Fluorescence Characteristics of Random Gain Media Fabricated from Coumarin Dye and ZnO Nanoparticles Hosted in PDMS Polymer

Bahaa C. Khallaf

Department of Physics, College of Science, Koya University, Kurdistan, IRAQ

Abstract

In this work, the addition of different concentrations of ZnO nanoparticles (0.1 mg, 0.5 mg, and 1 mg) to the Coumarin laser dye (10^{-5} M) hosted by PDMS polymer forming random gain media was studied throughout its effect on the fluorescence characteristics of such media. An optimum range of ZnO nanoparticles concentration was determined as the maximum fluorescence intensity was produced. Such optimum value may determine the maximum scattering mean free path, which is required to achieve the maximum amplification by the multiple scattering that represents the base for this type of lasers.

Keywords: Random gain media; Coumarin dye; Zinc oxide nanoparticles; Fluorescence characteristics

Received: 19 June 2025; **Revised:** 24 July 2025; **Accepted:** 31 July 2025; **Published:** 1 October 2025

1. Introduction

Random lasers represent a unique class of light sources that have attracted considerable attention in recent years due to their unconventional feedback mechanisms, structural simplicity, and wide-ranging potential applications in photonics, sensing, imaging, and display technologies [1-3]. Unlike conventional lasers that require well-defined optical cavities with mirrors to provide feedback, random lasers rely on multiple scattering events within a disordered medium to achieve light amplification, which makes them simpler to fabricate and more versatile in terms of material design [4-6]. One of the key advantages of random lasers is their low fabrication cost, as they do not require complex resonator geometries, and their emission properties can be easily tuned by modifying the composition or morphology of the gain medium. In this context, organic dyes such as Coumarin derivatives have emerged as excellent candidates for random gain media because of their high fluorescence quantum yield, strong absorption in the ultraviolet region, and efficient emission in the visible spectrum [7-9]. Coumarin dye, in particular, offers excellent photostability compared to other organic dyes, a broad gain bandwidth, and the ability to be easily dissolved or embedded in various host matrices, making it highly suitable for random lasing applications. However, organic dyes alone often suffer from issues such as aggregation and concentration quenching at higher loadings, which limit their efficiency and stability; therefore, incorporating nanoparticles into the gain medium provides a means of enhancing scattering, improving light confinement, and in some cases contributing to energy transfer mechanisms that further enhance the lasing efficiency [10-12].

Among different nanoparticles, zinc oxide (ZnO) nanostructures are particularly advantageous because of their wide direct bandgap (3.37 eV), large exciton binding energy, and strong ultraviolet emission, which not only make them efficient scatterers but also active gain materials themselves [13,14]. ZnO nanoparticles can serve as both scattering centers to provide the required feedback and as active components to improve the photonic density of states, thus enhancing the emission intensity and lowering the lasing threshold [15]. Furthermore, ZnO is chemically stable, non-toxic, and can be synthesized through low-cost, scalable methods, making it a practical choice for hybrid dye-nanoparticle random lasers [16].

The choice of host material also plays a critical role in determining the performance and stability of random lasers, and polydimethylsiloxane (PDMS) has emerged as an excellent host matrix for embedding both dyes and nanoparticles [17,18]. PDMS is a flexible, optically transparent, chemically inert, and biocompatible polymer with high optical transmittance in the visible region, which allows efficient light propagation and emission collection. Its elastomeric nature enables the fabrication of flexible and mechanically robust random laser devices, while its compatibility with soft lithography techniques makes it possible to design microstructured or patterned random laser architectures [19,20]. Moreover, PDMS prevents aggregation of dye molecules and nanoparticles by providing a uniform dispersion medium, thereby reducing quenching effects and improving the photostability of the hybrid system. The hydrophobic and inert surface of PDMS also minimizes interactions that can lead to photodegradation of Coumarin dye, prolonging the operational lifetime of the random laser. The combination of Coumarin dye, ZnO nanoparticles, and PDMS therefore offers a synergistic approach to designing efficient, stable, and tunable random lasers: the dye provides the optical gain, the nanoparticles enhance scattering and potentially contribute to lasing action, and the PDMS host ensures stability, uniformity, and mechanical flexibility. Such hybrid systems can find use in low-cost coherent light sources, optical sensors for environmental and biomedical applications, lab-on-chip devices, and flexible photonic platforms, underlining their importance in advancing both fundamental photonics research and practical optoelectronic technologies [21-27].

In this work, the effect of ZnO nanoparticles concentration in Coumarin dye dissolved in PDMS polymer on the fluorescence characteristics of these random gain media was studied.

2. Experimental Work

Figure (1) shows the FE-SEM image of the ZnO nanoparticles used in this work to fabricate random gain media. This image provides a high-magnification view (120,000x) of ZnO nanoparticles, showcasing their morphology, size distribution, and tendency toward aggregation. The image reveals a typical nanostructure for synthesized powders, consisting of non-uniform, irregularly shaped primary particles that are tightly clustered, indicating a significant degree of agglomeration. The agglomerates form a porous network rather than a densely packed structure. Several measurements are overlaid, ranging from approximately 5.43 nm to 18.49 nm, which highlights the polydisperse nature of the particle size. However, these measurements appear to be taken across small clusters or large individual particles, suggesting that the fundamental particle size is likely in the low single-digit to mid-nanometer range, consistent with the dense appearance of the background material.

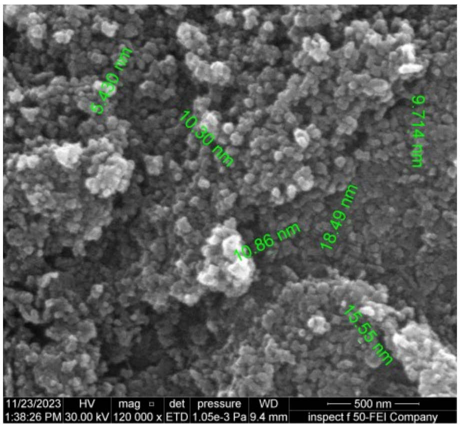

Fig. (1) FE-SEM image of ZnO NPs used in this work

Fabricating random gain media by adding ZnO NPs to a Coumarin dye solution in a PDMS polymer involves a multi-step experimental procedure. The primary goal is to create a well-dispersed, homogeneous composite material that can exhibit amplified spontaneous emission. First, a stock solution of Coumarin dye (1×10^{-5} M) is prepared by dissolving the dye powder in a suitable solvent. Separately, the ZnO NPs are weighed with high precision to achieve the desired concentrations (0.1 mg, 0.5 mg, and 1 mg). These nanoparticles are then dispersed in a small volume of a solvent (often an alcohol like ethanol or isopropanol) and subjected to ultrasonication for 60 minutes. This crucial step breaks up agglomerates and ensures a uniform dispersion of the nanoparticles, which is vital for preventing light scattering and maintaining optical quality. The dispersed ZnO NPs solution is then slowly added to the Coumarin dye solution. This mixture is then added to a pre-polymer of PDMS (Polydimethylsiloxane). The entire mixture is thoroughly stirred, often with a magnetic stirrer, to ensure the dye and nanoparticles are uniformly distributed throughout the viscous PDMS pre-polymer. A curing agent, typically a cross-linker, is added to the PDMS mixture at a specific ratio of 1:10. The mixture is then degassed, often in a vacuum chamber, to remove any air bubbles introduced during the mixing process. This is a critical step to ensure a bubble-free, optically transparent final product. The liquid mixture is then poured into a circular mold and left to cure. The curing process solidifies the PDMS, trapping the Coumarin dye and the ZnO NPs within a solid matrix. Figure (2) shows the fabricated samples.

Once the PDMS has fully cured and cooled, the solid random gain medium is removed from the mold. The final product is a transparent or semi-transparent solid film or block. The material is then characterized using various spectroscopic techniques. Fluorescence spectroscopy is used to measure the fluorescence intensity and emission spectrum using an F96 fluorospectrophotometer.

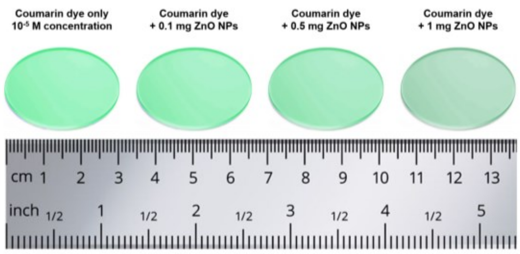

Fig. (2) Samples fabricated in this work

3. Results and Discussion

Figure (3) explains the effect of ZnO nanoparticles on the fluorescence of Coumarin dye hosted in a PDMS polymer as a classic example of concentration-dependent optical properties, where a low concentration of nanoparticles enhances fluorescence while a higher concentration causes quenching. It's clear from the plot that adding ZnO nanoparticles to the Coumarin dye solution has a quenching effect on the fluorescence intensity. This phenomenon is most pronounced at the highest ZnO NP concentration (1 mg), where the fluorescence intensity is at its lowest. Conversely, the fluorescence intensity is highest for the pristine Coumarin dye solution, with a progressive decrease as the ZnO NP concentration increases from 0.1 mg to 1 mg. This quenching effect is likely due to non-radiative recombination pathways introduced by the ZnO nanoparticles.

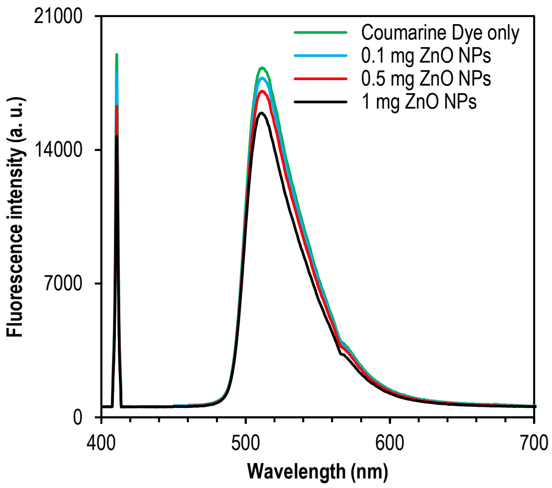

Fig. (3) Variation of fluorescence intensity with the concentration of ZnO NPs in Coumarin dye dissolved in PDMS host (excitation wavelength is 410nm)

The ZnO NPs may act as defects or energy transfer sites that provide alternative decay channels for the excited state of the Coumarin dye molecules, reducing the efficiency of the radiative emission process. The data suggests an inverse relationship between the concentration of ZnO nanoparticles and the fluorescence intensity of the Coumarin dye, demonstrating that for a Coumarin dye-based random gain medium, a lower concentration of ZnO NPs is preferable to maintain strong fluorescence characteristics.

4. Conclusions

In conclusion, adding ZnO NPs to Coumarin dye hosted by PDMS polymer results in an increase in fluorescence intensity as a consequence of increasing scattering rate and hence amplification of the emitted signal. However, further increase of nanoparticles may lead to a decrease in the fluorescence intensity due to the saturation effects accompanying such increase as a result of decreasing the scattering mean free path to the limit preventing the light signal from getting the required amplification.

References

[1] A.S.L. Gomes, "Nanocomposite-based random lasers: A review on basics and applications", in **Nanophotonics, Nanocomposites for Photonic and Electronic Applications**, Elsevier (2020) 45-79.

[2] A. Stassinopoulos et al., "Random lasing from surface modified films of zinc oxide nanoparticles", *Appl. Surf. Sci.*, 247(1-4) (2005) 18-24.

[3] A.A. Mahmood, H.M. Mikhlif and O.A. Hammadi, "Fluorescence Characteristics of Highly-Pure Nanoparticles Embedded in Dye Complexes for Random Laser Design", *Iraqi J. Appl. Phys.*, 18(2) (2022) 27-32.

[4] A.G. Ardakani and P. Rafieipour, "Random lasing emission from WO_3 particles dispersed in Rhodamine 6G solution", *Physica B: Cond. Matter*, 546 (2018) 49-53.

[5] A.A. Moahmmed Ali and M.A. Hameed, "Fabrication of Solid Random Gain Media in Visible Region from Rhodamine Dye Solutions Containing Highly-Pure Titanium Dioxide Nanoparticles", *Iraqi J. Appl. Phys.*, 18(1) (2022) 3-8

[6] B.K. Nasser and M.A. Hameed, "Narrow Emission Linewidth of Highly-Pure Silicon Nitride Nanoparticles in Different Dye Solutions as Random Gain Media", *Nonl. Opt. Quantum. Opt.*, 53(1-2) (2019) 99-105.

[7] C. Bouvy et al., "Quantum Size Effect and very localized random laser in ZnO@mesoporous silica nanocomposite following a two-photon absorption process", *J. Non-Cryst. Solids*, 355(18-21) (2009) 1152-1156.

[8] C.B. de Araújo, L.R.P. Kassab and D.M. da Silva, "Optical properties of glasses and glass-ceramics for optical amplifiers, photovoltaic devices, color displays, optical limiters, and Random Lasers", *Opt. Mater.*, 131 (2022) 112648.

[9] C.C. Alves et al., "One axis guided random laser emission from a glass capillary composite", *J. Lumin.*, 211 (2019) 426-430.

[10] H.G. Fahad and O.A. Hammadi, "Characterization of Highly-Pure Silicon Dioxide Nanoparticles as Scattering Centers for Random Gain Media", *Iraqi J. Appl. Phys.*, 16(2) (2020) 37-42.

[11] A.A. Mahmood, O.A. Hammadi, K.R. Ibraheem, "Preparation and Photoluminescence Spectra of Organometallic Complexes Containing Nanoparticles as Random Gain Media", *Indonesian J. Chem.*, 22(1) (2022) 205-211.

[12] K. Meesombad et al., "Zn-doped TiO_2 nanoparticles for glutamate sensors", *Ceram. Int.*, 47 (2021) 21099-21107.

[13] L. Li, "Random lasers tuning by combining a dye-doped liquid crystal and CdS nanoparticles", *Optik*, 134 (2017) 1-8.

[14] M.A. Hameed, "Effects of Solvent Properties on Absorption and Fluorescence Characteristics of Two Organic Dyes Used as Random Gain Media", *Iraqi J. Appl. Phys.*, 17(2) (2021) 15-18.

[15] M.R. Hashem and M.A. Hameed, "High-purity narrow emission line display of titanium dioxide nanoparticles in laser dyes as random gains", *Optik*, 260 (2022) 169058.

[16] M.R. Hashem and M.A. Hameed, "Fluorescence Characteristics of Coated-Cell Dye Solutions Containing Highly-Pure Nanoparticles as Random Gain Media", *Iraqi J. Appl. Phys.*, 18(1) (2022) 35-38

[17] Q. Li, K.M Ho and C.M Soukoulis, "Mode distribution in coherently amplifying random media", *Physica B: Cond. Matter*, 296(1-3) (2001) 78-84.

[18] R.C. Polson and Z.V. Vardeny, "Spectral analysis of near threshold random lasers", *Synth. Metals*, 162(3-4) (2012) 276-280.

[19] S. Shrestha, B. Wang and P. Dutta, “Nanoparticle processing: Understanding and controlling aggregation”, *Adv. Colloid Interface Sci.*, 279 (2020) 102162.
[20] S.F. Haddawi, H.R. Humud and S.M. Hamidi, “Signature of plasmonic nanoparticles in multi-wavelength low power random lasing”, *Opt. Laser Technol.*, 121 (2020) 105770.
[21] S.J. Musevi et al., “Offer a novel method for size appraise of NiO nanoparticles by PL analysis: Synthesis by sonochemical method”, *J. Saudi Chem. Soc.*, 20 (2016) 245-252.
[22] T. Okamoto, K. Imamura and K. Kajisa, “Inverse design of two-dimensional disordered structures for spectral optimization of random lasers”, *Opt. Commun.*, 508 (2022) 127775.
[23] Y. Dong et al., “Influence of particle size on the magneto-refractive effect in PbS quantum dots-doped liquid core fiber”, *Opt. Mater. Exp.*, 12(5) (2022) 1883-1849.
[24] Y. Li and L. Li, “A coherence random lasing for gain media based on lnP/ZnS quantum dots”, *Opt. Commun.*, 517 (2022) 128350.
[25] Y. Wan, “Coherent random lasing behavior in low-dimensional active weakly scattering random systems”, *Optik*, 127(22) (2016) 10919-10925.
[26] R. Carminati and J.C. Schotland, “Principles of Scattering and Transport of Light”, Cambridge University Press (2021), 125, 132-133, 207-208, 261, 354.
[27] J.K. Schindler, “The Electromagnetic Scattering of Broad Bandwidth Random Signals by a Discrete Target”, Office of Aerospace Research (MA, 1968), 13.

