Spectroscopic analysis of surface plasmon resonance in pyrromethene 580 laser dye

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Abstract

In this work, spectral properties of (pyromethane 580) PM 580 laser dye were studied and study the effect of addition Au: Ag Nanoparticles .In this study, studied the spectral properties of the liquid dye (pyromethane 580) PM 580 dissolved in ethanol solvent with different concentrations ($1x10^{-3}$, $5x10^{-4}$, $1x10^{-4}$, $5x10^{-5}$, $1x10^{-5}$, $1x10^{-6}$) M and the ideal concentration was chosen at $1x10^{-6}$ M. Also, nanoparticles were prepared from the noble metals (gold and silver) (Au: Ag) NPs immersed in 3 ml of polyvinyl alcohol (PVA) using a pulsed laser Nd-YAG with wavelengths (532 nm) with a number of 500 pulses and different energy (400, 600, 800, 1000) mJ. The spectral and structural properties of the mixture (laser dye and nanoparticles) were also studied. The results of the spectral properties of the dye solution showed that the peak of the absorption spectrum and the peak of the fluorescence spectrum of the liquid dye shift towards the shorter wavelengths (blue shift) when the concentration decreases, while the relative intensity decreases with the decrease in concentration While the fluorescence spectra were increased when the concentration was decreased, Observed by varying amount of Au: Ag NPs, the intensity of absorption and fluorescence are increasing with increasing this amount.

Keywords: Nanoparticles; Pyrromethene 580 dye; quantum yield; Absorpence
DOI Number: 10.14704/nq.2022.20.10.NQ55012 **NeuroQuantology 2022; 20(10): 101-112**

1. Introduction

The study of the photophysics of organic dyes has received great technological interest because of their use as the active media in tunable lasers and in the development of photoelectronic devices[1]. Lasing compounds are classified according to their chemical structure and the region that emit in them spectrum into the different classes: polymethane where the emission range about 700-1000 nm, Xanthene with emission range around 500-700 nm, and other classes [2]. Moreover, laser dyes have wide applications not only in photonics but also as fluorescent probes, molecular sensors, light-harvesting arrays and information storage, among other uses[3]. Therefore, the study of the photophysical properties of laser dyes is an important tool for the improvement of their photonic, photoelectronic and photosensor applications. There are several commercially available laser-dye families covering the spectral region from UV to near-IR[4, 5]. Generally, the visible radiation emitted by most organic dyes has helped to be used as an effective medium in dye lasers. These fluorescent dyes contain a high concentration of active atoms of the volume unit when compared to the invasive medium[6]. They can be pumped with a wide variety of excitation sources, can emit in pulsed and continuous-wave forms and, owing to their wide gain band, can supply ultrashort pulses in the femtosecond timescale and can be tuned over a can increase the losses in the resonator cavity by the inner filter (i.e. the reabsorption effects)[11].

- High thermo- and photostability of the dye, enhancing the operative time o the active media

The active medium in the organic dye laser is an organic fluorescent material, The laser dye: an unsaturated hydrocarbon compound, containing a conjugated chain of carbon atoms, with alternating single and double bonds, which is called the chromophore system [12]. Typical energy levels in a dye laser consist of two types of electronic levels: single-bonded electronic levels (S0. S1.S2) and other triple-bonded electronic levels (T1.T2). Each of these levels is in the form of a broad beam that includes vibrational levels. When the active medium is pumped, the dye molecules move from the stable level (S0) to the first excited electronic level (S1), meaning that these atoms will absorb energy and as a result, a process of irritation will occur for the liquid atoms leading to the transfer of those atoms to higher levels and when these atoms fall The molecules catalytically reach a stable level emitting a laser beam as shown in Figure (1)[13].

Fluorescence quantum yield is one of the key photophysical quantities that are amenable to direct experimental determination [14]. In order to evaluate absolute quantum yield, we have to consider both the radiative and the non-radiative processes occurring in the medium [15].

The knowledge of fluorescence quantum yield of organic dyes and its concentration dependence are essential for selecting efficient laser media. certain spectral range. These properties provide special applications for dye lasers in different fields, such as spectroscopy, optics, medicine, telecommunications, etc.[7,8]. A chromophoric system must fulfil certain characteristics to be considered a laser dye:

- Strong absorption bands, enhancing the population inversion during the pumping process.
- Low probability of non-radiative deactivation processes from the emissive excited state, reducing the losses in the resonator cavity. The intersystem crossing probability is of special interest, since it can quench the emission from the fluorescent excited state and mainly populates the long-lifetime lowest triplet state (T1). The triplet–triplet (T–T) absorption band, which can overlap with the lasing gain band, and the accumulation of molecules in the T1 state, can strongly reduce the lasing efficiency[9].
- Large Stokes shifts and low tendency of the dye to self-aggregate. In order to guarantee high efficiency in the pumping process, the active media of tunable lasers require high optical density samples. In these conditions, the dye aggregation can reduce the gain of the laser signal, since aggregates do not usually emit and are efficient quenchers of the fluorescence emission of monomers[10]. Moreover, the overlap between the absorption and fluorescencebands (governed by the Stokes shift)

with different energy (400, 600, 800, 1000) mJ and Laser wavelength 532 nm with 500 shots.Then , Adding solution of laser dye at concentration of 10^{-6} M of (PM 580) dye to (Au: Ag) NPs solution .

3. Results and Discussion

(Fig.1) shows the absorption spectra of Pyrromethene 580 dye solutions dissolved in Ethanol solvents at different concentrations (1x10^{-3}, 5x10^{-4}, 1x10^{-4}, 5 x 10^{-5}, 1x10^{-5} and 1x10^{-6}) M.Measurements of absorption spectra showed that the change in the concentration of (PM 580) affects the absorption spectra as shown in figure. In general, the intensity of absorbance increases with increasing the concentration of the dye in the solutions, the lowest concentration of 1x10^{-6} M exhibited the minimum intensity (0.37) at a wavelength of 520 nm, and the highest concentration 1x10^{-3} M, exhibited the maximum intensity (1.71) at wavelength 524 nm. It is clear from the above results that the peak of the absorption spectrum tends towards the shorter wavelength (blue shift) when decreasing the concentration. We also note that when the concentration increases, the intensity of the absorbance increases and the Full width at half maximum (FWHM) an increase with increasing concentration, due to the increase in the number of molecules, which in turn leads to an increase in the absorption potential, and this absorption of dyes correspond to the law of Beer-Lambert, which states that the amount of absorbed light is proportional to the number of particles and concentration of the medium along the path. Fig (2) explain the relation between Relative intensity (Absorbance) and λ_{max} , and FWHM. Table (1) shows the effect of different concentrations on the absorption

Conventional measurements require the use of accurate luminescence standard sample and comparison of the give sample with a standard for which the fluorescence yield is known [14].The main Aim of this work is to prepare Au:Ag nanoparticles and study their characteristics. These nanoparticles are added to pyrromethene 580 laser dye solution and their effect on the spectroscopic characteristics was studied.

2. Experimental Work

The pyrromethene 580 (PM580) laser dye solution was prepared by dissolving the required amount of the dye in the solvents ethanol where prepared different concentrations as (1x10^{-3}, 5x10^{-4}, 1x10^{-4}, 5 x 10^{-5}, 1x10^{-5} and 1x10^{-6}) M. Au : Ag NPs prepared by use Gold and silver plates with a purity of 99.9% were used as targets. The purity was measured by the (SKY RAY EDX P370) device. The target has a dimension of (2×2 cm^2). The surface of the target was polished with smooth paper and washed with ethanol and deionized water (DIW) before each ablation process to remove the ablation traces obtained from the previous ablation process. In this work, the PVA solution was used as the liquid medium. PM 580 was supplied from British Drug Houses (BDH), Sigma-Aldrich and used without further purification, PVA from DBH Chemical LTD Pooled England. The solvent used was Ethanol with a purity of 100%.The powder is weighted using an electronic balance type (mettler AE 166) German – mode having a sensitivity four digits. Then, different amounts of (Au:Ag) nanoparticles was dispersed in 3 m1 of PVA prepared by PLAL (Pulse Laser Ablation in Liquid)

FWHM.

spectra - it also shows the relative intensity and wavelength values and

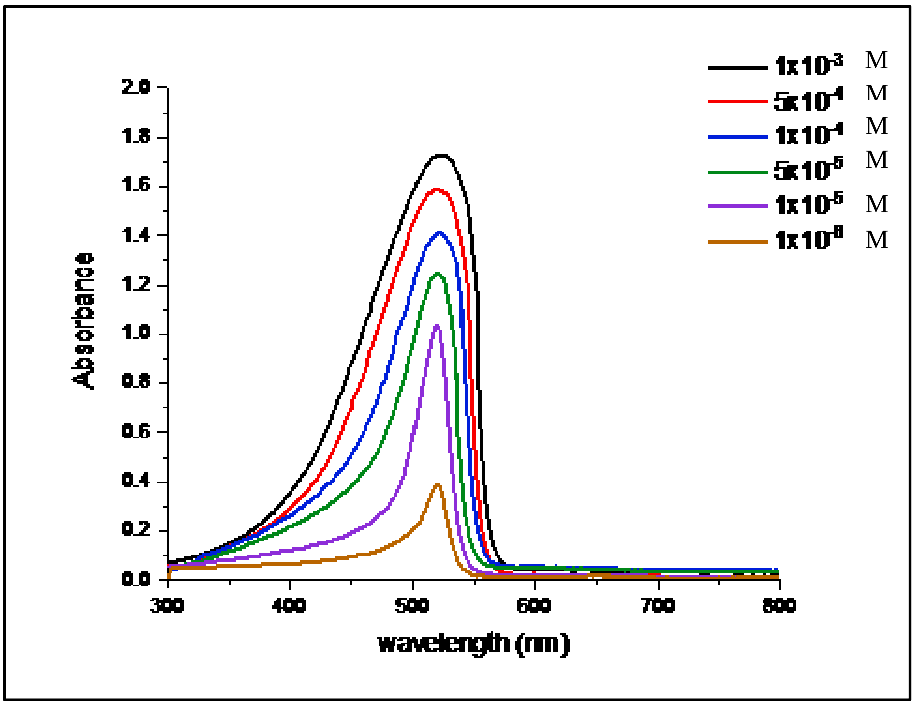

Fig. (1) The absorption spectra of different molar concentrations of Pyrromethene 580 dye solution in Ethanol

Table (1) Absorption spectra and wavelength max and FWHM of dye solutions dissolved in ethanol at different concentrations.

Concentration (M)	$\lambda\ max$ (nm)	FWHM (nm)	Relative intensity (abs) (a.u)
1x 10^{-3}	522	105	1.72
$5x10^{-4}$	521	91	1.58
$1x10^{-4}$	520	77	1.40
$5x10^{-5}$	520	56	1.24
$1x10^{-5}$	519	35	1.02
$1x10^{-6}$	519	24	0.38

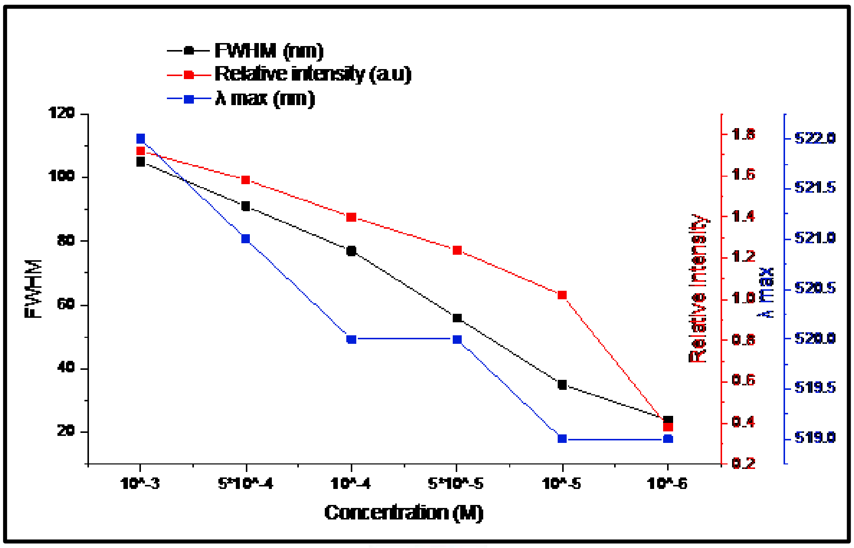

Fig (2) explain the relation between Relative intensity (Absorbance) and λ_{max} .and FWHM

(Fig.3) shows

theFluorescence spectra of Pyrromethene 580 dye solutions dissolved in Ethanol solvents at different concentrations (1x10^{-3}, 5x10^{-4}, 1x10^{-4}, 5 x 10^{-5}, 1x10^{-5} and 1x10^{-6}) M.where the emission intensity peaks varied from one concentration to another. By studying the fluorescence spectra, the emission peak at the lowest concentration (1x10^{-6}) M was (543 nm), While the emission intensity was (0.92) and the highest concentration (1x10^{-3}) mole/l was (564 nm), While the emission intensity was (0.19). This means, increasing the concentration leads to decrease in the intensity and shift Peak position to Long wavelength (red shift), and increasing concentration to (1x10^{-3}) M M es a shift in the fluorescence wavelengths due to the excimer or dimmer formed in solutions by collision diffusion processes, leading to a decrease in the quantum efficiency of the fluorine, since its fluorescence causes a shift towards the longest wavelength (red wavelengths) because of the loss of energy due to non-Radiative transitions like internal conversion and intersystem crossing, but the increase in concentration resulted in an increase in fluorescence intensity as shown in (Fig.3)

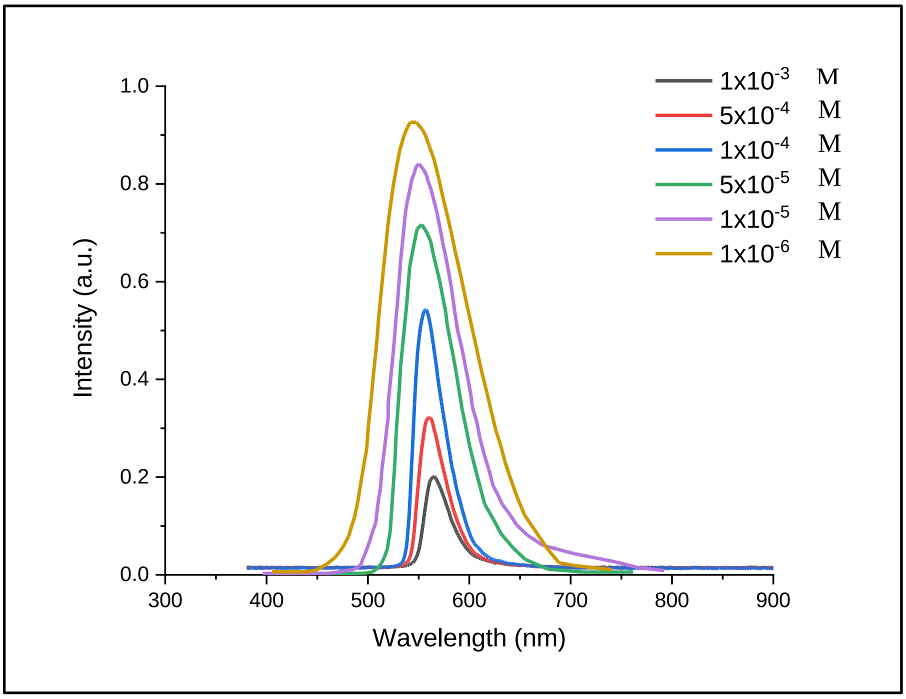

Fig (3) Fluorescence spectra of PM 580 in ethanol solvent at different concentration

Table (2): Fluorescence at the max wavelengths and lifetime and the quantum efficiency for PM 580 dye solution at different concentrations

Concentration (M)	$\lambda\, max$ (nm)	Relative intensity (Flu)(a.u)
1x 10^{-3}	566	0.19
5x10^{-4}	559	0.32
1x10^{-4}	557	0.53
5x10^{-5}	553	0.71
1x10^{-5}	550	0.83
1x10^{-6}	545	0.92

Through our results for the absorption and fluorescence spectra of PM 580 dye in Ethanol solvent (liquid models) at concentraition 1x10^{-6}M, it was shown in (Fig.4) that the peak of the absorption spectrum does not match the peak of the fluorescence spectrum, and this is attributed to non-radiative processes (such as internal transformation and inter-crossing). Since the molecule loses part of its energy before returning to the stable state, we find that the absorption energy is higher than the energy of fluorescence. The results also show that increasing the concentration causes the shift of the peak of the absorption spectrum and the peak of the fluorescence spectrum towards longer wavelengths. This is due to the increase in the field of turbulence between the molecules as a result of the increased concentration, in addition to the formation of the dimer resulting from the assembly of dye molecules, which leads to its absorption at higher energies than it is for monomer and its emission at lower energies.

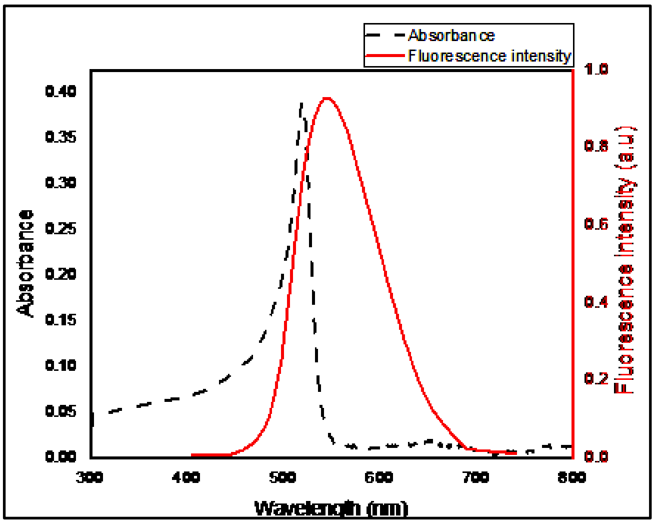

Fig (4) The Stokes shift when Dye Concentration (1x10^{-6})M.

(Fig.5) show absorbance spectra of Au: Ag NPs prepared by PLAL with laser wavelength532nm, with laser energy at (400, 600, 800 and 1000) mJ, If pure gold and silver nanoparticles were mixed in the same solution, two plasmon bands should be observed,This enhancement in the intensity of absorption can be explained by the increase in the concentration of metals nanoparticles formed in solution during the ablation processو The height and the width of the absorption peaks were found also to be dependent upon the laser energy. given for an increase in the NPs concentration, the absorbance is dependent on the concentration of the suspension based on the Beer-Lambert law. However, the formation of more than one gap in nanoparticles can lead to an increase in concentration resulting in Fermi level diffusion and an increase in the permissible states that represent an energy gap.Table (3) explains peaks of Absorptions values for samples produced by various laser energies.

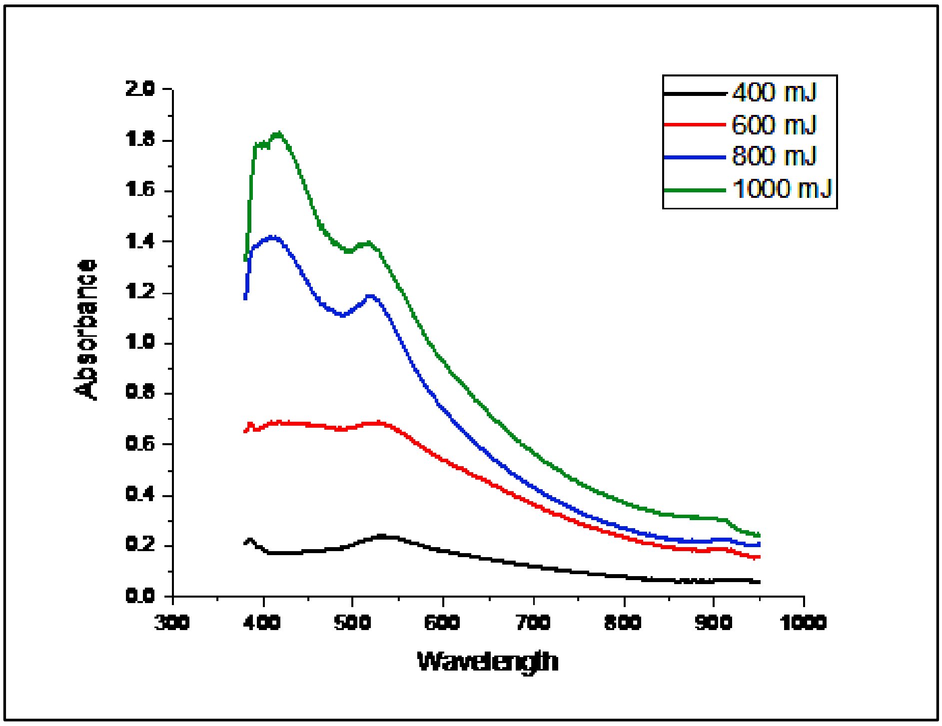

Fig. (5) The absorption spectra of Au: Ag (Core/shell) Nanoparticles with different Energy in laser wavelength 532 nm

TEM images of Au: Ag NPs their particle size distribution are illustrated in Fig (6). The Au: Ag NPs were synthesized by laser ablation in PVA solution with laser wavelength (532 nm), and with laser energy of 1000 mJ and 500 pulses.

Fig (6) shows increasing magnifications of TEM image for Au/Ag NPs synthesized by pulsed laser ablation in PVA solution with laser energy at 1000mJ and with 500 pulses and wavelength 532 nm, Ag/Au NPs. It can be seen that the nanoparticles are in the form of a core and a shell. The resulting particles for gold are spherical with an average size of (30 nm). When the silver target is ablated in the gold colloidal suspension, the formation and growth of Au/Ag core-shell particles take place. It is interesting to note that the particles in the proximity of the geometry of the plasma plume expansion become large particles compared to other particles, and then once the size increases, which in turn causes more Au ions to get attached to the particle due to the increase in surface area.

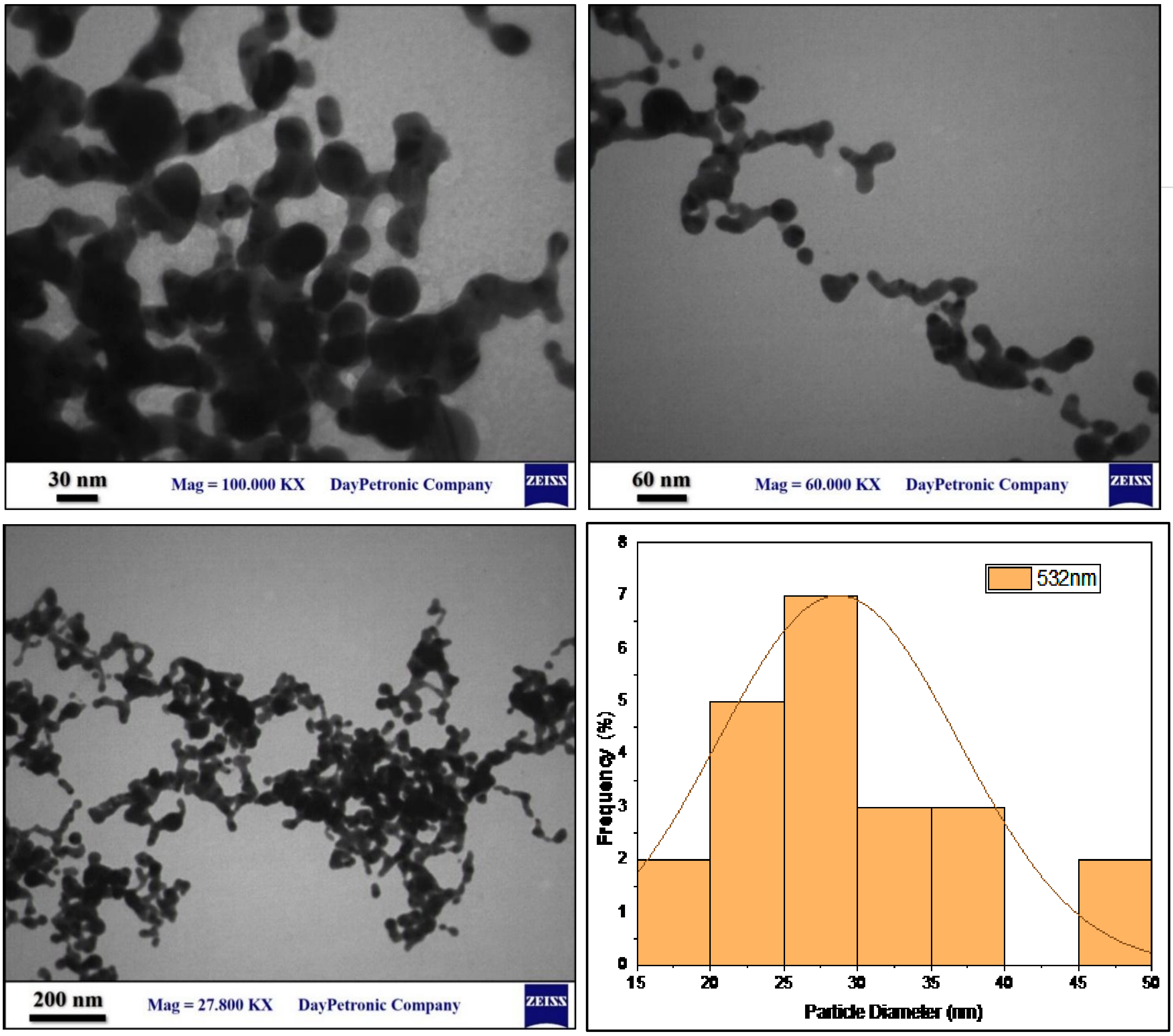

Fig (6): TEM image for Au/Ag NPs synthesized by 532 nm

Table (3) explain values of absorption for Au, Ag, and Au: Ag produced by various laser energies

Energy pulses (mJ)	Au: Ag
400	0.24 : 0.21
600	0.68 : 0.69
800	1.17: 1.41
1000	1.38: 1.83

(Fig.7)and (Fig.8), shows the absorption and Fluorescence spectra of PM 580 solution dissolved in Ethanol with different amount masses of (Au: Ag) Nanoparticles obtained by laser ablation of metal plates immersed in PVA with different energy puls (400, 600, 800, 1000) mJ and laser wavelength (532 nm). Where adding Nanoparticles solution of (Au: Ag) Nanoparticles to the dye solutions of ($1x10^{-6}$) M concentrations.

Table (4) shows the results of Absorption spectra and wavelength max and FWHM of dye solutions dissolved in ethanol ($1x10^{-6}$) M concentrations with (Au, Ag, Au: Ag) Nanoparticles. The intensity of the absorption was found to increase with the increase in the energy used to synthesize the nanoparticles and the highest absorption was found when nanoparticles obtained by laser ablation at 1000 mJ were added to the dye solution. This is attributed to the average minimum free path scattering rate, and this means the free crossing of nanoparticles in the dye solution. Also, the absorption spectra were significantly narrowed with a subsequent increase in intensity, which is attributed to the contribution of the nanoparticles to trapping the emitted photon and thus increasing the photon flux (amplification) within a narrow spectral range. A shift towards shorter wavelengths (about 4 nm) was observed as the energy to generate nanoparticles was increased from 400 to 1000 mJ in the dye solution. Accordingly,.

Through our results, (Fig.9) show the absorption and fluorescence (Stokes Shift) spectra of PM 580 dye in Ethanol solvent (liquid and nanoparticles), it was shown that the peak of the absorption spectrum does not match the peak of the fluorescence spectrum, and this is attributed to non-radiative processes (such as internal transformation and inter-crossing). Since the molecule loses part of its energy before returning to the stable state, we find that the fluorescence energy is higher than the energy of absorption. The results also show that increasing the energy of the pulse causes the shift of the peak of the absorption spectrum and the peak of the fluorescence spectrum towards shorter wavelengths. The absorption peak was centered at 516 nm while the fluorescence peak was centred at 541 nm with a shift of 25 nm. This shift is slightly equal to that measured for the PM 580 dye only, The results of the quantum efficiency of fluorescence also showed that it increases with the decrease in the molar concentration of the dye solution and it also increased at adding nanoparticles, where it increased from (61%) in the case of the dye solution at a concentration of 1 x 10^{-6}M molar to (82%) in the case of Au: Ag Nanoparticles.

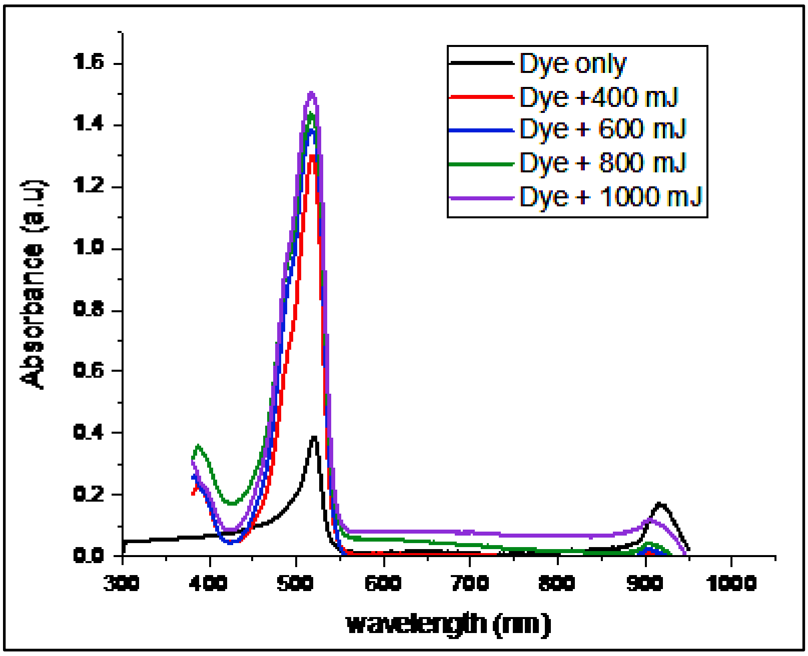

Fig (7): The Absorption spectra of 10^{-6} M molar concentration of PM 580 dye with (Au: Ag 532) NPs recorded at a different Energy pulse

Table (4) explain the values of intensity (Absorbance) and λmax, for 10^{-6} M of PM 580 dye with (Au: Ag) Nanoparticles

Energy pulses (mJ)	**Laser wavelength (nm)**	**Au: Ag + Dye**		
		Abs	**λ_{max} (nm)**	**FWHM (nm)**
400	**532**	1.29	518	42
600		1.37	517	52
800		1.43	516	54
1000		1.50	516	54

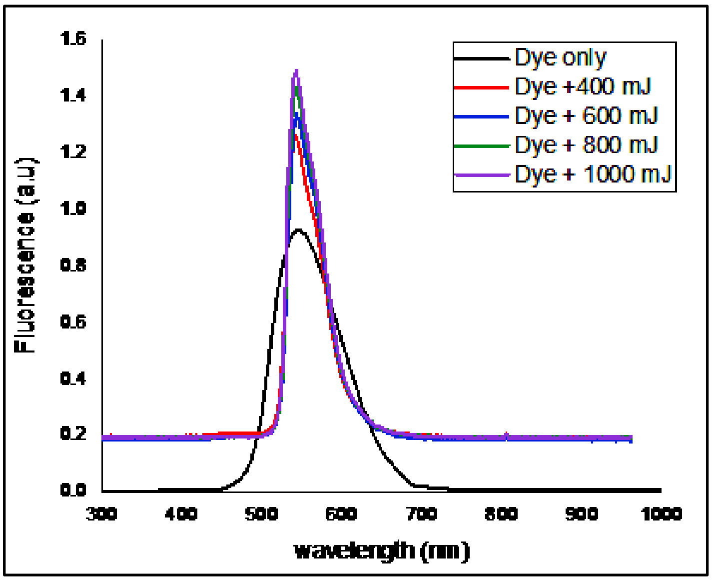

Fig (8): The fluorescencespectra of 10^{-6} M molar concentration of PM 580 dye with (Au: Ag 532) NPs recorded at a different Energy pulse

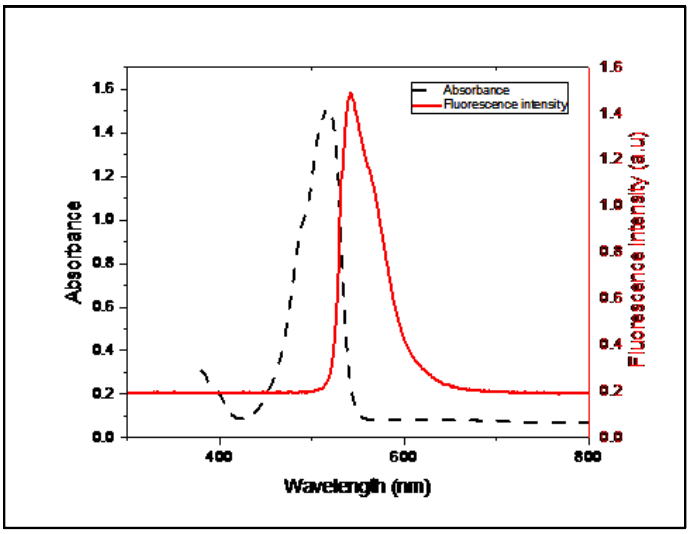

Fig (9) The Stokes shift for (Au: Ag 532)with 1000 mJ

4.Conclusion

In concluding remarks, Gold and Silvernanoparticles were employed in Pyrromethene 580 dye solution dissolved in ethanol with 10^{-6} M concentration to act as a gain medium. The highest increase in fluorescence intensity was reasonably measured as an amount of Au:Ag NPs at 1000 mJ nanoparticles were added to the dye solution. These results can effectively be used to design and fabricate gain media with low production cost, high spectral quality and good reliability for wavelength narrowing and tuning.

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