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RESEARCH PAPER

Enhancement Surface Plasmon Resonance in the Visible Region by Different Active Media

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ABSTRACT

In this study, the effect of types and concentrations of nanoparticles on the performance of plasmonic active media has been addressed, especially the intensity of their emission spectra, and the effect of the three different dye concentrations and the concentration of the Au NPs and Ag NPs were studied, separately, and it appeared through the experiment that the appropriate concentration of the dye must be chosen for each specific range of the concentrations of the Au NPs and Ag NPs. and it was found through the study that adding different concentrations of nanoparticles improves the plasmonic in the active media.

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INTRODUCTION

Plasmonic nanostructures of noble metals have been used in recent years in a wide range of rare optical properties that can be controlled by studying the effects of type, shape, size, and concentration of nanoparticles within the active media [1]. The noble material has conductive electrons on the surface, these free electrons vibrate coherently in a specific region when the light source of the appropriate wavelength illuminates the metal nanostructures. The absorption and scattering of the noble metal nanoparticle cross-sections are enhanced by the visible active gain media [2, 3]. The visible light that emits from the active media helps to study different parameters which have important effects and have broad applications in optoelectronics, nonlinear optics, lasers, and spectroscopy [4]. Plexcitonic nanostructures as a combination of plasmonic and excitonic buildings offer small mode volumes due to plasmonic arm and strong coupling even at the level of a few emitters at room temperature owing to an efficient selection of excitonic ones [5,6]. The strength of coupling between two oscillators can be classified into strong and weak coupling regimes. The strength of coupling is characterized by comparing the rate of energy transfer between the matter and the cavity and the decay rates of the individual states [7, 8]. The strong coupling in the active media can be considered a basic tool to control the emission spectrum parameters, due to the enhanced concentration of the scattering centers within the active media and that can be influenced due to the adjacency of an emitter in excitonic media near a plasmonic surface [9, 10]. The emission spectrum is enhanced by coupling between the host of the exciton such as the dye medium and the LSPR of metallic NPs to obtain an

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overlap between the emission spectrum of the dye and the LSPR of the nanoparticles spectrum [11]. This enhancement can be provided the necessary conditions for strong coupling. In the weak plasmon-exciton coupling regime, the inherent nature of SPP and exciton modes are not modified and thereby increase the absorption or emission rates of the molecules, all these phenomena depend on the concentration of nanoparticles inside the active media, and on the type of used dye [12]. In this work, the plasmonic effects on the emission spectrum of two types of noble materials (gold and silver nanoparticles) will be studied, and each type with five different concentrations inside the active media, these concentrations are mixed with three types of active media which cover a wide range in the visible region.

MATERIALS AND METHODS

Sample preparation

the laser ablation in a liquid method it is one of the most common methods for generating nanomaterial's, where in this method the focus of the laser pulses with suitable energy on the surface of a solid target immersed in liquid so the interaction of laser pulses with the target which is being in a plasma cloud with a high transfer of kinetic energy and contains ions, gatherings, or atoms. And then all energy is reflected through the surface, and in this case, it is noted that the reflectivity depends on the wavelength and material of the laser used. The absorbent energy of the model changes from photons to electrons and then to the lattice, and then is radiated in the material. Increasing the number of laser pulses on the target, the concentrations of nanoparticles in the liquid will be increased, the ablation procedure was performed with five different number of laser pulse 100, 200, 300, 400 and 500P for each Au and Ag target, in order to get different concentrations of nanoparticles, as shown in the Fig. 1, the Q-switched Nd: YAG laser operating at a wavelength (1064 nm), the pulse width of (5 ns), and repetition rate of (10 Hz) was focused on the surface of the target and shot for 30 min. To produce gold and silver nanoparticles. A reflective mirror has been placed tilted in relation to the vertical plane to change the direction of the laser beams that were directed at the target by a lens (focal length of 20 cm).

Preparing the dyes

The dye solutions have been prepared by dissolving the amount of three different kinds of dyes (methyl orange (MO), Rohdamine6G (Rh6G), and methyl blue (MB) dye) in a distilled water solvent. This amount of powder dye was dissolved in a specified volume of the solvent used, and the concentration of these three dye solutions was calculated depending on the following formula

$$w_m = \frac{C \times V \times M_w}{1000} \quad (1)$$

Where, The weight of the dye required to obtain the desired concentration (gm)

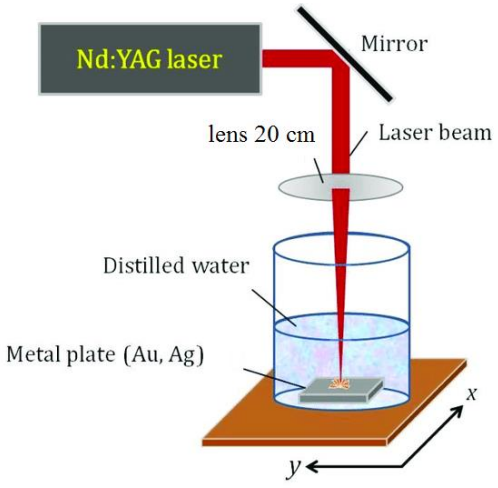

Fig. 1. The experimental setup of the preparation of Au NPs and Ag NPs by laser ablation.

: the concentration (M)

: the volume of the solvent (ml)

: Molecular weight of the dye used (gm/mol)

To reduce the error in the sample preparation process, a solution of each dye (MO, Rh6G, and MB) with a higher concentration (1×10-3 M) in distilled water solvent will have been prepared, which was in the volume of 10 ml was prepared from the solvent, and a solution of each dye (Rh6G, MB, MO) was prepared. As shown in Fig. 2 these high concentrations have been diluted to different low concentrations (10-4,0.5x10-4,10-5,0.5x10-5 M) by using the following relationship, known as the dilution relationship:

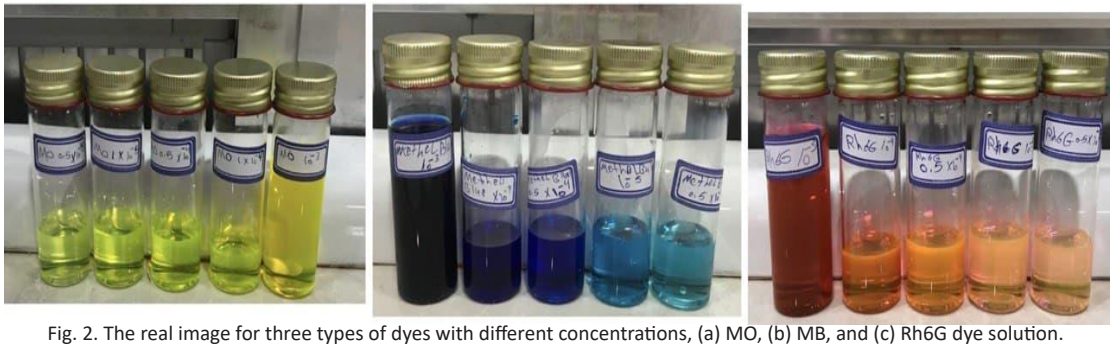

Fig. 2. The real image for three types of dyes with different concentrations, (a) MO, (b) MB, and (c) Rh6G dye solution.

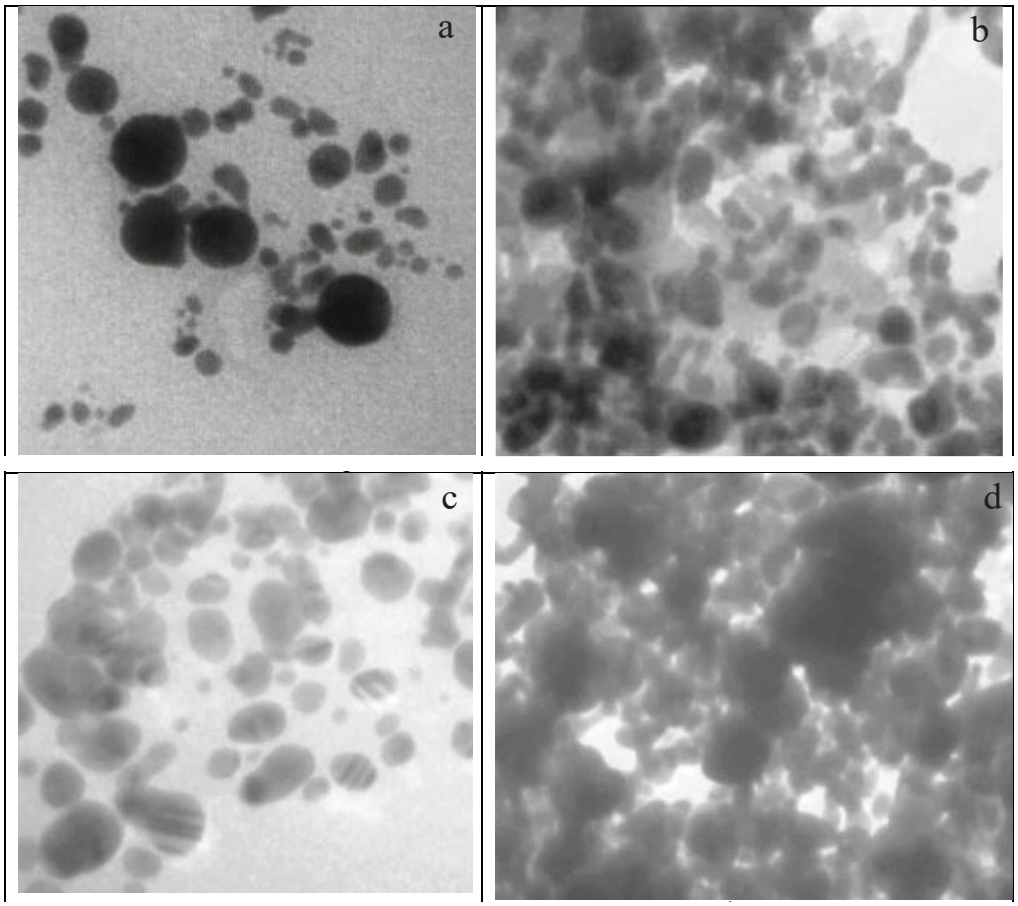

Fig. 3. TEM images of the colloidal solutions with low and high concentrations: (a and b) Au NPs 500 and 900, (c and d) Ag NPs (500 and 900 P), respectively

$$C_1 \times V_1 = C_2 \times V_2 \quad (2)$$

Where, C_1: first concentration (high) (M)

V_1: The necessary volume of the first concentrate (before dilution) (ml)

C_2 Second concentration (lightest) (M)

V_2: The volume required to be added to the first concentration to obtain the second concentration. (after dilution) (ml)

Preparation of the active media

To characterize the performance of plasmonic behavior under the influence of different concentrations and types of nanoparticles inside the dyes, the dyes (MO, Rh6G, and MB) with the nanomaterials (Au NPs and Ag NPs) are mixed with a volume ratio of 1:2. For ensuring homogeneity, 1ml of different concentrations for each (Au NPs and Ag NPs) with 2ml from the best concentration of the dyes (1×10-5 M) were mixed, and these active media were put in ultrasonic for 20 minutes.

RESULTS AND DISCUSSION

Structure characteristics

In Fig. 3 TEM images of low and high concentrations for each Al NPs and Ag NPs were prepared by ablation in liquid, Fig. 3a observed a low number of Au NPs with 500 P, when increase the pules ablation time and the number of nanoparticles increased as shown in Fig. 3b, In other words, increasing the number of laser pulses on the target lead to increases the ablation from the surface of the target, thus an increase in the number of particles inside the solution, the same behavior applies to Ag NPs, the concentration of nanoparticles inside the liquid with 900 pulses is higher than that in low pulses, as shown in Figs. 3a and b, respectively.

Optical properties

Absorption spectrum of Au NPs and Ag NPs

The absorption spectra of Au and Ag NPs with different concentrations were prepared by a pulsed laser ablation method when the energy was fixed at (500mJ) with a change in the number of pulses (500, 600, 700, 800, 900 plus), to study the effect of nanoparticles concentration on the emission spectra for the study plasmonic phenomenon. As shown in the Fig. 4a the absorption spectrum of Au NPs with different concentrations, and observed the plasmonic peak at (519.881nm), and by increasing the concentration the peak of the absorption spectrum has been increased, also in Fig. 4b the absorption spectrum of Ag NPs with different concentrations was shown, and the plasmonic peak was noticed at (406.60nm) and we noticed by increasing the concentration that intensity peak has been increased.

Absorption spectra of MO dye with and without NPs

In Fig. 5a show the absorption spectrum of methylene orange (MO) dye at different concentration without addition of nanoparticles is shown, and notice that when the dye concentration is increased, the absorption peak will be increase. The absorption spectra of MO with different concentrations ($1x10^{-6}$, $5x10^{-6}$, $1x10^{-5}$, $5x10^{-5}$, and $1x10^{-4}$ M) have been studied. The best absorption spectrum of MO was obtained at concentration $1x10^{-5}$ M at 486,684 nm. Thus, this concentration will be adopted for the remainder of our active medium. It is observed that the absorption spectrum of the MO dye shifts to the

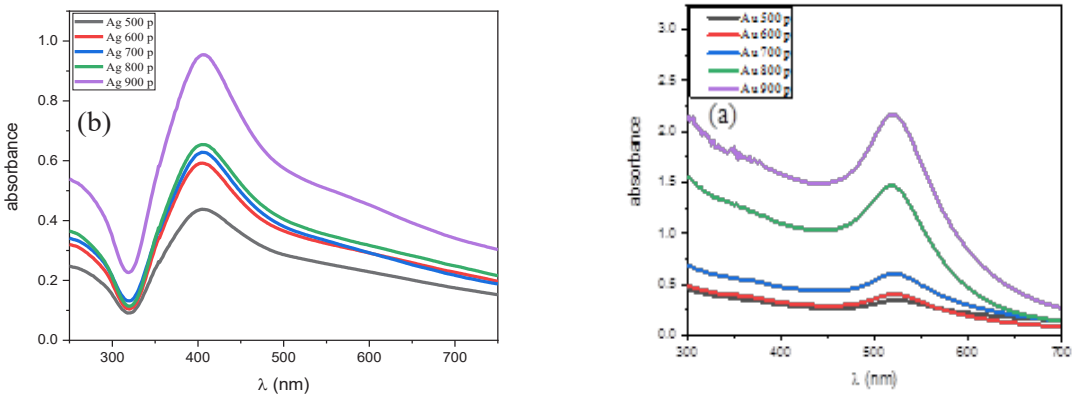

Fig. 4. absorption spectra with different concentrations of nanoparticles, (a) Au NPs and (b) Ag NPs.

shorter wavelength of 483.2 nm.

Figs. 5a and b showed the absorption spectrum of different concentrations of Ag and Au NPs mixed with MO dye, respectively. In this case, appears only one peak in the absorbance spectrum, the first one represents the absorption (SPR) peak of Ag NPs and which appears at (407 nm), these peaks will be enhanced by increased Ag NPs concentration, and the second peak for MO dye which appears at (490.788nm), and the absorption spectrum peaks moved toward redshift about (3nm) due to the increase in the nanoparticles concentration. In the higher concentrations observed quenching in the absorbance peak, this is due to the fact that increasing the concentration of nanoparticles has a certain limit within the dye, after that, it has a negative effect on the dye as shown in the red curve. Fig. 5c observed the absorption spectrum of different concentrations of Au NPs mixed with MO dye, in this case appear only one peak in the absorbance spectrum, the reason for the overlap between the absorption spectrum of Au NPs and Rh6G, they are close to each other, the absorbance peak appears at (491.005nm) with peaks moved toward redshift about (4nm), and observed quenching in absorbance peak with higher concentration as shown in the violet curve.

Absorption spectrum of Rh6G dye with and without NPs

The absorption spectra of Rh6G with different concentrations ($1x10^{-6}$, $5x10^{-6,}$ $1x10^{-5}$, $5x10^{-5}$, and $1x10^{-4}$ M) have been studied, and it appears from Fig. 6 that with increasing concentration, the absorption spectrum increases and regularly, where it was found that the highest value of the

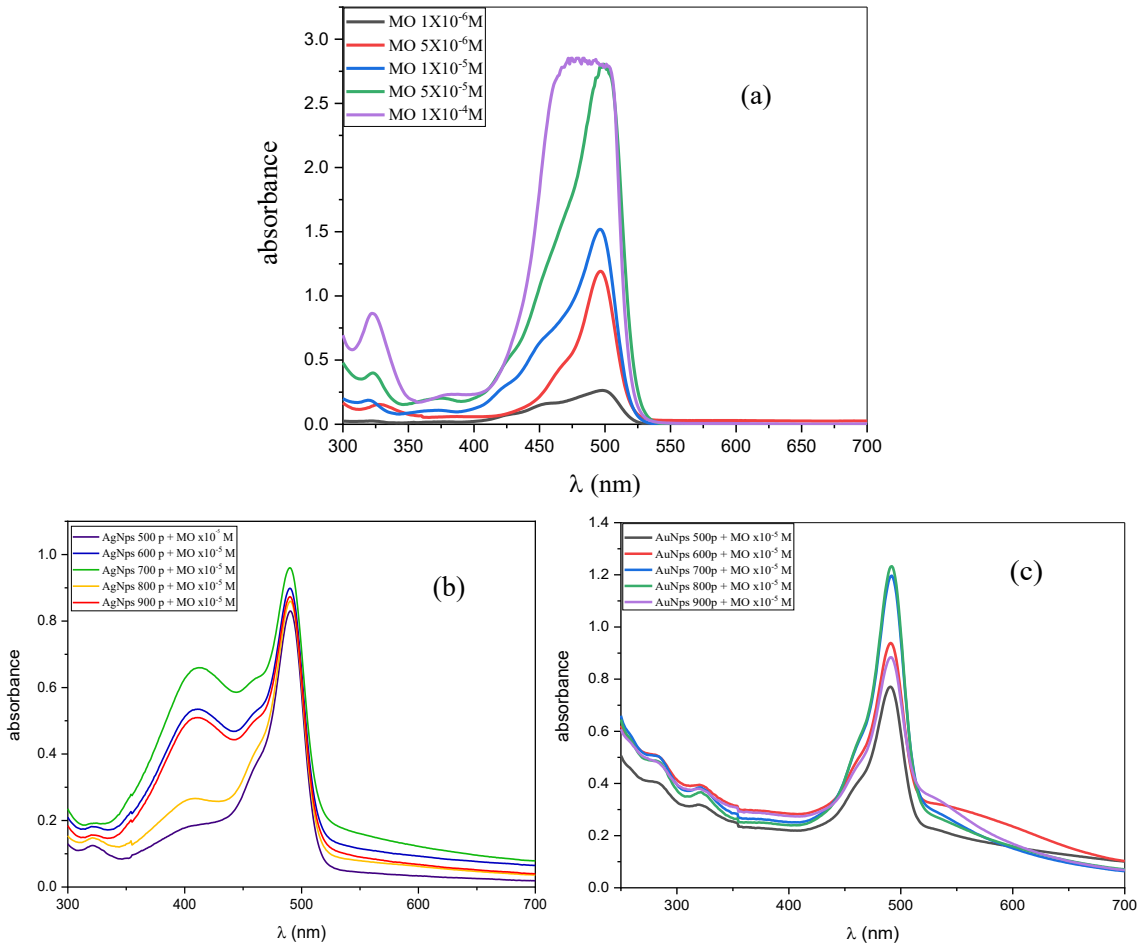

Fig. 5. a) Absorption spectrum of (MO) dye without nanoparticles c) Absorption spectra of the dye dissolved in water with nanoparticles, (a) Au NPs and (b) Ag NPs at a concentration of (MO) dye (1×10^{-5} M).

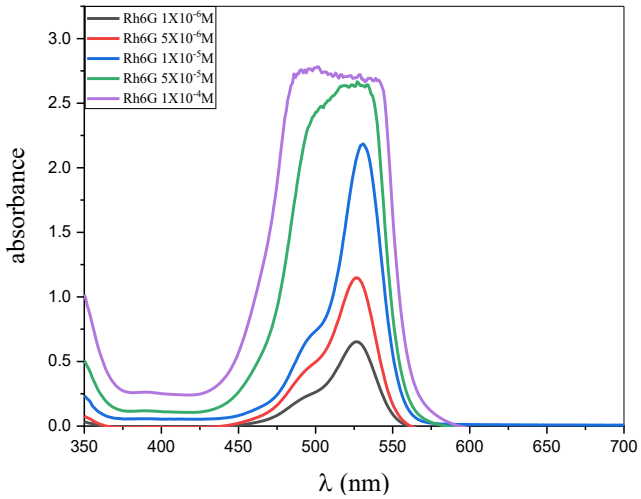

Fig. 6. Absorption spectrum of (Rh6G) dye without nanoparticles

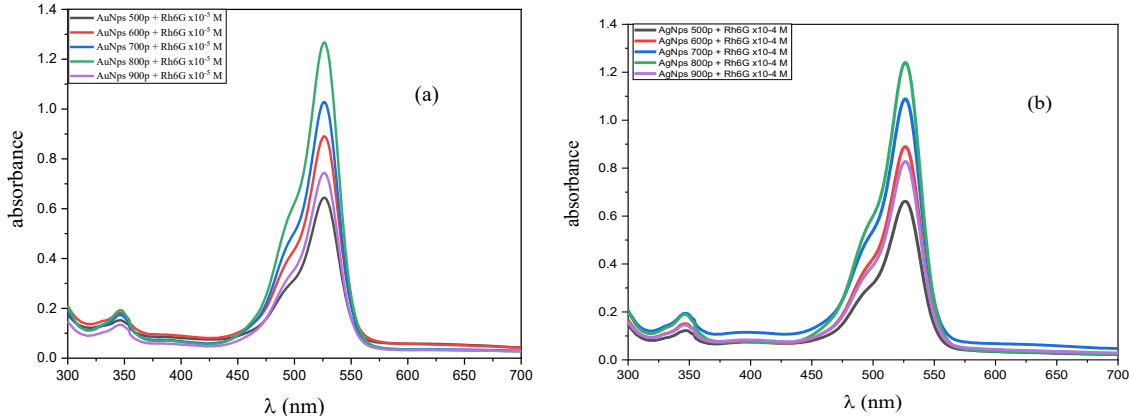

Fig. 7. Absorption spectra of the dye dissolved in water with nanoparticles, (a) Au NPs and (b) Ag NPs at a concentration of (Rh6G) dye (1×10^{-5} M).

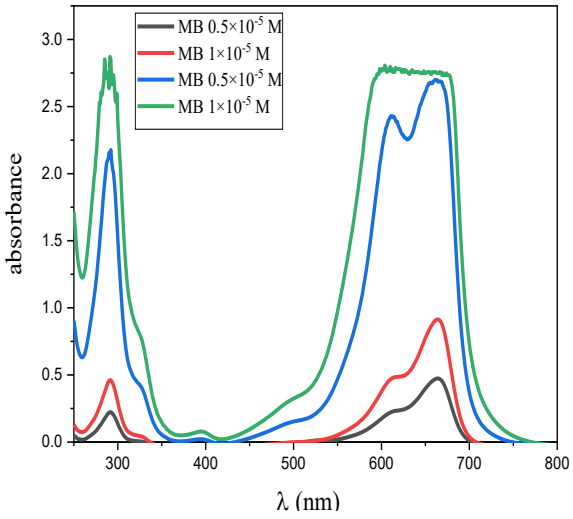

Fig. 8. Absorption spectrum of (MB) dye without nanoparticles

absorbance peak was at (532.837 nm), therefore, the best absorption spectrum of this dye was obtained at concentration 1 x10^{-5} M. Thus, this concentration will be used in our active medium.

In Figs. 7a and b the absorption spectrum of a (Rh6G) dye with concentration (1 × 10^{-5} M)

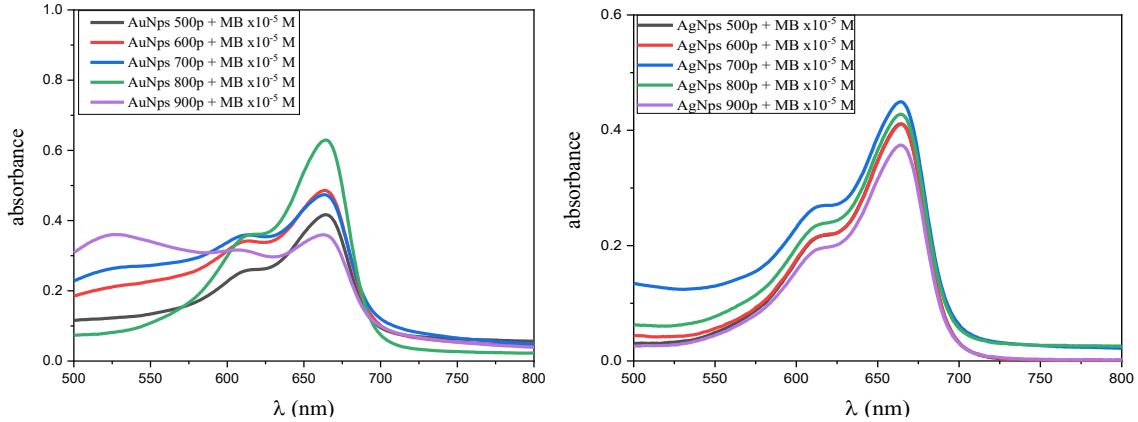

Fig. 9. Absorption spectra of the dye dissolved in water with nanoparticles, (a) Au NPs and (b) Ag NPs at a concentration of (1×10^{-5} M) of (MB) dye.

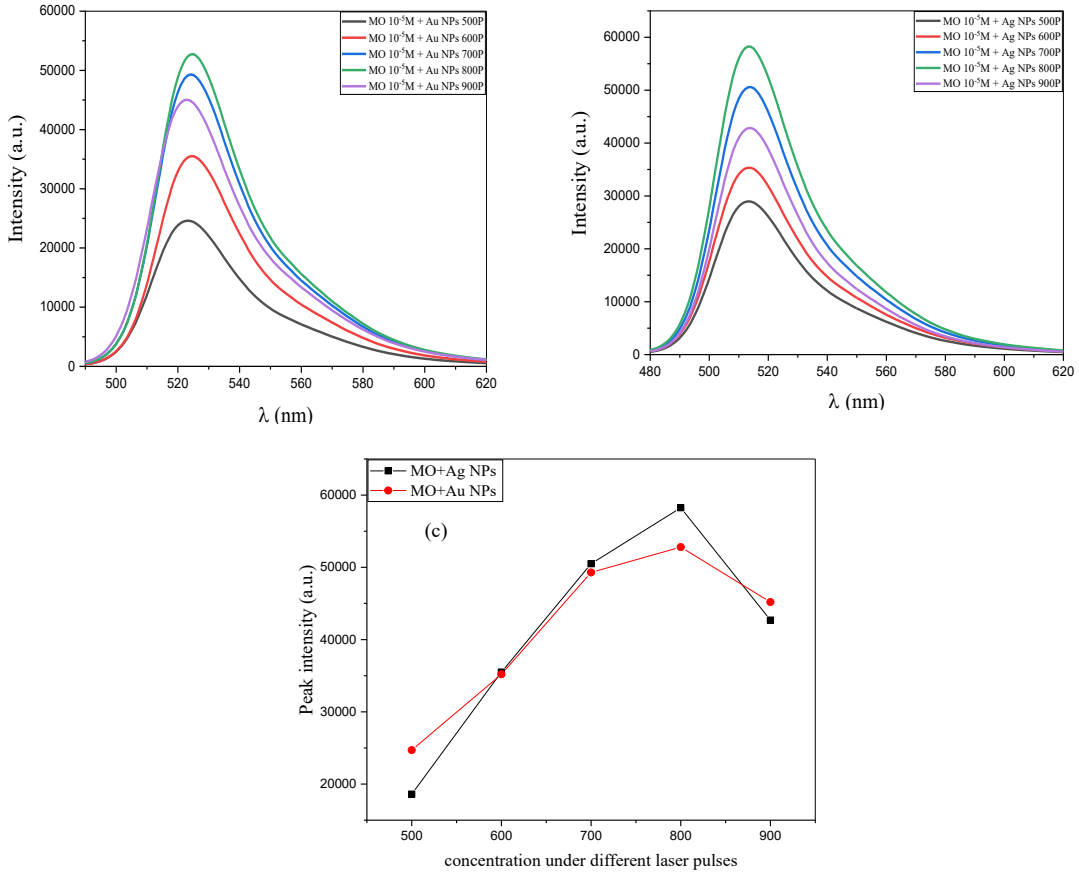

Fig. 10. Fluorescence spectrum of the MO dye at a concentration (1×10^{-5}M) mixed nanoparticles, (a) Au NPs, and (b) Ag NPs (c) the peak intensity of MO mixed with (Au NPs, Ag NPS) with different concentrations.

mixed with different concentrations of (Au NPs and Ag NPs) is shown. It is noted that when the concentration of Au NPs within the dye, the absorbacnce spectrum will be increase, for this reason the the plasmonic spectrum appears, while it decreases when the concentration is increased to (900P), and this indicates that the concentration of Au NPs inside the medium has overshadowed the concentration of the dye as shown in Fig. 7a. The same behavior can also be observed when adding Ag NPs inside the dye as shown in Fig. 8b.

Absorption spectra of MB dye with and without NPs

The absorption spectrum of different concentrations of m-blue dye in water solvent (1x10-5 M) has been recorded using UV-vis spectral analyzer. In this dye, there are two absorption peaks at (292 and 665 nm), and the best concentration (1×10^{-5} M) has been chosen as shown in Fig. 8.

In Fig. 9, the absorption spectrum of MB dye mixed with nanoparticles Au NPs and Ag NPs at a concentration of (1×10^{-5} M) is shown. It is noted that when the concentration of the dye increases, the peak increases and the plasmonic spectrum appears, after that the absorbance peak decreases with higher concentration.

Plasmonic phenomena for Au NPs and Ag NPs mixed with different dyes

Plasmonic effected by Au NPs and Ag NPs mixed with MO dye

The fluorescence spectrum of methylene orange (MO) dye mixed with nanoparticles (Au NPs, Ag NPs) at a concentration of (1×10^{-5}M) is shown in

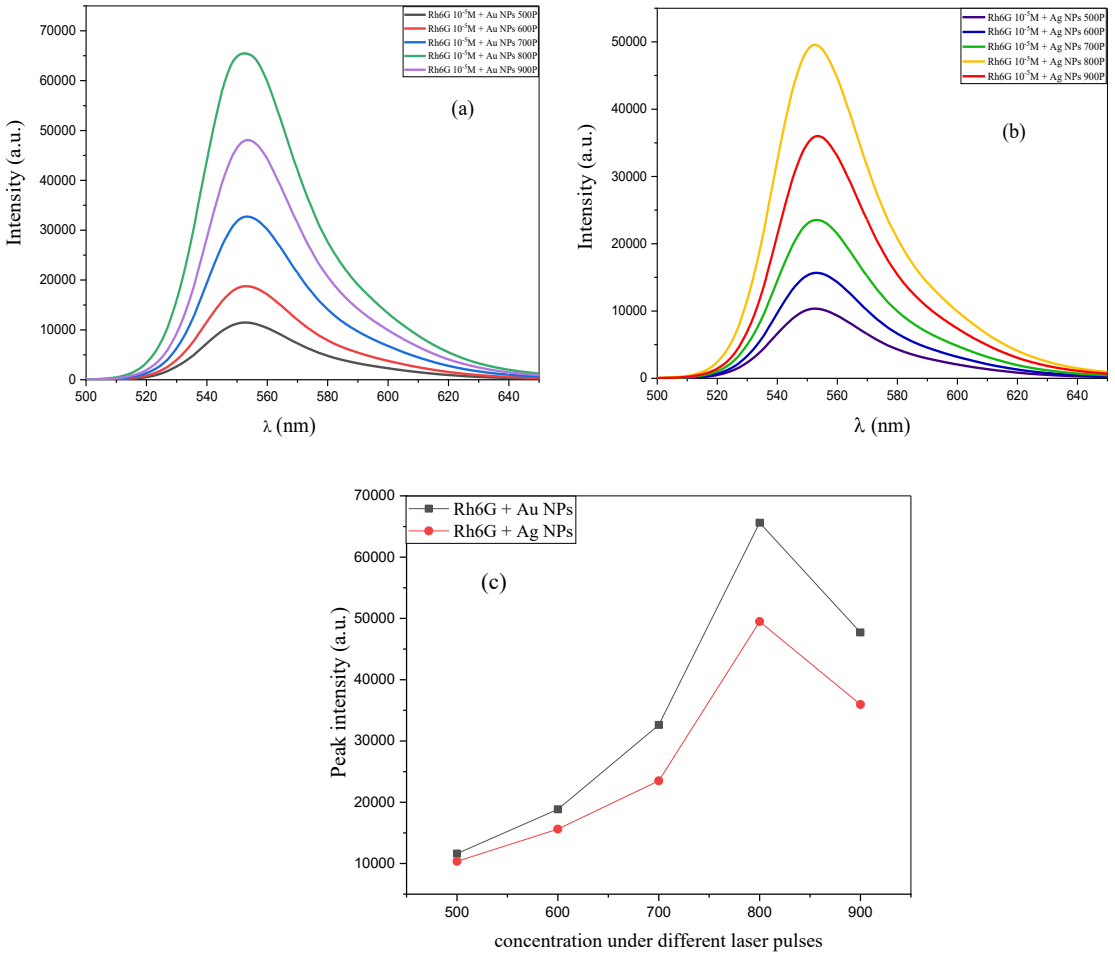

Fig. 11. Fluorescence spectrum of (Rh6G) at a concentration (1×10^{-5}M) with (a) Au NPs and (b) Ag NPs with different concentrations (c) the peak intensity of Rh6G mixed with (Au NPs, Ag NPS) with different concentrations.

Fig. 10a. It is noted that when the concentration of the dye increases, the intensity increases and the plasmonic spectrum appears. Fig. 10b shows that increasing the concentration of nanoparticles (Au NPs) mixed with (MO) dye will increase the emission spectrum and the best concentration mixed with MO dye will be noted At (Au NPs 800p) and the highest intensity was (52648 a.u.) at the wavelength (524.514nm). In Fig. 10b, notice that the best concentration also appears at (Ag NPs 800p) and its highest intensity is (58176 a.u.) at the wavelength (513.292 nm), and the intensity reaches a certain limit and then a drop occurs at the concentration (900p). From these results, we concluded the plasmonic phenomena in MO dye mixed with Ag NPs are better than that mixed with Au NPs as shown in Fig. 10 c.

Plasmonic effected by Au NPs and Ag NPs mixed with Rh6G dye

In the Fig. 11, the fluorescence spectrum of Rhodamine 6G (Rh6g) dye mixed with

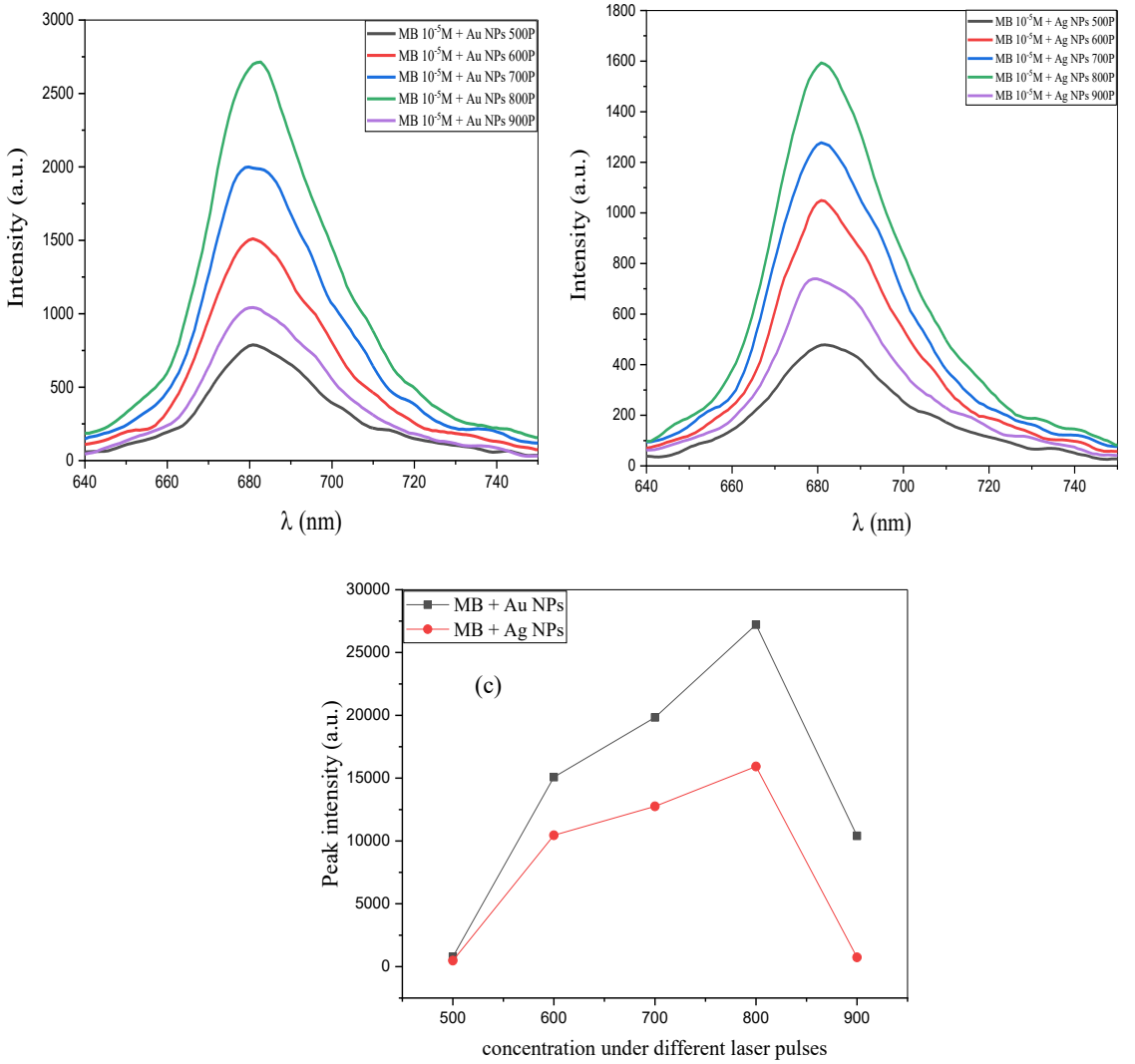

Fig. 12. Fluorescence spectrum of (MB) at a concentration (1×10^{-5}M) with (a) Au NPs and (b) Ag NPs with different concentrations (c) the peak intensity of MB mixed with (Au NPs, Ag NPS) with different concentrations.

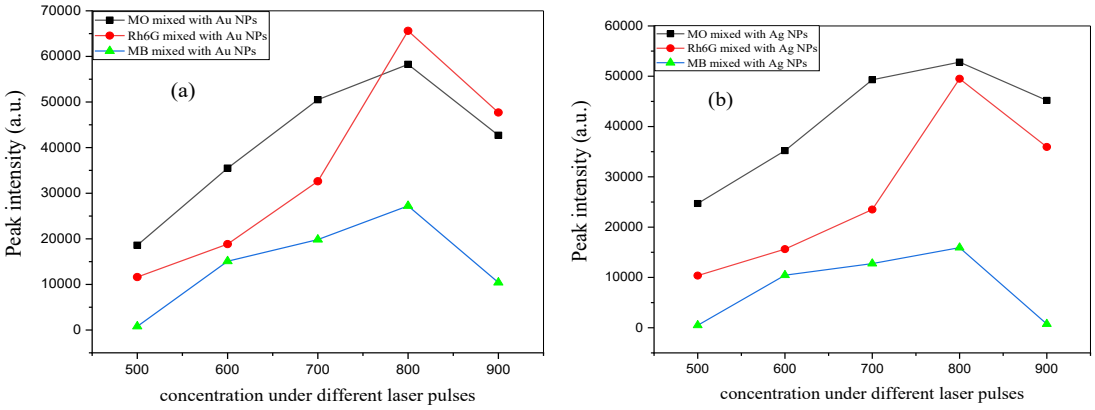

Fig. 13. Comparison of the peak intensity for three active media with different concentrations of (a) Au NPs and (b) Ag NPs of Au NPs

nanoparticles (Au NPs, Ag NPs) at a concentration of (1 × 10^{-5}M). It is noted that when the concentration of the dye increases, the intensity increases and the plasmonic spectrum appears. The effect of plasmonic nanoparticles on the fluorescence spectrum of Rh6G dye mixed with different concentrations of Au NPs and Ag NPs will be studied, and the intensity of the fluorescence spectrum is clearly increased when adding Au NPs to the Rh6G dye, the Au NPs with 800P showed the best fluorescence spectrum with the value of the plasmonic peak appearing at (65428 a.u.) and therefore strengthened our selection of it as the best suitable concentration for plasmonic active media as shown in the Fig. 11a. However the verse is reflected in relation to the higher concentration of Au NPs 900P where a decrease in intensity fluorescence is observed with an increase in the concentration of the dye as shown in the violet curve, and this can be attributed to the increasing concentration of Au NPs within the dye affects negatively the plasmonic spectrum of the dye. The same behavior for Ag NPs mixed with Rh6G dye observed the best concentration was with Ag NPs 800P, with the value of the plasmonic peak appearing at (49646 a.u.), and the plasmonic peak will be decreased with higher Ag NPs concentration 900P as shown in the red carve in the Fig. 11b.

From Fig. 11c observed, plasmonic peak of Au NPs was higher than that of Ag NPs, due to the absorption spectrum of Rh6G close to the absorption spectrum of Au NPs, for this reason, enhanced SPR on the near surface of the Au NPs, so It has better to use Au NPs in the dye medium to enhance the scattering and thus efficiency better than Ag NPs.

Plasmonic effected by Au NPs and Ag NPs mixed with Rh6G dye

Figs. 12a and b shows the fluorescence spectrum of methylene blue (MB) dye mixed with nanoparticles (Au NPs, Ag NPs) with a fixed dye concentration at (1 × 10^{-5}M). The value of plasmonic peak intensity appears at (27070 and 15886) for Au NPs 800P and Ag NPs 800P) respectively, and this value will be decreased when adding the higher concentrations for each one.

It is noted the plasmonic peak intensity of MB dye mixed with Au NPs has a higher intensity than that of Ag NPs, due to the absorption peak of Ag NPs far away from the MB dye absorption, as shown in Fig. 12 c.

Figs. 13 a and b allows a comparison between the plasmonic peak intensity of three active media containing different ratios of Au NPs and Ag NPs. The active medium with Rh6G dye mixed with Au NPs shows higher plasmonic peak intensity, while the rest active media systems have low plasmonic peak intensity for the active medium with MO dye mixed with Ag NPs shows higher plasmonic peak intensity, while the rest random laser systems have low plasmonic peak intensity.

CONCLUSION

The increase in the Au NPs and Ag NPs concentration is not free, but it is limited within a certain range because the excessive concentration of the nanoparticles may lead to the quenching of fluorescence, which in turn causes a shorter lifetime and lowers quantum yield. and the type of nanoparticles within the active media selected as scattering centers of the dye has a great effect on the properties of the plasmonic active media, as

the experiment has shown that the active medium with Rh6G dye mixed with Au NPs shows higher plasmonic peak intensity, while the rest active media systems have low plasmonic peak intensity, for the active medium with MO dye mixed with Ag NPs shows higher plasmonic peak intensity, while the rest random laser systems have low plasmonic peak intensity.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Haddawi SF, Humud HR, Hamidi SM. Signature of plasmonic nanoparticles in multi-wavelength low power random lasing. Optics & Laser Technology. 2020;121:105770.
2. Liang C-C, Liao M-Y, Chen W-Y, Cheng T-C, Chang W-H, Lin C-H. Plasmonic metallic nanostructures by direct nanoimprinting of gold nanoparticles. Opt Express. 2011;19(5):4768.
3. He GS, Zhu J, Yong K-T, Baev A, Cai H-X, Hu R, et al. Scattering and Absorption Cross-Section Spectral Measurements of Gold Nanorods in Water. The Journal of Physical Chemistry C. 2010;114(7):2853-2860.
4. Barnes WL, Dereux A, Ebbesen TW. Surface plasmon subwavelength optics. Nature. 2003;424(6950):824-830.
5. Cao E, Lin W, Sun M, Liang W, Song Y. Exciton-plasmon coupling interactions: from principle to applications. Nanophotonics. 2017;7(1):145-167.
6. Haddawi SF, Humud HR, Monfared SA, Hamidi SM. Two-dimensional plasmonic multilayer as an efficient tool for low power random lasing applications. Waves in Random and Complex Media. 2021;34(3):1640-1649.
7. Reitz M, Mineo F, Genes C. Energy transfer and correlations in cavity-embedded donor-acceptor configurations. Sci Rep. 2018;8(1).
8. Mendes Duarte R, Klaric Felic G. Corrigendum to "Analysis of the Coupling Coefficient in Inductive Energy Transfer Systems". Active and Passive Electronic Components. 2016;2016:1-1.
9. Bergman DJ, Stockman MI. Surface Plasmon Amplification by Stimulated Emission of Radiation: Quantum Generation of Coherent Surface Plasmons in Nanosystems. Phys Rev Lett. 2003;90(2).
10. Jain PK, Huang X, El-Sayed IH, El-Sayed MA. Review of Some Interesting Surface Plasmon Resonance-enhanced Properties of Noble Metal Nanoparticles and Their Applications to Biosystems. Plasmonics. 2007;2(3):107-118.
11. Zehentbauer FM, Moretto C, Stephen R, Thevar T, Gilchrist JR, Pokrajac D, et al. Fluorescence spectroscopy of Rhodamine 6G: Concentration and solvent effects. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2014;121:147-151.
12. Cao H, Zhao YG, Ho ST, Seelig EW, Wang QH, Chang RPH. Random Laser Action in Semiconductor Powder. Phys Rev Lett. 1999;82(11):2278-2281.