Dye-Doped Fe₃O₄ Nanoparticles for Magnetically Controlling Random Laser Parameters at Visible Wavelengths: Literature Review and Experiment

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ABSTRACTS

The development of light-controlled electronic devices requires new possibilities of optical control via tuning of laser input parameters. Here, Fe₃O₄ superparamagnetic nanoparticles (SNPs) were doped with dye, and the controllability of parameters of a random laser, including the wavelength, threshold energy, and intensity under the absence and presence of an external magnetic field was studied. The prepared dye laser (Rh-640) showed strong magnetic controllability and switch ability under different pumping energies (1‒7 mJ), as well as good responsivity and durability at visible wavelengths. The applied magnetic field was utilized to modify the distribution of Fe₃O₄ SNPs with different concentrations and scattering behavior, altering the generation of coherent loops and laser action properties. Thus, it was possible to employ the magnetically controllable random laser in a variety of technological applications, including biology and optical communications.

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1. INTRODUCTION

Despite the conventional lasers that require a rigid optical resonator, it is possible to fabricate random lasers based on the feedback of mirror-free scattering centers (Liao et al., 2017). Random lasers can be equipped with superior qualities that are difficult to be achieved using conventional lasers (Bachelard et al., 2014). By representing the light amplification via stimulated emission with the feedback provided by disordered scattering, random lasers have remained an attractive topic for many researchers in the field of laser physics. These lasers have unique intrinsic properties such as simple structure and large angular emission without the need for external cavities (Ejbarah et al., 2020). Therefore, great efforts have been devoted to realizing random lasers in different materials with a wide wavelength range from ultraviolet to mid-infrared and the terahertz frequency (Knitter et al., 2013). Nevertheless, the mechanism of controlling the direction of the random laser emission has remained the biggest challenge for researchers in this field. While simplicity and randomness present an obstacle to the control of random lasers (Bachelard et al., 2014; Kedia and Sinha 2017; Perumbilavil et al., 2018), several approaches have been proposed to overcome these constraints. In this regard, three characteristics of random lasers should be taken into consideration, involving the wavelength control, laser threshold, and intensity of the emitted laser beam (Rashidi et al., 2021).

The wavelength control is one of the most important advantages of a random laser. This is because of the possibility of controlling the wavelength of the random laser either through the so-called previous control, including the adjustment of the absorption state, or the appropriate selection of the size, type, and shape of the nanomaterial in addition to the shape and thickness of the cell. Alternatively, it has also been possible to control the random laser through the so-called post-control, being carried out by controlling external parameters such as the temperature, shed electric field, and optics (Ye et al., 2017). As for the random laser directionality, several techniques have been utilized to control this important characteristic using optical waveguides, low-dimensional cavities, and a specific structure for the random laser (Turitsyn et al., 2014; Schönhuber et al., 2016; Wetter and Jimenez-Villar 2019; Kumar et al., 2021).

Concerning the third characteristic, several strategies have been employed to control the laser threshold, including the use of an appropriate concentration of nanomaterial and dye mixtures, improving the size of the scattering centers and the mean free path, and tuning of the refractive index between the gain and scattering media (Meng et al., 2009; Cerdán et al., 2012; Lin and Hsiao 2014; Tommasi et al., 2016). The fourth characteristic (the intensity of the random laser emission) has also been investigated under the influence of many factors, including the optimization of the selection of the dye and the nanomaterial, the size, and type of the nanomaterial, the concentration of both the dye and the nanomaterial, the pumping power, and the type of source (Lau et al., 2005; Popov et al., 2006; Wiersma 2008; Chen et al., 2011; Yu 2015).

Amongst the nanomaterials, nanoparticles (NPs) with superparamagnetic behavior have become interesting because they can be easily controlled under an external magnetic field owing to their extremely low coercive field and high saturation magnetization (Chung and Fu 2011; Brojabasi et al., 2015; Jing et al., 2021). For example, magnetite (Fe₃O₄) superparamagnetic NPs (SNPs) have shown these features significantly (Bajpai and Gupta 2010; Koo et al., 2019). In fact, at room temperature, by exceeding the Brownian rotation time over the Néel relaxation time, Fe₃O₄ SNPs lose their magnetization.
following the removal of the magnetic field, revealing their superparamagnetic properties (Taylor et al., 1986; Nguyen et al., 2021). Nevertheless, these SNPs have not yet been doped with dyes to be employed in the control of random laser parameters.

In this paper, Fe₃O₄ SNPs are doped with dye (Rh-640), followed by their utilization in a random laser. Under the absence and presence of an external magnetic field, the three characteristics of the random laser (the wavelength, threshold, and intensity) are studied and discussed separately. This study gives insights into the magnetic controllability of the random laser parameters using dye-doped Fe₃O₄ SNPs.

2. LITERATURE REVIEW

Brojabasi et al., (2015) studied magneto-optical transmission in ferrofluids consisting of different Fe₃O₄ NP sizes. The average diameters of Fe₃O₄ NPs were reported to be 15, 30, and 46 nm, respectively. Initially, the external field was absent, observing only a bright circular spot on the screen. The external field was then applied to the ferrofluids. By increasing the intensity of the external field, a straight-line scattering pattern with spotty parts was seen as justified by the aggregation process. This process was induced by the external field.

It was also found that the intensity of the transmitted light was enhanced in the initial state, followed by reaching a maximum value. Beyond this value, the transmitted intensity was inversely reduced as a function of field intensity, reaching a minimum value. Interestingly, decreasing the average diameters of the NPs in the ferrofluids increased both the critical field intensities to higher values. The authors attributed the observed phenomena to the formation of particle chains and column structures in the aggregation process. In other words, at a constant concentration, ferrofluids with smaller sizes of NPs required stronger field intensities to form chains of particles.

Tsai et al., (2017) designed and fabricated magnetically controllable random lasers (MCLRs). Under a prescribed magnetic field (0, 1066, and 2008 Gauss), they used a random medium composed of stilbene 420 laser dye as a gain medium and a mixture of TiO₂ and Fe₃O₄ NPs as scatters. The wavelength excitation was a Q-switched Nd:YAG laser (266 nm, 3–5 ns pulse, 10 Hz). The Fe₃O₄ NPs possessed magnetic controllability due to their susceptibility with good responsivity and durability for the magnetic field.

The applied magnetic field was used to manipulate the distribution of Fe₃O₄ NPs, which in turn altered the formation of the coherent loops and the properties of laser action and provided strong optical confinement and feedback for laser action. At a zero magnetic field, the slope of spontaneous emission intensity was relatively small. With increasing the magnetic field, two thresholds were observed, reaching 12.4 and 25.4 mJ/cm², being above the value of the first threshold (12.1 mJ/cm²). The results showed that the lasing threshold initially decreased to a minimum value, and was then enhanced by increasing the magnetic field. On the other hand, beyond the first threshold value, the corresponding to a Full width at half maximum (FWHM) was significantly reduced from 11.2 to 5.7 nm, representing the occurrence of amplified spontaneous emission. By further increasing the magnetic field to the second threshold (25.4 mJ/cm²), the FWHM decreased to 0.3 nm, implying the appearance of laser action under the magnetic field effect. Thus, the lasing emission of the MCLRs can be switched on/off with great responsivity and durability by installing/removing the magnet.

Some researchers fabricated a magnetically tunable random laser (Dai et al., 2019). In this case, polymer-dispersed liquid crystal (PDLC) in the capillary was achieved by employing doping magnetic NPs at varied pump energies. They used 532 nm laser pulses (10 ns &10 Hz) focused on the samples.
with a cylindrical lens (f=20 cm). The external magnetic field was applied by a cylindrical magnet. The intensity of the magnetic field was tuned by varying the distance between the magnet and the capillary. Experimental results showed the lasing threshold was enhanced with increasing doping concentration (0, 0.01, 0.02, and 0.03 wt%) of the NPs. The respective thresholds were 9.5, 11.5, 12.3, and 18.5 μJ. As well, this effect was due to the larger absorption of NPs with a higher concentration. By increasing the applied external magnetic field, the blue shift of emission spectra was observed following an increase in the NP concentration. Furthermore, the blue shift was induced by the shorted resonator cavity, followed by a decrease in the mean free path (MFP) with an increasing concentration of NPs. Meanwhile, the dye molecules drifted away from the gain volume, resulting in a reduction in the dye concentration. Consequently, the gain length of the sample was enhanced. In addition, the decrease in the dye concentration was able to reduce self-absorption, thereby leading to the blue shift of the envelope center of the laser spectrum. Some researchers used the Fe$_3$O$_4$@SiO$_2$ core-shell NPs as scatters in Rhodamine B solutions (Ye et al., 2015). The average diameter of the NPs was 200 nm, whereas the thickness of the SiO$_2$ shell was 50 nm. The pump source employed was the second harmonic of an Nd:YAG laser (532 nm, 10 ns, 10 Hz). The first threshold was found to be at 100 μJ/pulse in the absence of a magnetic field. Additionally, well-separated sharp spikes with linewidth smaller than 0.2 nm appeared around 590 nm, indicating the occurrence of coherent random lasing. Nevertheless, threshold energy was reported to be 120 μJ/pulse in the presence of a magnetic field. It was because most of the NPs in the solution was effectively separated from the pump region under the application of the magnetic field. It was revealed that the Fe$_3$O$_4$@SiO$_2$ doped dye solution possessed a magnetically controllable feature. Also, the sharp spikes disappeared when the diameter of Fe$_3$O$_4$ NPs was relatively large (about 100 nm), whereas the laser peaks existed when the diameter of Fe$_3$O$_4$ was relatively small (about 12 nm). Accordingly, this kind of random laser had potential applications in the fabrication of magnetic sensors and integrated optical devices.

3. METHOD

3.1. Sample Preparation

The dye samples of the random laser were prepared as follows: The dye used in this experiment (Rh-640, a dark green crystal powder in appearance with a concentration of 5×10$^{-4}$ M, purchased from Sigma Aldrich) was dissolved in methanol to obtain the laser gain medium. Afterward, Fe$_3$O$_4$ SNPs (1.3×10$^{17}$ cm$^{-3}$ in density, purchased from VCN materials, Iran) were mixed with the dye solution. Two samples of the random medium were then prepared by doping 70% of Rh-640 dye with 30% of Fe$_3$O$_4$ SNPs (sample-1), and 50% of Rh-640 dye with 50% of Fe$_3$O$_4$ SNPs (sample-2). These samples consisting of the dye and SNPs were ultrasonically dispersed in methanol for 30 min before each experiment.

3.2. Experimental Setup and Characterization

The experimental setup used for magnetically controlling the random laser is schematically depicted in Figure 1. The random suspension media were placed in a quartz cuvette with a thickness of about 10 mm at the magnetic system center and kept inside a solenoid. The magnetic field was fixed at 125 G. A Q-switched frequency-doubled Nd:YAG laser (532 nm, 5 ns pulse width, 10 Hz pulse repetition rate) was oriented at 90° concerning the normal to the cuvette face. The dye laser emission from the front face of the cuvette was collected using a lens (f = 5 cm) oriented at 30° concerning the normal to a fiber-coupled spectrometer (Ocean Optics USB2000+UV-VS-ES with a spectral resolution of ~ 0.3 nm). The direction of the magnetic field was parallel to the light propagation.
4. RESULTS AND DISCUSSIONS
4.1. Morphology and Structure of Fe₃O₄ SNPs

Morphological and structural characteristics of the Fe₃O₄ SNPs are shown in Figure 2. From the field-emission scanning electron microscopy (FE-SEM) image in Figure 2(a), these SNPs are observed to have spherical-like morphology. According to the inset of Figure 2(a), the size distribution of the SNPs is found to range between 20 and 40 nm. Additionally, the mean size of the Fe₃O₄ SNPs is about 27 nm. The X-ray diffraction (XRD) pattern of the SNPs is depicted in Figure 2(b), indicating the reflections of (220), (311), (400), (422), (511), (440), and (622) planes at 2θ of 30.4, 35.6, 43.5, 53.9, 57.4, 63.0, and 75.0°, respectively (Maarouf et al., 2022). The crystal structure of the SNPs is then confirmed to be from magnetite (Fe₃O₄) without the presence of impurity or secondary peaks. Based on the Scherrer formula (Taylor et al., 1986), the average crystallite size along the main peak (i.e., (311)) is calculated to be about 22 nm, which is following the mean size observed using the FE-SEM analysis. The Fourier transform infrared (FTIR) spectrum of as-synthesized Fe₃O₄ SNPs is shown in Figure 2(c). The strong absorption band centered at 465 cm⁻¹ confirmed that the main phase of the SNPs was magnetite. The peak was attributed to the vibration and torsional modes of Fe-O bonds. It was reported that bulk Fe₃O₄ had the Fe-O absorption band at 570 cm⁻¹. Herein, this band was shifted toward a higher wavenumber since the localized electrons were rearranged on the SNP surface along with an enhanced surface bond force constant (Leong et al., 2016).

The presence of the broad peaks at approximately 1644 and 3446 cm⁻¹ was assigned to the bond stretching of O-H and bending vibrations of H₂O molecules, respectively. Due to the formation of Fe₃O₄ SNPs in the aqueous solution, bare and unreacted Fe and O atoms on the SNP surface may bind with OH⁻ and H⁺ respectively, thereby producing a hydroxyl group (-OH). In turn, the resultant hydroxyl group can lead to the surface functionalization of Fe₃O₄ SNPs, arising from its reaction with other positive moieties (Asmara and Kurniawan, 2018).
4.2. Absorption and Fluorescence Spectra

The absorption spectra of the samples were measured using a UV-Vis spectrophotometer in the wavelength range of 220–1100 nm. Figure 3 shows the absorption spectra studied for pure Rh-640 dye with a concentration of 5 mM, pure Fe$_3$O$_4$ SNPs with a density of $1.3 \times 10^{17}$ m$^{-3}$, and 50% Rh-640:50% Fe$_3$O$_4$ mixture. From these results, one can infer that the pure Rh-640 dye possessed a wide absorption spectrum (500–630 nm) with a maximum absorption peak at the wavelength of 540 nm. In the case of the pure Fe$_3$O$_4$ SNPs, one can observe that the maximum absorption occurred at the wavelength of 229 nm (Maryanti et al., 2021). Furthermore, the absorption decreased in the wavelength range between 229–800 nm. The spectrum of the dye-Fe$_3$O$_4$ SNP mixture was indicative of a reduction and a shift to higher energy (a blue shift), without overlapping with the pump laser wavelength of 532 nm, and the absorption and emission spectra of pure Rh-640 laser and Fe$_3$O$_4$ SNPs. In turn, this can lead to the formation of strong scattering centers for the dye-doped SNPs.

Figure 4 shows the comparison between spontaneous emission spectra of pure Rh-640 dye and Rh-640 dye-Fe$_3$O$_4$ SNP mixture under pumping energy of 7 mJ recorded using a spectrofluorometer (Shimadzu, RF-5301 PC, Japan). It is observed that the peak of the emission spectrum of pure Rh-640 dye was at the wavelength of 600 nm. The spectrum of the mixture broadened towards a longer wavelength (a red shift) with significant differences in amplitude and bandwidth.
4.3. The Effect of Magnetic Field and Concentration

The effect of the magnetic field on laser parameters of Rh-640 dye solution with two different concentrations of Fe₃O₄ SNPs was investigated, and the results obtained are shown in Figures 5 and 6. Figure 5 shows the evolution of emission spectra of sample-1, consisting of 70% Rh-640 (with a concentration 1×10⁻⁵ M), and 30% Fe₃O₄ SNPs (with a particle density of 2.87×10¹⁷ cm⁻³) at different pumping energies (ranging between 1‒7 mJ) in the absence and presence of a magnetic field (125 G). Moreover, the peak intensities and full width at half maximum (FWHM) values were extracted as a function of pumping energy.

As inferred from Figure 5(a), no reasonable change in the slope occurred due to the absence of the magnetic field and lower scattering of SNPs. Therefore, a noticeable threshold activity cannot be observed. However, by applying an external magnetic field, a significant change in the threshold energy was seen as it tended to be optimized to surpass the loss and consequently achieve the RL emission (Figure 5(b)). Meanwhile, FWHM values changed between 25.2–21.5 nm with increasing the pumping energy from 1 to 7 mJ in the absence of the magnetic field (Figure 5(c)). Under the applied magnetic field of 125 G, increasing pumping energy from 1 to 7 mJ decreased the FWHM from 17 to 15 nm (Figure 5(d)). Accordingly, the magnetic field and pumping energy influence both FWHM and peak intensities of the emission spectra, and threshold energy.
Figure 5. The emission spectra of 70% Rh-640 dye-30% Fe₃O₄ SNP mixture at different pump energies in (a) the absence and (b) the presence of a magnetic field (125 G). The variations of peak intensity and FWHM as a function of pumping energy in (c) the absence and (d) the presence of a magnetic field.

On the other hand, Figure 6 shows the emission spectra of sample-2, consisting of 50% Rh-640 dye and 50% Fe₃O₄ SNPs at different pump energies (1–7 mJ) in the absence and presence of the magnetic field. Increasing the concentration of scattering centers enhanced the random lasing behavior, followed by the increase in the peak intensity and the narrowing of bandwidth at 0 G and 125 G, respectively (Figure 6 (a) and (b)). These results indicate that the effects of pumping energy and magnetic field on the random laser parameter (including the emission spectrum intensity and FWHM) for sample-2 (Figure 6 (c)) at 0 G were very similar to that explained for sample-1. With the improvement of some parameters, the threshold energy was reduced to 1.89 mJ (Figure 6 (d)) whereas it was 2 mJ for the sample at 125 G.

For better clarity, increasing the concentration of scattering centers initiated an improvement in the random lasing behavior, leading to increases in the peak intensity, narrowing of bandwidth, and a decrease in the threshold energy. The higher concentration necessarily leads to a reduction in the scattering mean free path \( l_s \), which can be calculated using the following relation: \( l_s = 1/(\rho \sigma) \) (Kamil et al., 2020), where \( \rho \) is the particle density and \( \sigma \) is the scattering cross-section. In this way, the \( l_s \) of the dye-doped Fe₃O₄ SNPs was calculated to be 14.1 mm for sample-1 and 10.4 mm for sample-2. Essentially, two scattering regimes can exist based on the magnitude of \( l_s \): the weakly scattering regime \( (l_s \geq L) \) and the diffusive regime \( (L > l_s > \lambda) \), in which \( L \) is the sample size (10 mm) and \( \lambda \) is the emission wavelength (600 nm).
Therefore, \( I_s \) values obtained in this study are indicative of dye-doped \( \text{Fe}_3\text{O}_4 \) SNPs with weak scattering behavior. It should be noted that another factor affecting the value of \( I_s \) is the magnetic field, according to the literature (Shima et al., 2009). Tables 1 and 2 show improvements in the value of random laser parameters by changing the magnetic field from 0 to 125 G for the two samples, thereby indicating enhancements in the amplification of the random laser.

![Figure 6](image)

**Figure 6.** The emission spectra of 50% Rh-640 dye-50% \( \text{Fe}_3\text{O}_4 \) SNP mixture at different pump energies in (a) the absence and (b) the presence of a magnetic field (125 G). The variations of peak intensity and FWHM as a function of pumping energy in (c) the absence and (d) the presence of a magnetic field.

**Table 1.** Random laser parameters by changing the magnetic field from 0 to 125G (Sample1).

<table>
<thead>
<tr>
<th>Magnetic field (Gauss)</th>
<th>Threshold pumping energy ( P_{\text{th}} ) (mJ)</th>
<th>FWHM(_{\text{below}}) (nm)</th>
<th>FWHM(_{\text{above}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.1</td>
<td>25</td>
<td>21.5</td>
</tr>
<tr>
<td>125</td>
<td>2</td>
<td>17.5</td>
<td>15</td>
</tr>
</tbody>
</table>

**Table 2.** Random laser parameters by changing the magnetic field from 0 to 125G (Sample2).

<table>
<thead>
<tr>
<th>Magnetic field (Gauss)</th>
<th>Threshold pumping energy ( P_{\text{mb}} ) (mJ)</th>
<th>FWHM(_{\text{below}}) (nm)</th>
<th>FWHM(_{\text{above}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.8</td>
<td>25</td>
<td>22.5</td>
</tr>
<tr>
<td>125</td>
<td>1.89</td>
<td>19.1</td>
<td>15</td>
</tr>
</tbody>
</table>
4.4. The Effect of Response Time on The Emission Wavelength

Generally, the wavelength emission spectra of dye lasers are affected by the concentrations of the scattering centers (NPs), leading to shifts that might be in the direction of red or blue shifts, and a jump from blue to red shifts depending on the NP and dye concentrations (being high, low, or moderate), respectively (Zhang et al., 2017). Figure 7 shows the investigation of the effect of the response time (0‒30 s) on the emission wavelength in the presence of the applied magnetic field (125 G). Red shifts (about 6 nm) took place with increasing the response time from 0 to 25 s. Furthermore, a jump to the blue shift was observed with the increase in the response time from 25 to 30 s. This wavelength shift was supposed to be caused by Fe₃O₄ SNPs that can form chains and change their concentration along the direction of the external magnetic field with increasing response time.

4.5. Transition from Incoherent to Coherent Random Laser

In random laser systems, it is possible to transit from incoherent to coherent modes. This is mainly indicated when spikes appear and their number increases in the corresponding emission spectrum. According to Figures 5, 6, 7, and 8(a), one can notice the effect of the magnetic field, pumping energy, and the concentration of the dye-doped SNPs on the appearance of the spikes and the increase in their numbers to more than 10 spikes with an FWHM of approximately 1 nm. Alternatively, Figure 8(b) shows the following three regions: Region (I), representing the amplified spontaneous emission; and Regions (II) and (III), indicating the change in the intensity of emission spectra and FWHM. The change in Region (II) may represent a transition from the amplified spontaneous emission to the incoherent random laser. Moreover, the occurrence of the super linear change of Region (III) could arise from a transition from incoherent to coherent random laser modes.

Figure 7. The tuning of wavelength by varying the response time of the magnetic field at constant pumping energy (6mJ/pulse).
Figure 8. (a) The emission spectra and (b) variations of peak intensity and FWHM as a function of pumping energy in the presence of a constant external magnetic field of 125 G.

5. CONCLUSION

The effect of a relatively weak magnetic field (125 G) on the emission spectra of Rh-640 dye solution containing spherical-like Fe₃O₄ SNPs with an average size of 27 nm was investigated at room temperature. The controllability of the random laser parameters in the presence of the magnetic field was evaluated and confirmed up to acceptable values. Sharp spikes were observed in the emission spectra, resulting from the presence of the applied magnetic field and numerous scattering centers formed by SNPs in the excited region. It was also found that the emission strength increased with increasing the density of the scattering centers. A linear function was established between the spectral shift and the response time (0‒30 s) of the magnetic field, allowing for a transition from the amplified spontaneous emission to incoherent random laser as well as from incoherent to coherent random laser modes.

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7. AUTHORS’ NOTE

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. The authors confirmed that the data and the paper are free of plagiarism.

8. REFERENCES


