

Study the Impact of Silica Nanoparticles on the Properties of Several Dyes for the Fabrication of a Random Laser Gain Medium

Noor Y. Khudair*, Mohammed K. Dhahir

Institute of Laser for Postgraduate Studies, University of Baghdad, Baghdad, Iraq * Email address of the Corresponding Author: <u>Noor.Yasir2101m@ilps.uobaghdad.edu.iq</u>

Article history: Received 16 Mar 2023; Revised 25 Aug 2023; Accepted 4 Sep 2023; Published online 15 Dec 2023

Abstract: Random laser gain media is synthesized with different types of dye at the same concentration $(1 \times 10^{-3} \text{ M})$ as an active material and silicon dioxide NPs (silica SiO₂) as scatter centers through the Sol-Gel technique. The prepared samples are tested with UV–Vis spectroscopy, Fluorescence Spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), and Energy Dispersive X-ray Diffraction (EDX). The end result demonstrates that doped dyes with silica nanoparticles at a concentration of 0.0016 mol/ml have lower absorbance and higher fluorescence spectra than pure dyes. FESEM scans revealed that the morphology of nanocrystalline silica is clusters of nano-sized spherical particles in the range (25-67) nm. It is concluded that the various dyes with SiO₂ as a scattering center can be proposed to build laser media.

Keywords: Random lasers, sol-gel, silica (SiO₂), dyes, nanoparticles.

1. Introduction

Since the introduction of the first laser in 1960, the manufacturing of high-efficiency laser systems has been one of the most fundamental difficulties in laser physics [1–2]. Lawandy et al. demonstrated in the early 1990s a stimulated emission from laser dye containing microparticles, hence the phrase "random laser" [3], which led to several theoretical [4–5] and experimental [6–7] studies on the amplification of light in diffusive media.

The mechanisms of random lasers (RLs) are based on multiple light scattering. In random lasers, as opposed to two highly reflecting mirrors in conventional lasers, the resonant cavity is constructed by repeated multiple scattering. In an active medium with a disordered distribution of scattering particles or domains, fluorescence photons may be multi-scattered thousands of times in random directions before leaving the medium. When scattering photons propagate via a narrow circuit, recurrent multiple scattering may either produce incoherent or coherent feedback [8]. RL has several advantages such as small size, low cost, flexible shape, and many others; It has several applications in integrated optics [9], temperature



64

sensing [10], document encoding, material labeling, high-density optical data storage [11], tumor diagnostics [12-13], liquid crystal display [14], and liquid flow monitoring [15]. Many random laser mediums have been widely demonstrated, including ZnO powders [16-17], Rare-earth ion-doped crystalline powders [18-19], conjugated polymers [20-21], dye-doped liquid crystals [22-23], dye-doped polymer films enhanced by silver or gold nanoparticles [24-25], a few biological issues doped with laser dye [26-27], and organic dye solutions doped with dielectric scatters [3–28].

Laser dyes are one of the organic luminescent materials with high molecular weight that can be used as an active medium because they are composed of carbon atom chains connected alternately by a single and double band called chromfore [29], while many tiny particles such as TiO_2 particles, zinc oxide (ZnO) [30], silica (SiO₂), tungsten oxide (WO₃), alumina (Al₂O₃) [31], and others can be used as scatter.

The goal of this work is to create random laser gain media by doping silica nanoparticles (SiO₂) with different types of dye (Rhodamine B, Rhodamine 101, Crystal Violet, and Fluorescein) at the same concentrations $(1 \times 10^{-3} \text{ M})$ in the Sol-Gel method and studying its characterization features.

2. Experimental work

The fabrication of random laser gain media through the sol-gel technique includes mixing 3 ml of ethanol as a solvent (purity 99.9%), 3 ml of tetraethylorthosilicate (Glentham Life Sciences Ltd., 99% purity) as a precursor material, 3 ml of deionized water (pH = 1 by adding 0.15 ml of HCl as a catalyst), and 0.6 ml (0.0001g dissolved in ethanol) from Rhodamine 610 and Rhodamine 640 dyes (supplied by Lambda Physik), Crystal Violet dye (supplied by Avonchem Limited) and Fluorescein dye (supplied by Sinopharm Chemical Reagent) to make all the prepared samples at a concentration of $(1 \times 10^{-3} \text{ M})$.

The mixtures are stirred for 15 minutes at 100°C on the magnetic stirrer, and then the samples are aged and dried at room temperature for around 4 days in closed glass vials to produce four disk samples of random laser gain media. Energy Dispersive X-ray Diffraction (EDX) with XFlash 6L10, Field Emission Scanning Electron Microscopy (FE-SEM) with Inspect TM F50, UV-Visible spectrometry with a Shimadzu UV-VIS 1800 spectrophotometer, and F96 Shanghai Leng Guang Fluorescence Spectrophotometer were used to analyze the structural and optical characteristics of random laser gain media in the Sol-Gel technique.

3. Results and discussion

3.1 Morphological properties

As shown in Fig.1, SEM images indicate clusters of spherical, bright spots (circles and inset picture) that correspond to silicon oxide (SiO₂) nanoparticles with a mean particle size of around (25–67) nm for all prepared samples. By exhibiting peaks corresponding to the energy levels for each element in the test, EDX was used to confirm the structural purity of the samples.

As shown in Fig.2, all of the samples contain Si as the highest peak in the spectrum, indicating that it is the most concentrated element; the presence of an O peak also confirms the stoichiometry of the silica NPs compound. The other peaks reflect the constituent elements of the dyes in the samples.

3.2 Optical properties

Using UV-Vis spectroscopy, the optical characteristics of the samples were determined. Fig.3 displays the absorption spectra of pure and doped dyes (Rh 101, Rh B, C.V., Fluorescein) with silica at the same concentration $(1 \times 10^{-3} \text{ M})$, where the absorption spectra moved to a longer wavelength in the visible region (red shift) after it was doped with SiO₂. This indicates the aggregation of nanoparticles in the dye solution [32], resulting in a shift in wavelengths. While Fig.4 shows the optical transmission spectra of pure and silica-doped dyes, the absorbance spectra for all samples exhibit the opposite pattern.





Fig. 1: SEM image of dyes (a) Rh 101, (b) Rh B , (c) C.V , (d) Fluorescein doped with SiO₂ NPs.



Fig. 2: EDX results of dyes (a) Rh 101, (b) Rh B, (c) C.V, (d) Fluorescein doped with SiO₂ NPs.



Fig. 3 Optical absorbance spectra of pure and doped dyes at the same concentration with SiO_2 for (a) Rh 101 (b) Rh B (c) C.V (d) Fluorescein.



Fig. 4: Optical transmittance spectra of pure and doped dyes at the same concentration with SiO_2 for (a) Rh 101 (b) Rh B (c) C.V (d) Fluorescein. [This is what the results revealed, and they are presented as is].

Fluorescence spectra were acquired using an F96 Shanghai Leng Guang Fluorescence Spectrophotometer. Fig. 5 displays the fluorescence spectra of pure and doped dyes (Rh 101, Rh B, C.V., Fluorescein) with silica at the same concentration $(1 \times 10^{-3} \text{ M})$, where the fluorescence spectra became higher after it was doped with SiO₂ with a concentration of 0.0016 mol/ml since nanoparticles can exhibit unique optical and electronic properties that are not present in bulk materials, which means that they can absorb light energy and transfer it to the host material, leading to higher fluorescence



Fig. 5: Optical fluorescence spectra of pure and doped dyes at the same concentration with SiO_2 for (a) Rh 101 (b) Rh B (c) C.V (d) Fluorescein.

4. Conclusion

Using the sol-gel process, several dyes with SiO_2 as a scatter are successfully used to create random laser gain media. FESEM images show that the SiO_2 particles generated in the entire sample are in the nano range (100 nm), EDX demonstrates that Si is the most prevalent element in every sample, UV-Vis spectra demonstrate that all pure dyes have a higher absorbance than when they are doped, and the Fluorescence Spectrophotometer demonstrates that the fluorescence spectra became higher after it was doped with SiO_2 in all samples. [The proposed opinion will be applied to future studies].



References

[1] M. Maeda, Laser dyes: properties of organic compounds for dye lasers. Academic Press, 1984.

[2] S.K. Turitsyn et al., "Random distributed feedback fibre lasers", Phys. Rep., 542(2),133-193(2014).

[3] N. M. Lawandy, R. M. Balachandran, A. S. L. Gomes, and E. Sauvain, "Laser action in strongly scattering media," Nature, **368** (6470), 436–438 (1994).

[4] W. L. Sha, C.-H. Liu, and R. R. Alfano, "Spectral and temporal measurements of laser action of Rhodamine 640 dye in strongly scattering media," Opt. Lett., **19**(23), 1922–1924 (1994).

[5] G. Van Soest, F. J. Poelwijk, R. Sprik, and A. Lagendijk, "Dynamics of a random laser above threshold," Phys. Rev. Lett., **86**(8)1522 (2001).

[6] S. John and G. Pang, "Theory of lasing in a multiple-scattering medium," Phys. Rev. A, 54(4), 3642 (1996).

[7] G. A. Berger, M. Kempe, and A. Z. Genack, "Dynamics of stimulated emission from random media," Phys. Rev. E, 56(5), 6118, (1997).

[8] L. Ye, C. Zhao, Y. Feng, B. Gu, Y. Cui, and Y. Lu, "Study on the polarization of random lasers from dye-doped nematic liquid crystals," Nanoscale Res. Lett., **12**, 1–8 (2017).

[9] D. Wiersma, "The smallest random laser," Nature, **406**(6792), 133–135(2000).

[10] D. S. Wiersma and S. Cavalieri, "A temperature-tunable random laser," Nature, 414(6865),708–709 (2001).

[11] S. Murai, K. Fujita, T. Hirao, K. Nakanishi, K. Hirao, and K. Tanaka, "Scattering-based hole burning through volume speckles in a random medium with tunable diffusion constant," Appl. Phys. Lett., **93**(15), 151912 (2008).

[12] R. C. Polson and Z. V. Vardeny, "Random lasing in human tissues," Appl. Phys. Lett., 85(7), 1289–1291, (2004).
[13] Q. Song et al., "Random lasing in bone tissue," Opt. Lett., 35(9), 1425–1427 (2010).

[14] L.-W. Li and L.-G. Deng, "Random lasing from dye-doped chiral nematic liquid crystals in oriented and nonoriented cells," Eur. Phys. J. B-Condensed Matter Complex Syst., **86**(3), (2013).

[15] H. Cao, "Lasing in random media," Waves in random media, **13**(3), R1(2003).

[16] H. Cao, Y. G. Zhao, S. T. Ho, E. W. Seelig, Q. H. Wang, and R. P. H. Chang, "Random laser action in semiconductor powder," Phys. Rev. Lett., 82(11),2278(1999).

[17] C. T. Dominguez, M. de A. Gomes, Z. S. Macedo, C. B. de Araújo, and A. S. L. Gomes, "Multi-photon excited coherent random laser emission in ZnO powders," Nanoscale, **7**(1), 317–323 (2015).

[18] X. Xu, W. Zhang, L. Jin, J. Qiu, and S. F. Yu, "Random lasing in Eu³⁺ doped borate glass-ceramic embedded with Ag nanoparticles under direct three-photon excitation," Nanoscale, **7**(39),16246–16250 (2015).

[19] A. L. Moura, V. Jerez, L. J. Q. Maia, A. S. L. Gomes, and C. B. De Araújo, "Multi-wavelength emission through self-induced second-order wave-mixing processes from a Nd3+ doped crystalline powder random laser," Sci. Rep., 5(1),1–7 (2015).

[20] Y. Wang, X. Yang, H. Li, and C. Sheng, "Bright single-mode random laser from a concentrated solution of π -conjugated polymers.," Opt. Lett., **41**(2), 269–272 (2016).

[21] R. C. Polson, A. Chipouline, and Z. V. Vardeny, "Random lasing in π -conjugated films and infiltrated opals," Adv. Mater., **13**(10), 760–764 (2001).

[22] L. Wang, Y. Wan, L. Shi, H. Zhong, and L. Deng, "Electrically controllable plasmonic enhanced coherent random lasing from dye-doped nematic liquid crystals containing Au nanoparticles," Opt. Express, **24**(16), 17593–17602 (2016).

[23] J.-L.Zhu et al., "Random laser emission in a sphere-phase liquid crystal," Appl. Phys. Lett., **106**(19), 191903 (2015).

[24] Z. Wang et al., "Controlling random lasing with three-dimensional plasmonic nanorod metamaterials," Nano Lett., **16** (4), 2471–2477 (2016).

[25] T. Zhai et al., "Random laser based on waveguided plasmonic gain channels," Nano Lett., **11**(10), 4295–4298 (2011).

[26] D. Huang et al., "Low threshold random lasing actions in natural biological membranes," Laser Phys. Lett., vol. **13**(6),65603(2016).

[27] F. Lahoz et al., "Random laser in biological tissues impregnated with a fluorescent anticancer drug," Laser Phys. Lett., **12**(4),45805 (2015).

[28] L. Ye et al., "Random lasing action in magnetic nanoparticles doped dye solutions," Opt. Commun., **340**,151–154 (2015).

[29] F. S Abbas and N. F Ali, "Study the optical characteristics of epoxy panel doped with fluorescein-sodium dye," J. kerbala Univ., **10**(2),50–60 (2014).



[31] A. G. Ardakani and P. Rafieipour, "Random lasing emission from WO₃ particles dispersed in Rhodamine 6G solution," Phys. B Condens. Matter, **546**,49–53(2018).

[32] S. Rahayu, A. T. Dosi, and P. Wulandari, "Optimization of metal nanoparticles concentration in dye solution to enhance performance of dye sensitized solar cells," in Journal of Physics: Conference Series, **2243**(1), 12090 (2022).

دراسة تأثير جسيمات السليكا النانوية على خصائص عدة صبغات لتصنيع وسط كسب ليزر عشوائي

نور ياسر خضير * , محمد كريم ظاهر

معهد الليزر للدراسات العليا، جامعة بغداد، بغداد، العراق

*البريد الالكتروني للباحث:<u>Noor.Yasir2101m@ilps.uobaghdad.edu.iq</u>

الخلاصة: تم تصنيع وسائط كسب الليزر العشوائي من انواع مختلفة من الصبغات كمادة مضيفة نشطة وجسيمات اوكسيد السيليكون النانوية (السيليكا SiO2) كمر اكز تشتت من خلال تقنية السول- جل. تم فحص العينات المعدة عن طريق استخدام التحليل الطيفي للأشعة المرئية وفوق البنفسجية , التحليل الطيفي الفلوري , طيف المجهر الإلكتروني لمسح الانبعاث الميداني (FESEM) ، و طيف حيود الأشعة السينية المشتتة للطاقة (EDX). أظهرت النتائج النهائية ان الصبغات المشوبة بجسيمات السيليكا النانوية بتركيز Molo 16 mol/ml لها امتصاص اقل واطياف فلورة اعلى من الصبغات النقية , و كشفت فحصوصات FESEM أن مور فولوجيا السيليكا النانوية هي عبارة عن مجموعات من الجسيمات الكروية النانوية الحجم (25–67 nm). تم ستتناج أن الصبغات المختلفة التي تحتوي على SiO2 كمركز تشتت يمكن اقتراحها في بناء اوساط كسب ليزرية.

