RESEARCH PAPER

Efficient Random Laser in New Kind of Semi Plasmonic Nanostructures

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ABSTRACT

In this work, the effect of type scattering centers on the performance of random laser systems has been studied, in particular the intensity of their emission spectrum, the width of the emission spectrum (FWHM), and the laser threshold. The effect of the semi plasmonic nanoparticles concentration was studied, separately, and it appeared through the experiment that the appropriate concentration of the dye must be chosen and a specific range of the concentrations of nanoparticles within the dye, so the performance of the Ag NPs random laser is studied at five different concentrations (500, 600, 700, 800 and 900 Pulse) for each of them. It has been found that the greatest emission intensity in Al NPs (approximately 19000 a.u.), the lowest laser threshold (40 μJ), and the lowest FWHM (12.5 nm) was obtained at the concentration of 800P. It was observed that these properties improved further by reaching the intensity of 21400 a.u., while the laser threshold and FWHM decreased to (35 μJ) and (10.5 nm), respectively when the concentration became 800P also.

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INTRODUCTION

Many researchers in the past decade aroused research interest in many laser active media fields, and the brightest was in the random laser, where the theoretical studies conducted by the Russian scientist Letokhov on the light diffusion in random media indicate the possibility of light amplification by random scattering [1]. as The experimental studies have certain the significance of choosing nanoparticles inside active media that act as scattering centers due to their significant effect to enhance the gain which happening of this type of laser[2]. The multiple scattering in the random active gain media system serves as a feedback mechanism for transfer to the stimulated emission of radiation [3].

The difference between the random laser and the conventional lasers is centered on the mechanism of confining the photon inside the active medium, the process of confining photons inside the active media in the random lasers by the multiple scattering in random systems, and this is done by nanoparticles, which act as a scattering center when added inside the random media [4, 5]. The light scattering phenomenon is obtained from disordered that happen in different active media such as dye-doped nematic liquid crystal [6], semiconducting nanoparticles [7], Two-dimensional plasmonic random laser [8], organic dye-doped gel films [9], and so on. Since the properties of random lasers, including the peak intensity, line width, and lasing threshold can be

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influenced by multiple light scattering effects, size, type, and concentrations of nanoparticles [10]. Depending on the type of nanoparticle within active media, random lasers can be transfer from incoherent (non-resonant) to coherent (resonant). In case of using plasmonic nanoparticles more quickly than by using nanoparticles do not have this phenomena. So the plasmonic nanoparticles are rich in the surface plasmon resonance phenomena (SPR), which can be trapping of photons near the nanoparticles surface and leads to get random laser with high efficiency [11]. In the incoherent random laser, multiple scattering increases the paths of photons, thus, the feedback mechanism increases the photon lifetime in the active media. In the coherent random laser, the photon lifetime decreases and returns to its first position forming a closed path [12]. The plasmonic nanoparticles mixed with dye have Stokes shifts between their absorption and emissions, which can reduce self-absorption and lead to enhancing the threshold with low energy pumping [13]. The emission spectrum can be enhanced with the assistance of a plasmonic by coupling between the dye and LSPR of a plasmonic nanoparticle [14]. In this paper, the effect of two types of nanoparticles and each type with five different concentrations, and the range of the impact of each parameter will be studied on the properties of the random gain media to choose the suitable medium for the random laser system. These parameters will be discussed and their effect on the peak intensity, full width at half maximum (FWHM), lasing threshold, and the number of spikes as well as their impact on other factors such as scattering mean free path () and transport mean free path ( ). Which can be considered as the basic factors for understanding random laser behavior.

MATERIALS AND METHODS

Two different kinds of semi plasmonic materials such as Al and Mg NPs ware prepared by laser ablation in liquids (LAL) method, by (Al and Mg target (>99.99% purity, Sigma Aldrich, Germany) with thickness of Al target 2 mm and Mg target 3 mm, the semi plasmonic nanoparticles prepared with using first harmonic Q-switched Nd: YAG laser with different pulse, the pulse width of 5 ns and repetition rate of 1–10 Hz. These samples were prepared at a fixed energy at 200 mJ and variable repetition rate. In order to get different concentrations of for each type of semi plasmonic nanoparticles, the ablation procedure was performed with five different laser pulses 500, 600, 700, 800 and 900 mJ. It was found that increasing the laser pulse leads to the formation of a gradual increase in the concentration of the Al and Mg NPs. The laser source was focused on the target using special kind of a high reflective mirror and lens with length (25 cm) on a rotated Al and Mg metal target in a deionized water as shown in Fig. 1 The concentrations had been produced by the laser ablation were verified using a transmission electron microscopy (TEM). The optical properties

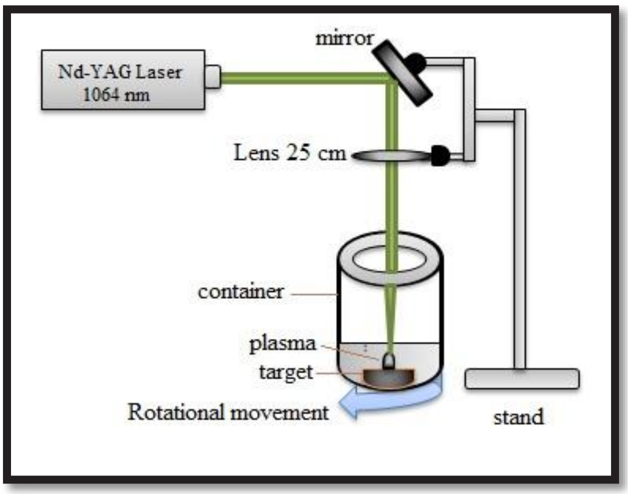

Fig. 1. Schematic of the experimental setup used for Au and Ag nanoparticles preparation by LAL

of were the optical properties of nanoparticle also studied by UV-Vis spectrophotometer.

Now to make active media, the laser dye solutions have been prepared by dissolving the required amount of Rh-B dye powder in ethanol solvent, and the concentration of Rh-B dye solution was calculated depending on Eq. 1:

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

Where C represents the concentration of dye solution reported in M (mol/L), W describes the weight in , refers to the molecular weight of the dye in grams/mole (g/mol)., and V describes the volume of solvent in liter (L The high concentration of the dye which was 5*10-3 M was prepared, and the other concentrations were obtained by dilution the amount of the solvent by using the dilution law. To obtain a gain medium for our random laser, the best concentration of the dye will be mixed with two types of the used semi plasmonic materials (five concentrations for each type), five different random media have been prepared for each type by mixing 2 ml Rh-6G with 1 ml from each concentration of Al and Mg nanoparticles to investigate the effect of nanoparticles concentration on random laser action, after that the sample will be ready to test, and to get the emission spectra of the lasing, a second harmonic generation of Nd: YAG laser has been used to disorder our active media by our tancu spectrometer as shown schematically in Fig. 2.

RESULT AND DISCUSSION

Structure properties

Fig. 3 a-f represents the images of the Al NPs and Mg NPs prepared by the laser ablation method in deionized water as a host medium. in the Fig. 3 a-c observed transmission electron microscopy (TEM) of Al NPs with low, model, and high concentrations which corresponds to (500, 700, and 900 P) with fixed energy pulses at (200 MJ), and also the images show the formation of Al NPs by size range 60-80 and 55-80 nm. In the same above condition, the (TEM) image of Mg NPs appears with a size approximately from 55-80 nm, and the sizes were determined by imageJ program.

Optical properties

Absorption spectra with different concentrations of the Al NPs and Mg NPs were measured straightway after ablation by the spectrophotometer as shown in Fig. 4. in the experimental part, semi Plasmonic NPs prepared at different repetition rate and at fixed energy (200 mj) have shown SPR absorption spectrum as indicated by their NPs concentrations. The Al NPs and Mg NPs exhibited large absorption in the ultraviolet range, and the edge of the absorption

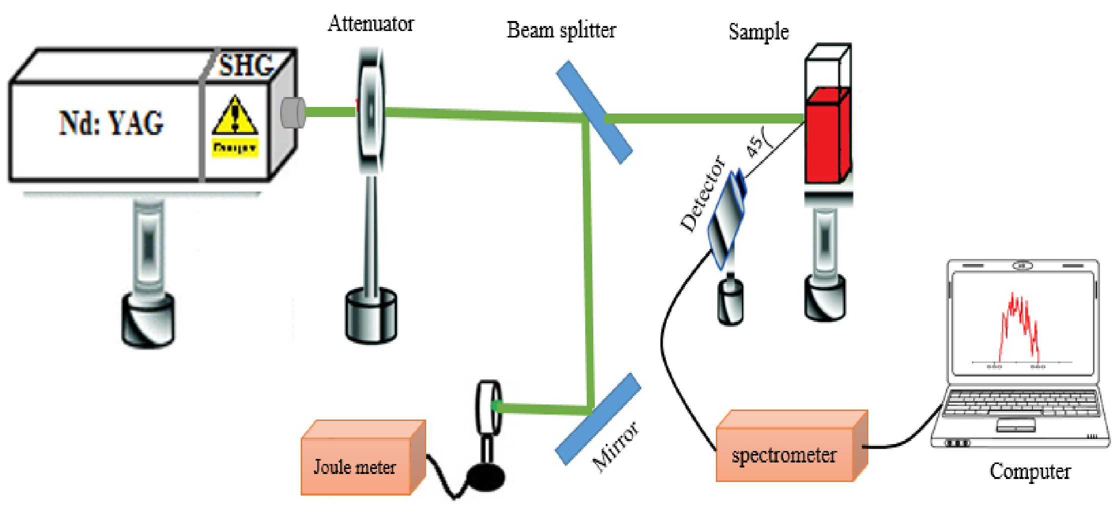

Fig. 2. Schematic of the experimental setup of testing the performance random laser

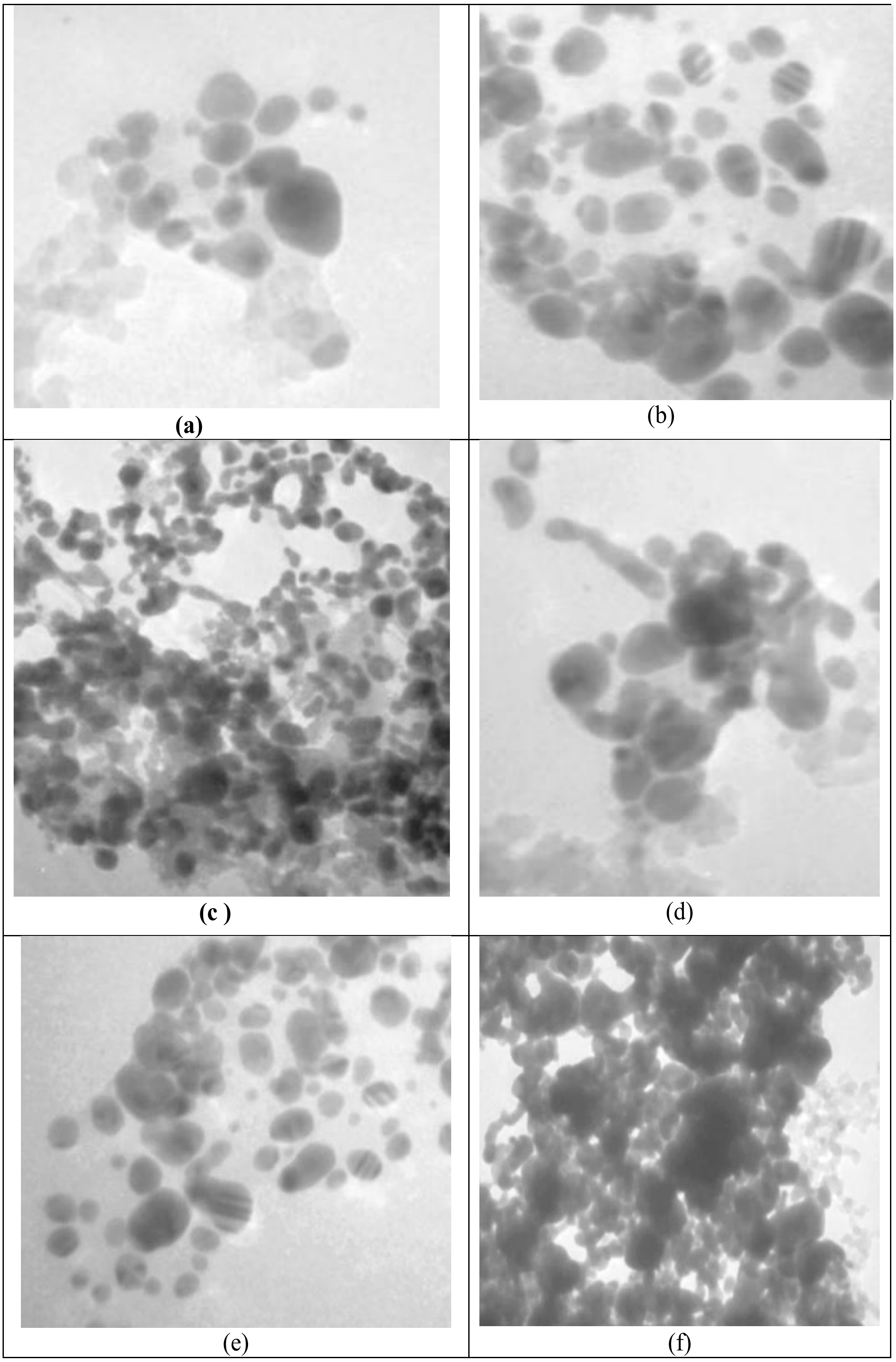

Fig. 3. TEM images of the colloidal solutions with different concentrations: (a-c) Al NPs (500, 700, and 900 P), (d-f) Mg NPs (500, 700, and 900 P) respectively

band extended towards the visible region. the absorption curve of Al NPs increased by increasing the number of laser pulses of nanoparticles in the solution as shown in Fig. 4a, the absorption spectrum of Al NPs of five concentrations, while observed the absorption carve with high concentrations (violet carve) more highest than low concentrations, Also, it is found that increasing the of Mg NPs concentrations gives rise to an increase in the absorption efficiency as shown in

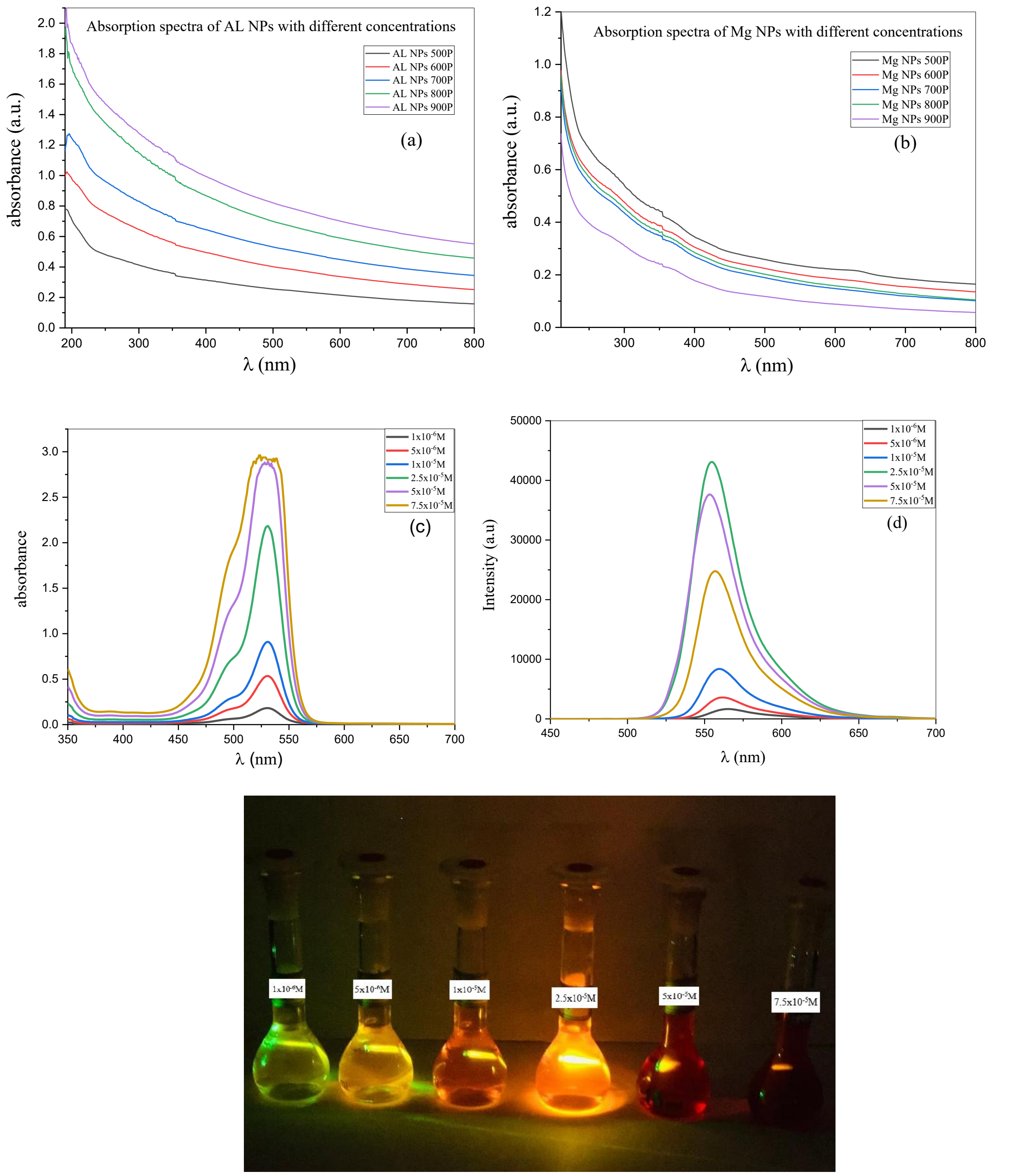

Fig. 4. The absorption spectrum of (a) Al NPs (b) Mg NPs, (c) Absorption spectra of Rh6G dissolved in ethanol with different concentration, (d) Fluorescence spectrum of Rh6G at different concentrations, e)Real image emission spectra due to different concentrations of dyes without nanoparticles.

Fig. 4b, and This behavior is obvious in the (black curve) is have highest absorption curve than from the lower concentrations.

The absorption spectra of Rh6G dye with different concentrations ($1x10^{-6}$, $5x10^{-6}$, $1*10^{-5}$, $2.5x10^{-5}$, $5x10^{-5}$, and $7.5x10^{-5}$ M) which dissolved in ethanol have been studied, as shown in Fig. 4c, and can be observed that with increasing the concentration of the dye in the ethanol solution, the absorption peak increase with its maximum peak at 530 nm. Therefore, the best absorption spectrum of Rh6G dye was obtained at concentrations $2.5x10^{-5}$ M at 530 nm. Thus, this concentration will be adopted for the remainder of our active random gain media after mixing with different semi plasmonic nanoparticles.

The fluorescence spectra for the different concentrations of Rh6G dye were illustrated in Fig. 4d using (Scinco fluorescence spectrometer), the intensity of the mission spectrum, increases with increasing dye concentration to a certain extent of focus afterwards behavior is reflected, a decrease in intensity fluorescence is observed with an increase in the concentration of the dye. The best emission spectrum appears in the concentrations $2.5x10^{-5}$ M for this reason this have been choose it as a suitable concentration for the active gain media based on the absorption spectrum.

We also tested the fluorescence of Rh6G dye at different concentrations under green laser source (532 nm), and that also confirmed to us the best concentration is $2.5x10^{-5}$M, as shown in the real fluorescence in the Fig. 4e.

Al NPs and Mg NPs absorb and scatter light with high efficiency due to a strong interaction of light with conduction electrons on the metal surface of the nanoparticle. When Al NPs and Mg NPs mixed with the best concentration of Rh6G dye ($2.5x10^{-5}$ M) and excited by the suitable wavelength, the same wavelength that it absorbed dye. Thus, these electrons are responsible for the collective oscillation on the surface to form the plasmonic phenomenon (SPR), and this phenomenon increases the absorption and scattering ratio inside active gain media, which leads to an increase in the emission spectrum when adding it to the active media with appropriate concentrations when the concentrations of nanoparticles are increased more than the appropriate limit, they affect to the fluorescence spectrum, causing quenching in the emission spectrum as shown in the Fig. 5. The best fluorescence spectrum in active random media appears with a concentration of Al NPs (800 P), and it has been seen in the violet carve in the Fig. 5a, and it has a peak intensity of the fluorescence spectrum at (35700 a.u.), also, observed the best concentration using Mg NPs was in the (800P) as shown in the red curve in the Fig. 5b, in this type of nanoparticle the peak intensity of the active medium was observed at (41650 a.u.). From this, we deduce the Mg NPs has more strong scatterers than Al NPs.

Random laser by Al NPs

The emission spectra of random active gain medium mixed with five concentrations of Al NPs and which it pumped by 532 nm have been investigated. As shown in the Fig. 6a the random laser properties observed with low concentration of Al NPs (500 P) mixed with Rh6G with (2.5x10-5 M), in this active random medium remarked the intensity enhanced gradually when the increased

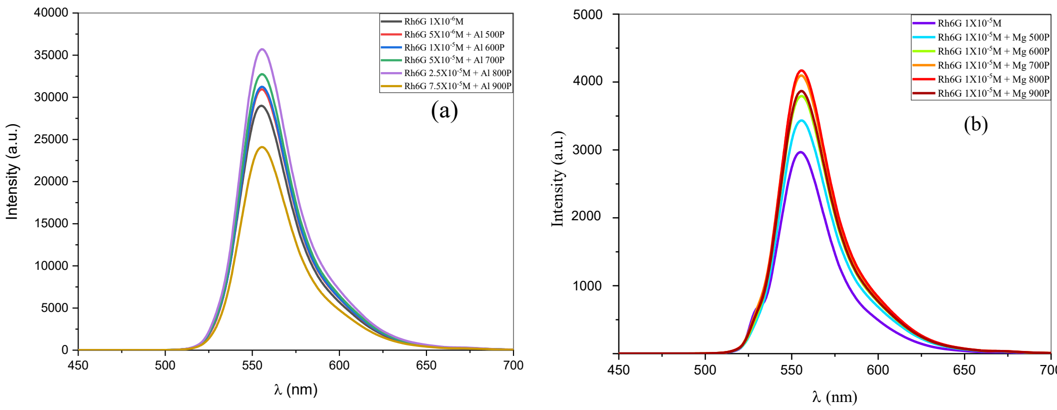

Fig. 5. Fluorescence spectrum of R6G mixed with different concentrations of nanoparticles, (a) Al NPs and (b) Mg NPs

energy pumping from (25 to 70 μJ), At the lowest pumping energy 25 μJ, It is noticed that there is no random laser appearing in this energy, when increased energy pumping on the active media, this lead to increases in the peak of intensity, and the FWHM decreases, this behavior refers to the emergence and incoherent random laser it was observed at a threshold equal 55 μJ, after enhanced energy pumping the peak intensity increased to reach (9600 a.u.) and FWHM (14

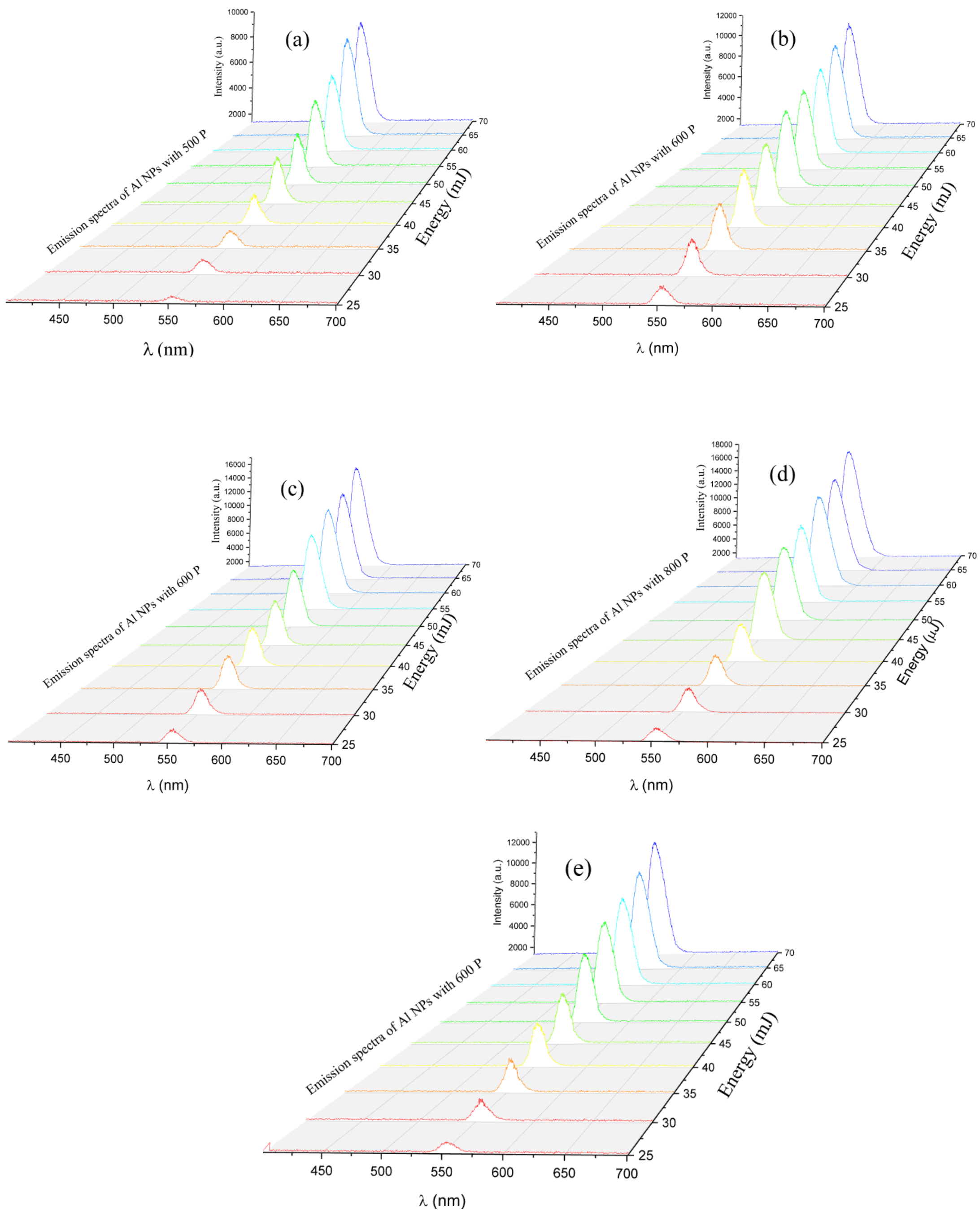

Fig. 6. The emission intensity of the five samples of Al NPs with concentrations 500P, 600P, 700P, 800P, and 900P as function of the pumping energy.

nm) and the number of spikes also increased in the emission spectrum with the width of these peaks can reach less than 1 nanometer, which is one of the most important indicators of the transition from incoherent random lasers to coherent random lasers. So the concentration of semi plasmonic nanoparticles within active media has a basic role enhance of emission spectrum, and it also clearly affects the transition from an incoherent to a coherent random laser.

After that, the 500 P of Al NPs will be replaced by the Al with 600P which as shown in Fig. 6b represents the random laser properties when increasing the concentration of Al NPs to 600P. the emission peak begins to narrower and its intensity rises more rapidly with increasing pumping energy, the lasing threshold is reduced to (50 μJ) in the new concentration, and the FWHM appears to be more narrow with the value of (13.1) with an increased number of spikes and has higher peak intensity than the previous concentration and its value is estimated (12700 a.u).

Now a third concentration of the gain medium will be generated by adding Al NPs 700P. As Fig. 6c exhibited that the properties of this random laser compared with previous concentrations have been enhanced. Therefore, increasing the concentration of Al NPs in the random medium will improve the properties of the random laser due to increase the scattering centers in this concentration, the

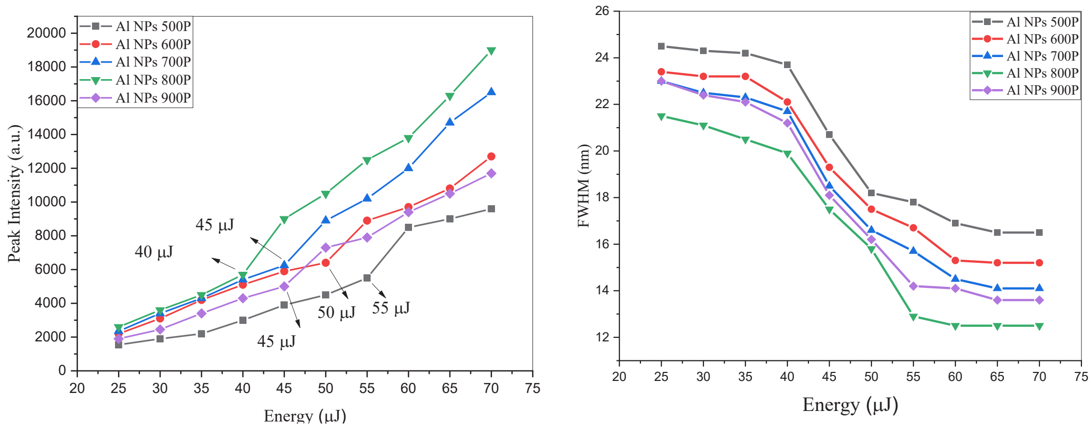

Fig. 7. (a) The peak intensity as function of pumping energy. (b) FWHM as function of pumping energy.

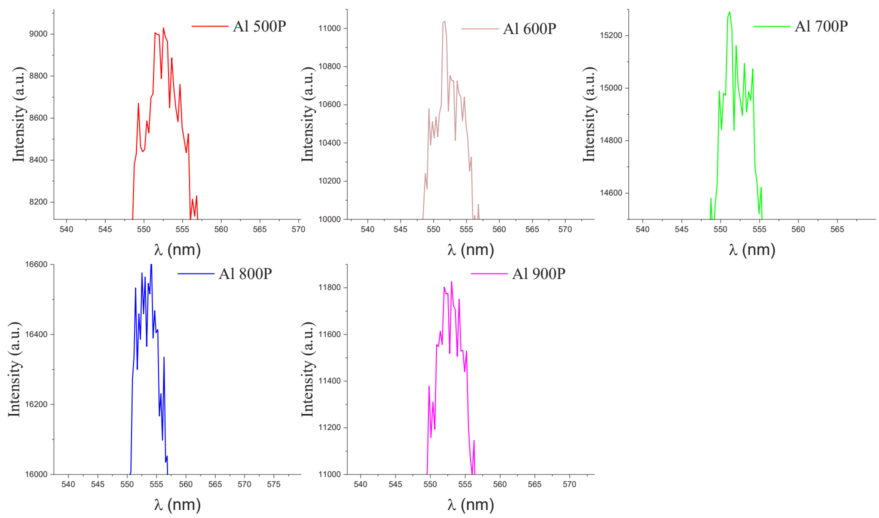

Fig. 8. The revolution of the spikes with different Al NPs concentrations

most important of which is the surface plasmon resonance. Where we notice a clear increase in the peak intensity reach (16500 a.u.), the lasing threshold at (45 μJ), and the value of FWHM about (12.9), also with an enhanced number of spikes at the top of the peak of the intensity.

We will continue to increase the concentration of the Al NPs 800P. It is observed from Fig. 6d that the peak intensity of the emission spectrum increase super linearly with increasing pumping energy to reach about (19000 a.u.), and the value of FWHM reaches (12.5)with more spikes in the peak of the intensity, as observed the best threshold in this concentration (40 μJ). The dramatic decrease in the lasing threshold in this concentration under test is due to the increased plasmonic scattering centers in the gain medium, which has the property of a surface plasmon that enables the material to be trapped photons near the surface, creating an improved gain area near the surface of the material and thus accelerates the occurrence of the random coherent laser. This result corresponds to the fluorescence spectrum, as shown in Fig. 5a.

The high concentrations of Al NPs 900P have a direct effect on the scattering mean free path as well as on lasing threshold, as observed the peak intensity was increased in the previous case but decreased in higher concentration. Thus, the more reduction of the scattering mean free path led to a lower lasing threshold. This leads to the confinement of the photon longer period inside the active medium due to the increase in the number of nanoparticles, and this increase does not allow the photon to transition to the dye which is considered the main source of the gain, thus leading to producing obstructs which don't allow to escaping the photons from the active medium easily. So the peak intensity in this case has value (11700 a.u.), and increase in the lasing threshold value reach to at (45 μJ) again, and the value of FWHM about (13 nm), this behavior can be seen in the Fig. 6e.

Fig. 7.a allows a comparison between the lasing thresholds for five different concentrations of Al NPs. The sample with Al NPs 800P shows a low pumping threshold of about 40 μJ, while the remainder of random laser systems has lasing thresholds is 55, 50, 45, and 40 μJ according to the ratio of the Al NPs concentrations in random media 500P, 600P, 700P, and 500P respectively. Where Fig. 7b shows that the (FWHM) narrows as the proportion of Al NPs concentrations increases except for the concentration of Al NPs 900P in the gain media. Moreover, when the pumping energy increases the width of the (FWHM) narrows until it reaches to settles.

In the Fig. 8, the effect of the concentration of Al NPs on the emergence of these spikes in addition to their number will be discussed. as it was observed that their emergence was related to the lasing threshold for the emitted spectrum of a random laser, when increased pumping energy is above the threshold, the gain is more than the loss in random cavities, and the photons in this case oscillate to add separate peaks to the emission spectrum, and the number of spikes with an increase in the width again in the emission spectrum reduces by increasing the concentrations of Al NPs to 900P despite the increase in the number of scattering centers.

For analysis, the parameters of mean free path can be calculate by Eq. 2 for each concentrations with the cell thickness of T, the transmitted intensity of the solvent (I_0) and the transmitted intensity of the solvent with Al NPs (I) should be investigated.

$$\text{Mean Free Path} = \frac{T}{\ln\frac{I_0}{I}} \tag{2}$$

then, it is observed that the mean free path for Al NPs with 800P concentration is smaller than that of lower concentrations NPs for this reason, It was obtained more gain in the emission spectra based on the suitable concentration of Al NPs with 800P

Table 1. Represents some of the random laser parameters

Sample	Peak intensity (a.u.)	FWHM (nm)	Threshold (μJ)	l_s (mm)
Al 500P	9600	16.5	55	0.79
Al 600P	12700	15.2	50	0.72
Al 700P	16500	14.4	45	0.66
Al 800P	19000	12.5	40	0.59
Al 900P	11700	13.6	45	0.68

was added to the dye, and this concentration has a direct effect on the scattering mean free path as well as on lasing threshold and peak intensity, In other words, we get the greatest gain in the active media when the value of the mean free path decreases. The peak intensity was low in the low and high concentration 900P. Thus, the increase in the scattering mean free path led to the high lasing threshold as shown in the Table 1.

Random laser by Mg NPs

As mentioned above, the scattering centers of these types of nanoparticles have high efficiency due to a strong interaction of light with conduction electrons on the surface of the nanoparticle. To investigate the effect change

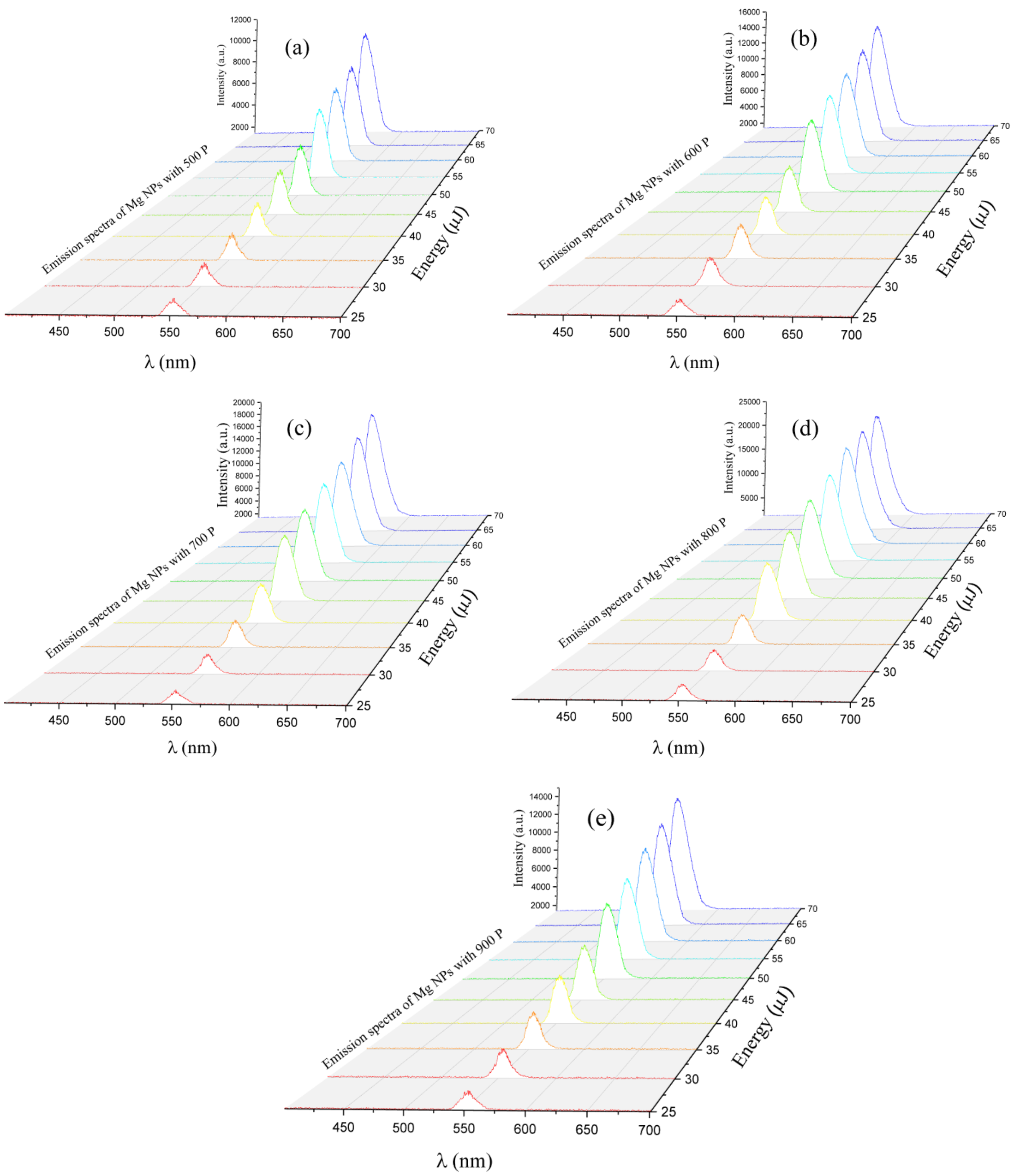

Fig. 9. The emission intensity of the five samples of MgNPs with concentrations 500P, 600P, 700P, 800P, and 900P as function of the pumping energy

in the Mg NPs concentration on random laser action, the emission spectra of five samples were measured as explained in the experimental setup in Fig. 2. Where it's recorded at different pumping energy, the measured results represented in Fig. 9 a-e are shown that the emission spectrum begins to increase gradually with increasing the Mg NPs concentration. The demeanor of the properties of random laser in relation to the first four concentrations of Mg NPs is a common behavior where the intensity increases and both the lasing threshold and FWHM decrease with increasing the concentration. But what is noticed, was a sudden change occurred when the Mg NPs concentration continued to increase to 900P, as the emission intensity decreased while the lasing threshold and FWHM increased and this can be attributed to the quenching of luminescence which occurs when the location of the metallic NPs become a very close to the dye molecules.

So, the intensity of the emission gradually increases from 10500, 13800, 17500, until it reaches to 215400 a.u. when the concentration of Ag NPs increases from 500, 600, 700 to 800P. But this increase in the emission intensity does not continue and a sudden drop occurs in it, so that it decreases to 13500 with Mg NPs 900P. The same goes for the lasing threshold, as it was

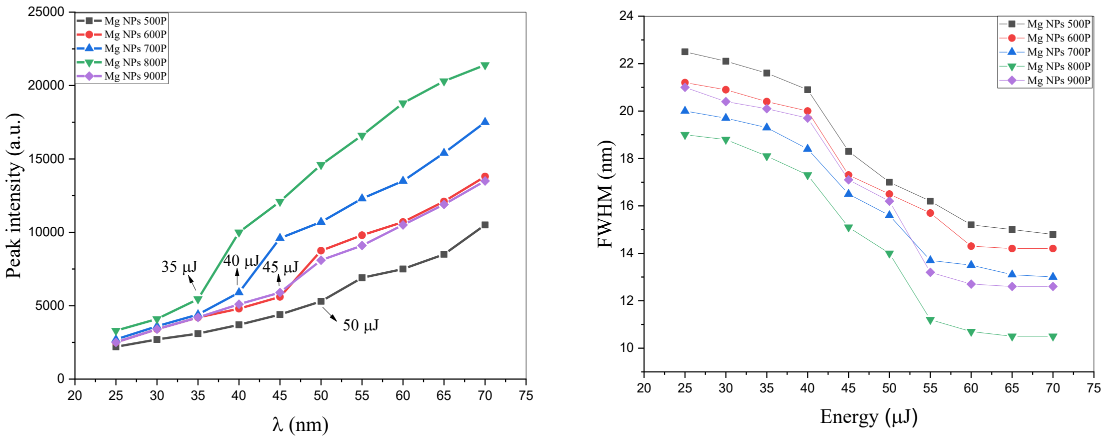

Fig. 10. (a) The peak intensity as function of pumping energy. (b) FWHM as function of pumping energy.

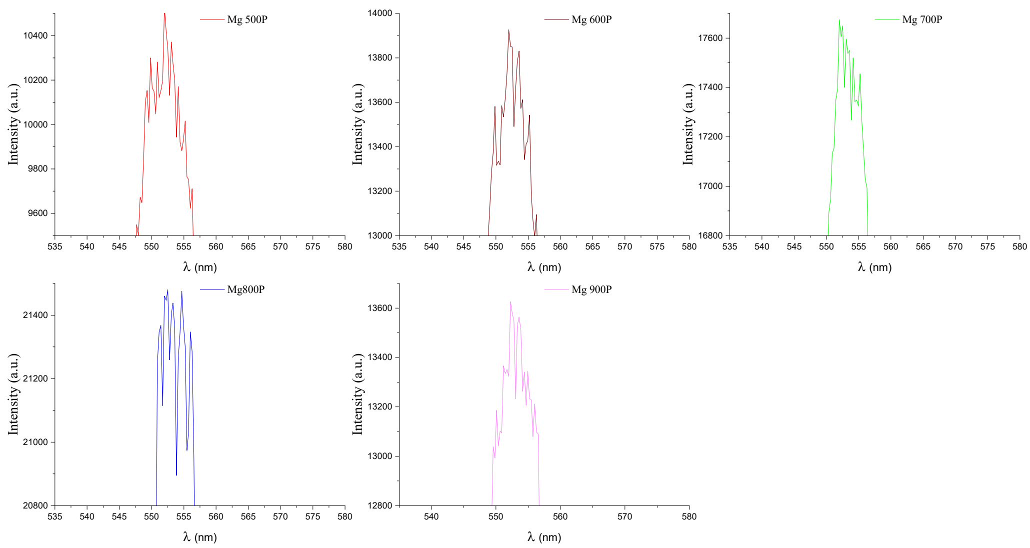

Fig. 11. The evolution of the spikes with different Al NPs concentrations

found that increasing the Mg NPs concentration leads to decrease in the lasing threshold from 50 to 35 μJ when the particle concentration increases from 500P to 800P. But at certain degree

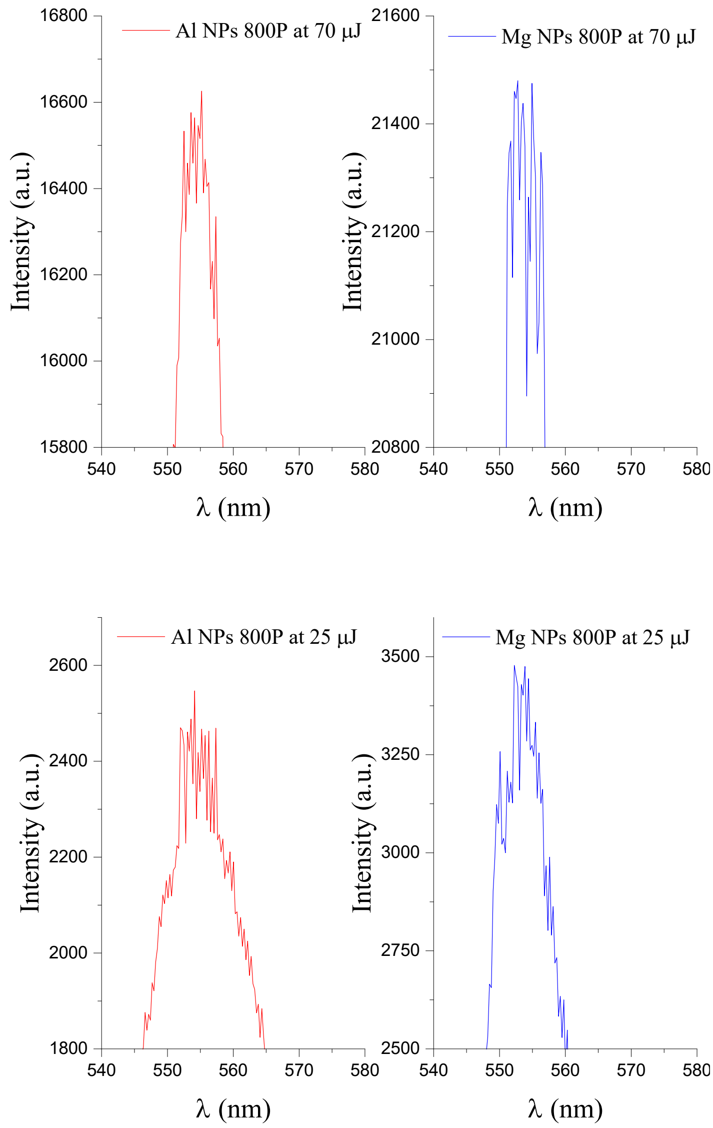

Fig. 12. The peak intensity and spikes with the effect of the type of the scattering centers for the low and high pumping energy.

Table 2. Represents some of the random laser parameters

Sample	Peak intensity (a.u.)	FWHM (nm)	Threshold (μJ)	l_s (mm)
Mg 500P	10500	14.8	50	0.71
Mg 600P	13800	14.2	45	0.63
Mg 700P	17500	13	40	0.58
Mg 800P	21400	10.5	35	0.53
Mg 900P	13500	12.6	40	0.65

of concentration, the lasing threshold begins to increase rapidly to reach 45 μJ with increasing the concentration to 900P as shown in Fig. 10a. As for the FWHM, Fig. 10b shows that the value of FWHM decreases from 14.8 to 10.5 nm when increasing Mg NPs concentration from 500 to 800P. After that, the FWHM value increases to reach 12.6 nm with increasing the concentration of the scattering particles to 900P.

The appearance of these spikes under the influence concentration of the semi plasmonic nanoparticles, they have been covered in some detail in the Al NPs, as it was observed that their emergence was related to the threshold of the random laser. As shown in Fig. 11 it has been found that these spikes grow clearly and their number increases with increasing the Mg NPs from 500 to 800P within the dye.

From Table 2 the value of the and FWHM will be reduced by increasing Mg NPs concentration since they are inversely proportional to their concentration, thus the higher the concentration, the lower their values.

CONCLUSION

In sum, the characteristics of the random laser can improve with increased semi plasmonic nanoparticles, but the increase in the semi plasmonic nanoparticles concentration within the dye 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 lower the quantum yield. The type of semi plasmonic nanoparticles selected as scattering centers in the random medium has a great effect on the properties of the random laser, as the experiment has shown that selecting these types of nanoparticles greatly improves the random laser performance compared to the dielectric materials. It is noticed the random laser with Mg NPs that shows better results than the Al NPs through the apparent increase in the intensity of the emission at the same pumping energy. Also, the pumping threshold of this type has materialized early compared to Al NPs, in addition, the appearance of spikes in this sample preceded the previous one.

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CONFLICT OF INTEREST

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

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