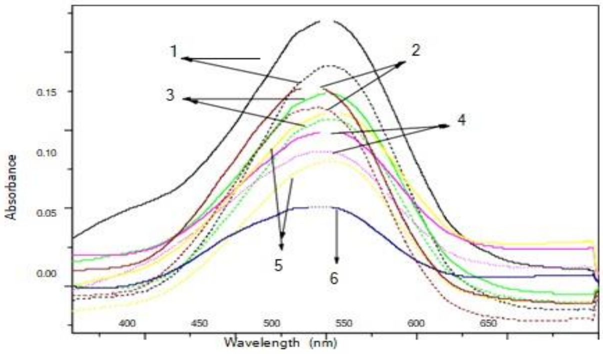

Fig. 3: Laser dye molecule Red Mega 480 in various solvent absorption spectra with and without silver nanoparticles (1-Methanol, 2-decanol, 3-ethanol, 4-Propanol, 5-butanol, 6-nonanol) (Line-Without, dashed line-with silver nanoparticles).

1. The integral of Coloumbic overlap.
2. Location(SPR)
3. Broadening of the band (inverse SPR lifetime) of the absorption spectrum of silver nanoparticles with dye.

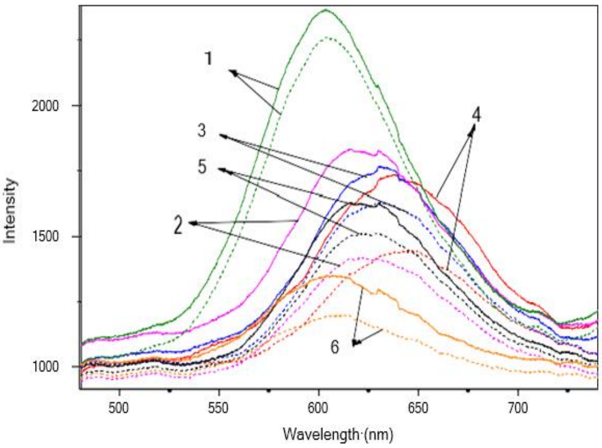

Fig. 4: Laser dye molecule Red Mega 480 in various solvent fluorescence spectra with and without silver nanoparticles (1-Methanol, 2-decanol, 3-ethanol, 4-Propanol, 5-butanol and 6-nonanol) (Line-Without, dashed line-with silver nanoparticles)

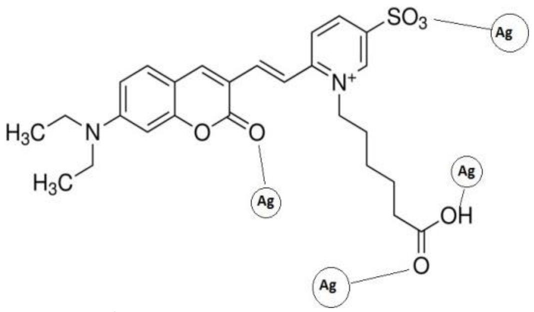

Fig.5: Attachment of silver nanoparticles with Red Mega 480 molecule.

The effect of Coulombic interactions on energy transmission has been investigated using two components.

1. The interaction of dye and AgNPs is determined by their relative densities of charge.
2. Dipole approximation during interaction

The electron concentrations on a probe molecule, dye dipole moments, and Ag-NPs account for the way in which energy transfers dye to silver nanoparticles, which induces a quench in optical absorption. Ultraviolet-visible spectra show a band range of 470-510nm which is assigned to π-π* transitions.

Based on the dye's chemistry, the attachment of AgNPs to dye’s molecules causes a heavy quenching of fluorescence [21, 23, 24]. The modifications in chemical and structural bindings and the complex fluorescence of AgNP’s in close proximity to a metal are explained by the broadening of a plasmon and the fluorescence rate of the molecules is a function of the distance between the probe molecule and the AgNPs. The fluorescence of a molecule is completely quenched when it comes into direct contact with the nanometal [22, 23, 25, 26]. In our situation, the interaction of AgNPs with dye molecules is slightly larger. The impact of silver nanoparticle on the sulphonyl and alcoholic group makes the quenching of absorbance and fluoresce intensity [27, 28] on the location of the surface plasmon region of alcohol series functional nanoparticles of silver was investigated through the application of the dye molecule for evaluating UV-Vis absorbance spectra in the range 450-800nm. Because particular interactions with the -OH group, the ester group of the Red Mega 480 dye chain, might have a substantial influence on the optical properties of AgNPs, alcohols were chosen as the solvent.

Energy may be confined to tiny spatial regions by surface plasmon resonance stimulation when the size of nanoparticles grows shorter compared to the wavelength of the stimulating light ($2R \ll \lambda$) [Reference??]. The optical characteristics of metal nanoparticles are greatly impacted by their size, shape, and surroundings, as well as resonant energy transmission between closely spaced metal nanoparticles and the surrounding molecule [2].

A non-radiative decay-based resonance energy transfer model [21, 29] provides a theoretical explanation for these quenching fluorescence findings. The spectral characteristics of molecules adsorbed on or encapsulated in metallic and dielectric particles have been explored experimentally and theoretically in recent years. When an excited particle oscillates in an incoming electromagnetic field, the excited system could possess a changing electrical dipole moment, resulting in radiation. The light radiation from the dipole moment provides an outlet for radiative decay [22]. These fields' joule heating and plasmon absorption, on the other hand, open non-radiative decay paths. The competition for radiant and nonradiative decaying energies affects the fluorescence emissions of molecules around particles. Fluorescence quenching occurs when nonradiative degradation takes over [32]. The observed yield of quantum particles always diminishes with a modest separation from a metallic nanoparticle because the radiative and nonradiative rates function differently at various distances.

The reported quenching of fluorescence is caused by the transfer of resonance energy between Red Mega 480 and AgNPs. This non-radiative decay may be studied using the Forster transfer of resonance energy (FRET) hypothesis [21, 30]. Due to physical adsorption, whenever AgNPs in the colloidal form are injected into a solution with Red Mega 480 dye molecules in various alcohol solvents, molecules preferentially cluster around silver particles. More molecules adsorb on the silver particles as the concentration of Red Mega 480 rises. The quantum yield of nanoparticles of silver is quite high.

$$Q = \frac{\Gamma^{R}}{\Gamma^{R}+\Gamma^{NR}} \tag{9}$$

Γ^{R} decay due to radiation rate; Γ^{NR} rate of non-radiative degradation.

The adsorption of AgNPs containing dye causes an increase in the non-radiative decay rate [21, 31], resulting in a loss in quantum efficiency or fluorescence quenching. Static quenching may also be attributed to dye interaction among AgNPs via nanometal complexes with the -OH alcoholic group or ester group [21, 32, 33, 34].

Conclusion

In Conclusion, silver nanoparticles are synthesized by the chemical reduction method. SEM and TEM analysis displayed the averaged particle size in the range of 4-12 nm. Further, absorbance and fluorescence quenching intensities with Red Mega 480 laser dyes using different alcohols, with and without the attachment of silver nanoparticles are seen. It is all because of size, energy transfer, and bonding with the probe molecule. This quenching of fluorescence with Red Mega 480 laser dye leads to innumerable usages, specifically in advancements in bimolecular labeling, printing technology, 3D graphics, glossy painting, and fluorescence patterning.

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