

Detection of Random Laser Action from Silica Xerogel Matrices Containing Rhodamine 610 Dye and Titanium Dioxide Nanoparticles

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ABSTRACT

The synthesis, structural characterization, and amplified spontaneous emission spectroscopy of dye-scattering particles in inorganic medium based on Rhodamine 610-TiO₂ nanoparticles confined in silica xerogel matrix have been reported. Optimum concentrations have been determined depending on the normal fluorescence spectra for laser dye, in order to provide amplification, and TiO₂ nanoparticles as scatter center. Random Laser has been studied under second harmonic Nd:YAG laser excitation. At the optimum concentrations, the results show that the values of bandwidth at full width half-maximum (FWHM) and the threshold energy are about 11 nm and 3 mJ respectively. The scattered and amplified probe light has been collected on a PC-interfaced CCD camera system.

Keywords: Random Lasers; Sol-Gel; Nanoscale Materials and Structures

1. Introduction

Laser action in random structures where light is multiply scattered and amplified becomes a subject of intense theoretical and experimental studies because of its important potential applications [1]. Following the pioneering theoretical work by Letokhov in the late 1960s [2], experiments by Markushe *et al.* on powdered Na₅La_{1-x}Nd_x(MoO₄)₄ [3] and Lawandy *et al.* on solutions containing an organic dye, Rhodamine 640, and TiO₂ particles [4] demonstrated scattering-assisted optical gain upon laser pumping.

Random lasing has been demonstrated with various material structures, including semiconductor [5], and rare earth based materials [6] in powder form, nanocomposite hybrids [7], organic dyes [8,9], liquid crystals [10] and biological tissues [11]. Many research works have been done on the preparation and characterization of disordered gain media based on organic dye and scattering particles doped into a solid-state organic host [12-15]. This type of disordered media has been to be bulks or films and based on external scatters.

Sol-gel method has been used to produce several types of inorganic host matrices doped with laser dyes. In this way, the ground powder of a silica gel containing 2 wt% R6G-SiO₂ nanoparticles prepared via the sol-gel method has been experimentally demonstrated one and two-photon pumped random lasing [16,17]. The advantages

of this dye random laser system have been specified in its solid-state nature, quenched disorder, high laser-like emission efficiency and the possibility of being functionalized for various applications such as biomedical sensors [18]. Also, a novel sol-gel method has been used to synthesize zinc oxide buffer layer for use in random laser media [19].

In the present study, sol-gel method has been used to synthesis silica xerogel as inorganic transparent solid host for both R610 dye as active dopant and TiO₂ nanoparticles as scatters. Suitable sol-gel parameters have been used to produce a suitable silica matrix that contains the suspended titanium nanoparticles. Consequently, the statistical spectroscopic studies of the concentrations of R610 dye and TiO₂ scatter center have been achieved to select the optimum required concentrations. At these optimum concentrations, the emission spectra at different energies of Nd:YAG, 2nd harmonic generation, has been investigated to determine the lasing threshold.

2. Experimental Details

2.1. Samples Preparation

The silica xerogel samples were prepared using sol-gel method. Two recipes, illustrated schematically in **Figure 1**, were prepared and mixed together. Tetraethylorthosilicate TEOS (Si(OC₂H₅)₄, Purity > 98%; supplied by Schuchardt, was used as SiO₂ precursor. For recipe 1,

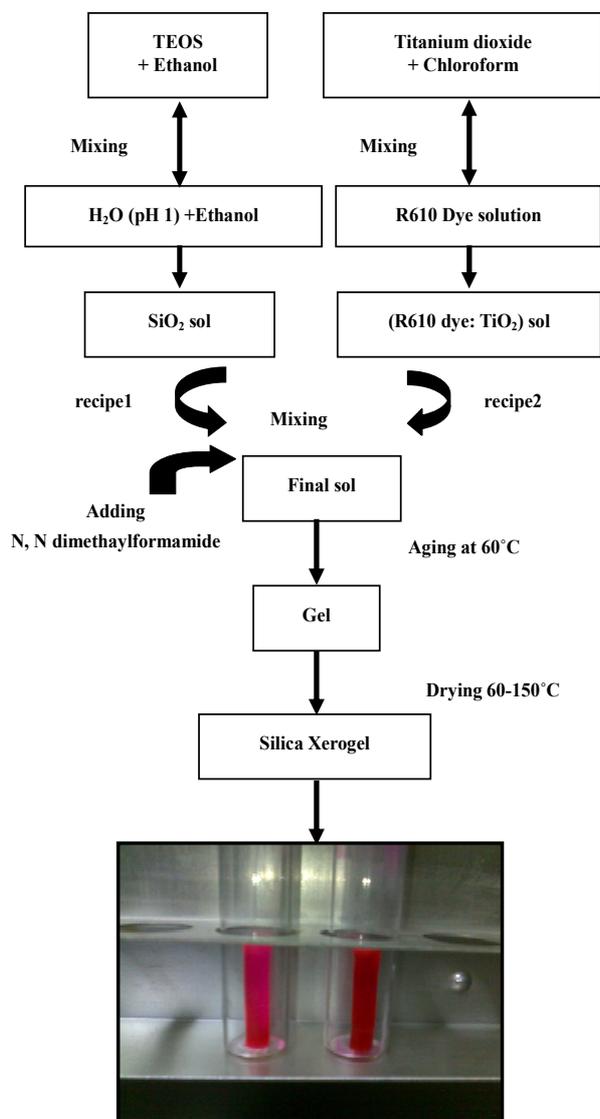


Figure 1. Sol-gel preparation scheme for R610 dye and TiO₂ nanoparticles doped silica xerogel, with photo of some prepared samples.

TEOS and pure ethanol were mixed at molar ratio of 1:4 to prepare silica solution. The catalyst solution was contained deionized water of pH1 (using hydrochloric acid HCl, 0.15 M) mixed with pure ethanol at molar ratio of 2:4. The catalyst solution was slowly added to silica solution with R-molar ratio (H₂O/TEOS) of 24:0.06. In recipe 2, Titanium dioxide (TiO₂) acquired from DuPont Inc., with the crystal structure of anatase was used as scatter center. TiO₂ particles were suspended in chloroform with different concentrations estimated from the known weight fraction of TiO₂ in suspension. R610 laser dye was dissolved in ethanol at concentration of 10⁻³ mol/l and then diluted to get the other concentrations: 2 × 10⁻⁴, 2 × 10⁻⁵ and 10⁻⁵ mol/l. After mixing the two recipes, N, N dimethylformamide (C₃H₇NO) was added as

drying control chemical additive. The gelation of monoliths was achieved by pouring the final sol into covered glass tube and kept it at 60°C.

2.2. Samples Characterization

The samples were prepared as bulk nature in rod shape. The diameter and length of rod samples were measured using digital micrometer (0 - 150 mm), Hardened. The diameter and length ranges were 3 - 4.5 mm and 13 - 18 mm respectively.

Titanium particle size determination was carried out with scanning electron microscope (SEM) after preparing TiO₂ suspension as film by spin coating process. The device of spin coating (achieved in our laboratory) was constituted of a metal body which holds the motor and the sample holder as well as the glass windows, the metal covers and the upper cover (sailing) has a hole for liquids delivery, variable legs for horizontal adjustment of the equipment using spirit level, variable power supply of 220 V input and variable output from 0 V to 220 V and A.C. motor 100 V, 220 W, maximum speed at 100 V is 8000 rpm. **Figure 2** shows topography image of TiO₂ film where the mean particle size was determined to be 52.49 nm.

Mid-IR spectra were obtained for the prepared samples using FT-IR spectrometer, Shimadzu, on KBr pellets of the samples. The characteristic vibrational bands of silica were determined in the spectra of silica xerogel samples doped with R610 dye and TiO₂ nanoparticles as shown in **Figure 3**.

The band centered at 462.88 cm⁻¹ is due to the bending vibrations of (Si-O-Si) groups, and the absorption band peaking at 805 cm⁻¹ is attributed to the symmetric stretching (Si-O-Si) groups, while the wide band at around 1070 cm⁻¹ is the characteristic Si-O-Si asymmetric stretching vibrations [20]. The band at 962 cm⁻¹ is

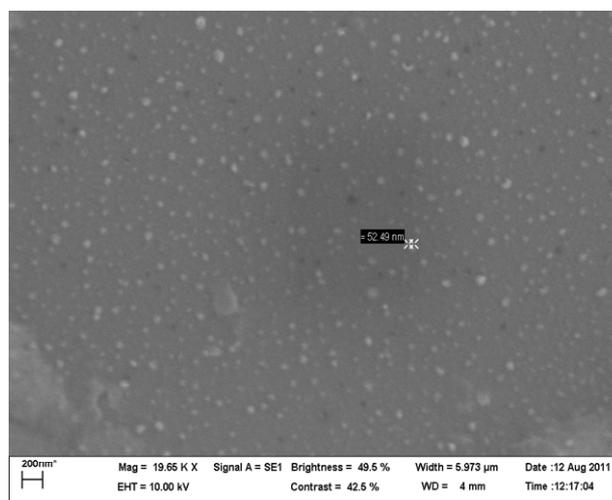


Figure 2. The SEM Micrographs of TiO₂ film surface.

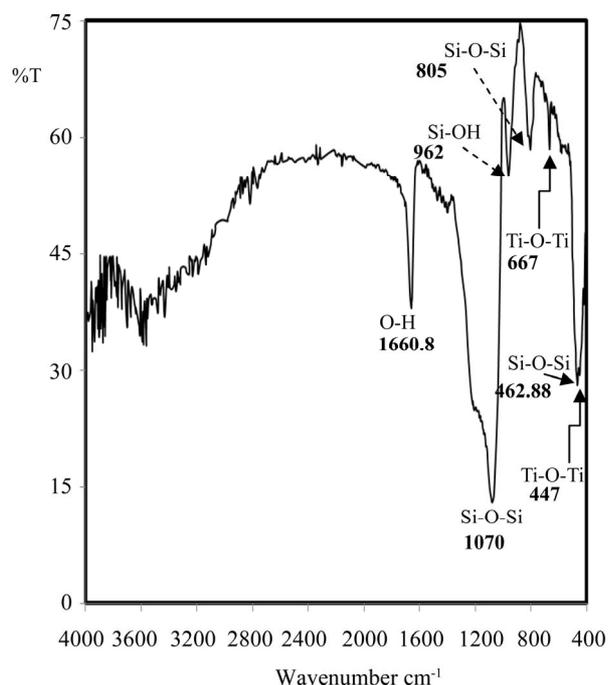


Figure 3. FT-IR spectrum of silica xerogel doped with 2×10^{-4} mol/l R610 dye and 4.5×10^{13} cm $^{-3}$ TiO $_2$.

ascribed to stretching vibration of silanol (Si–OH) groups [21], indicates the existence of these groups in the silica network. Because of the drying process at 150°C cannot completely trap the water molecules from the pores structure of silica xerogel, the absorption bands at 1660.8 cm $^{-1}$ is observed and due to bending vibrations of (O-H) bond in H $_2$ O molecules [22].

The important result, that could be seen from the FTIR spectra, is the existence of two absorption bands centered at around 447 cm $^{-1}$, that overlapped with bending vibration band of siloxan (462.88 cm $^{-1}$), and 667 cm $^{-1}$, assigned for Ti-O-Ti bonds [23,24]. This result indicates that there is randomly distribution of TiO $_2$ nanoparticles, interstitially as defects within the structure of silica matrix near the pores surfaces and thus act as scatter centers.

2.3. Experimental Setup

Figure 4 shows the experimental setup for measuring the spectra of amplified spontaneous emission (ASE). A quartz cell with 0.5 cm width and 3 cm length has been used as sample cell. The excitation source is Q-switched Nd:YAG 2nd harmonic generation ($\lambda = 532$ nm, with a pulse width of 6 ns, repetition rate of 6 Hz and focal spot size of ≈ 4 mm). Monochromator and photomultiplier tube were used, respectively, to select and detect the emission signals.

To explore the laser output characteristics (intensity distribution); a PC-interfaced CCD camera system (working in the spectral range of 400 - 1100 nm) was used with

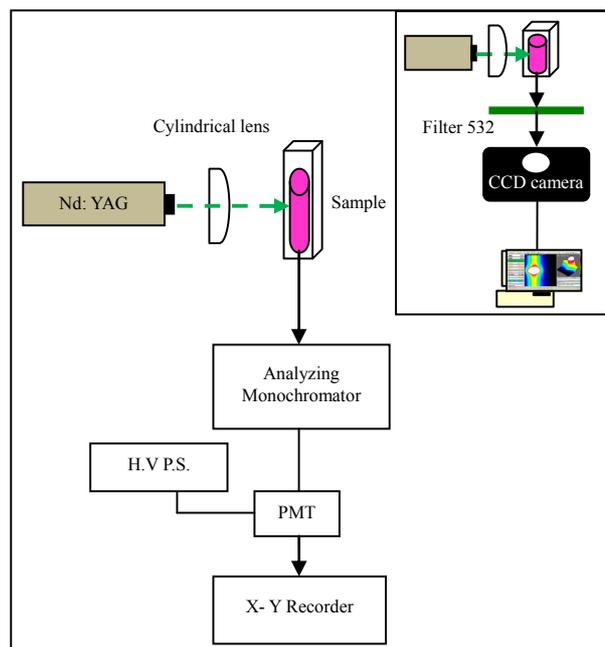


Figure 4. Schematic diagram of the experimental setup.

a 532 nm interference filter to rid the excitation wavelength as shown in the inset of **Figure 4**.

3. Result and Dissection

Firstly, the dropping in the fluorescence intensity was observed for the rod samples containing 10^{-3} and 2×10^{-4} mol/l of R610 laser dye and 4.5×10^{13} cm $^{-3}$ TiO $_2$ particle density as shown in **Figure 5**. This behavior can be seen with other concentrations of TiO $_2$ and due to the aggregation of dye molecules inside the pores structure of silica xerogel, and thus the concentration quenching can be occurred. The concentrations: 10^{-4} mol/l of R610 dye and 4.5×10^{13} cm $^{-3}$ TiO $_2$ particle density give the best results, in which high fluorescence intensity and hence narrow band width at FWHM (20 nm) can be observed comparing with 39 nm in the case of without doping of TiO $_2$ as shown in the inset of **Figure 5**. The values of bandwidth at full width half-maximum (FWHM) were determined using an Excel program that calculates the area under the curve and distribute them to the highest value of intensity.

These optimum concentrations of dye molecules and nanoparticles doped silica xerogel give a primarily indication that the amplification and multiscattering processes are performed parallel without noticeable effect on the dye response. Thus, TiO $_2$ nanoparticles scatter photons, increase the path length photons walking in the matrix of silica xerogel and consequently can cause amplified spontaneous emission (incoherent laser).

The emission spectra of rod sample, containing these optimum concentrations were recorded with different

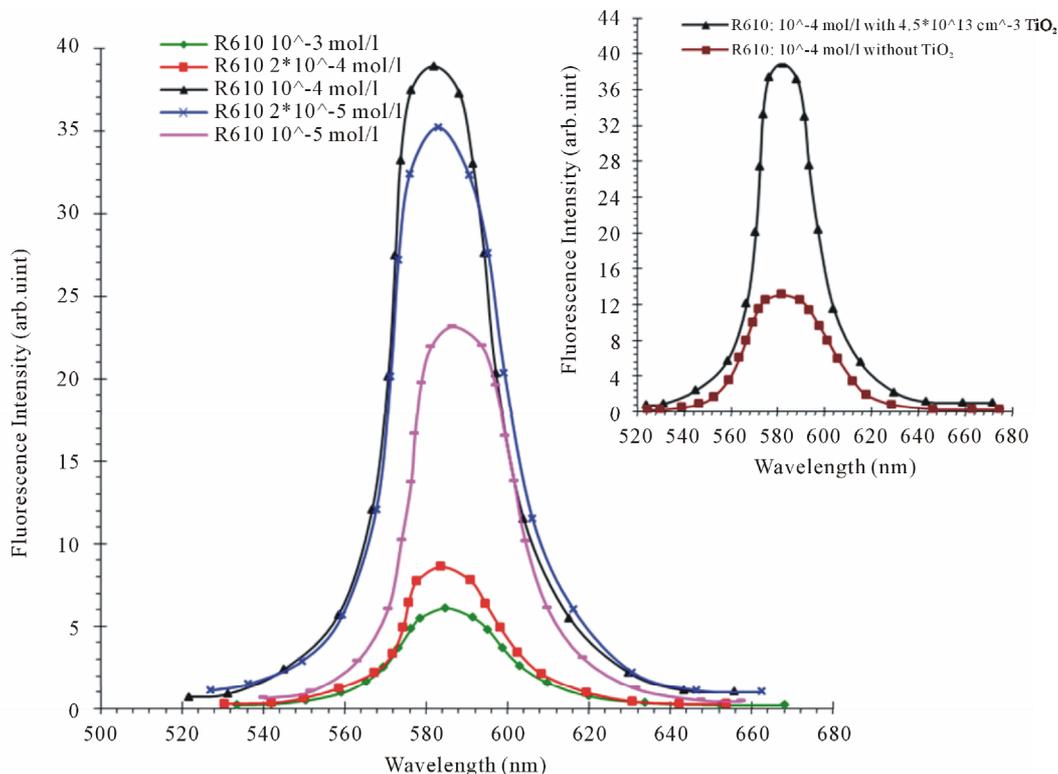


Figure 5. The fluorescence spectra of silica xerogel samples with $4.5 \times 10^{13} \text{ cm}^{-3} \text{ TiO}_2$ and different concentrations of R610 dye.

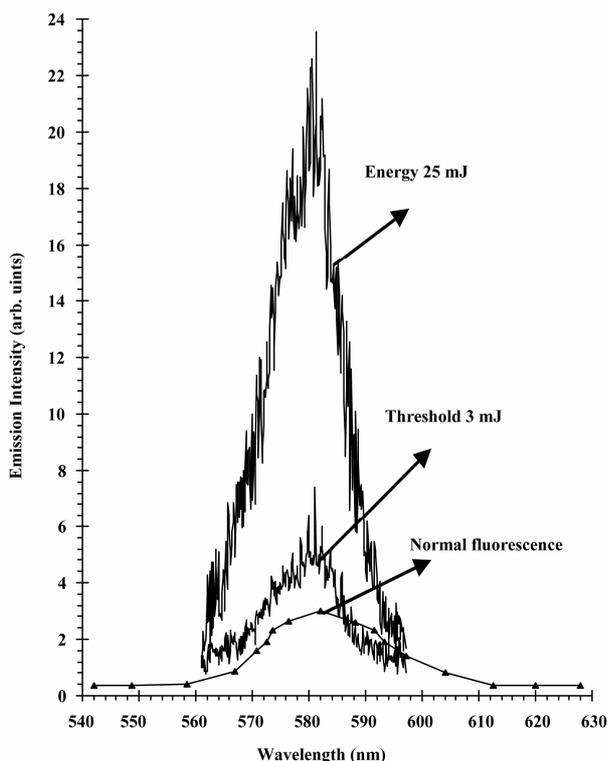


Figure 6. Emission spectra of silica xerogel sample with 10^{-4} mol/l R610 dye and $4.5 \times 10^{13} \text{ cm}^{-3} \text{ TiO}_2$ at two values of pump energy, in addition to normal fluorescence.

pumping energies (1 - 25 mJ). Thus, the threshold energy and the pumping energy that gives a minimum band width were determined. Figure 6 shows the emission spectra, obtained from the experimental setup, of silica xerogel rod containing: 10^{-4} mol/l of R610 dye and $4.5 \times$

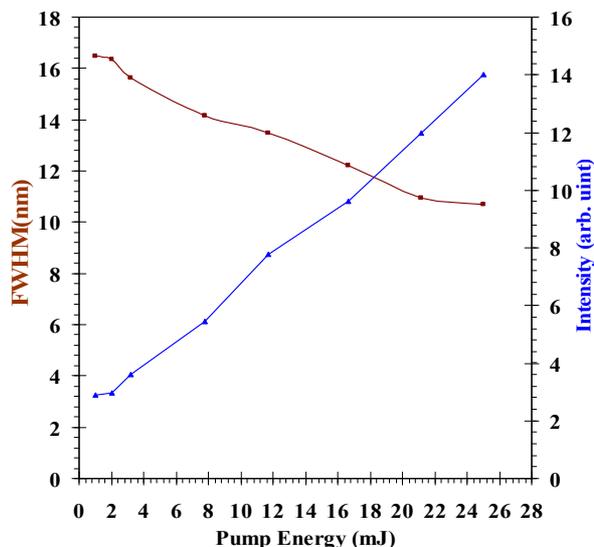
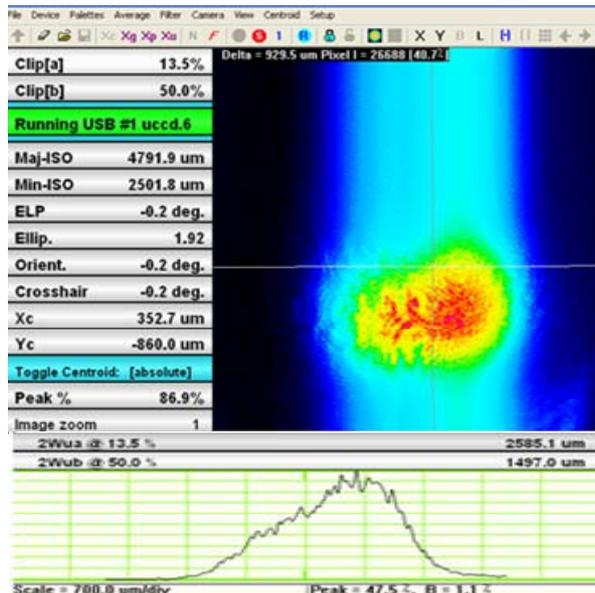


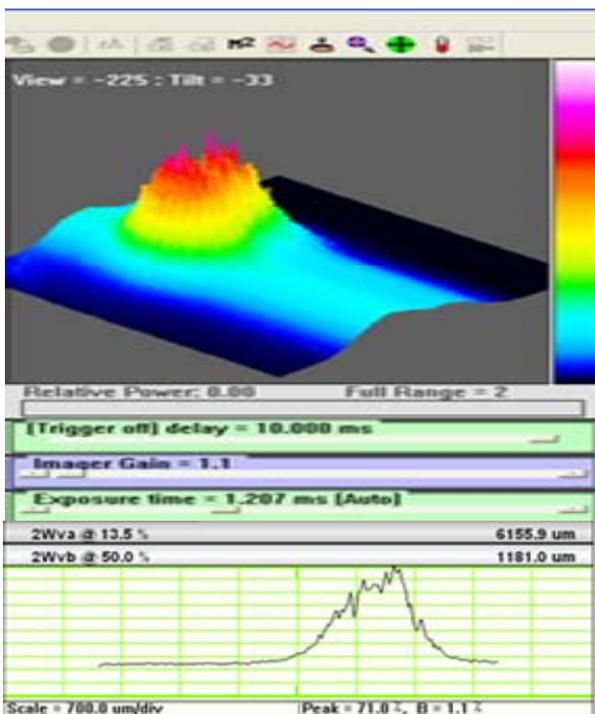
Figure 7. The relation of band width at FWHM and maximum intensity estimated from the emission spectra of silica xerogel sample with 10^{-4} mol/l R610 dye and $4.5 \times 10^{13} \text{ cm}^{-3} \text{ TiO}_2$ at different values of pumping energy.

10^{13} cm^{-3} of TiO_2 .

The R610 dye fluorescence was centered at approximately 582 nm as can be seen in **Figures 5** and **6**. The relation of both band width at FWHM and intensity at peak emission as a function of pumping energy can be illustrated in **Figure 7**. From this figure, it was found that



(a)



(b)

Figure 8. Photo of CDD camera for silica xerogel doped with 10^{-4} mol/l of R610 dye and $4.5 \times 10^{13} \text{ cm}^{-3}$ of TiO_2 : (a) 2D images; (b) 3D image.

the random laser threshold was 3 mJ and the minimum value of band width at FWHM (with maximum intensity) was 11 nm at 25 mJ pumping energy.

Figures 8(a) and **(b)** shows photo of a charge-coupled device (CCD) camera, as clarified in the inset of **Figure 4**, for the selected sample at optimum concentrations. This is the laser beam profile test which involves 2D and 3D images where the apparent spikes verify the results described in the ASE intensity spectra. By this test, it can be explored the random gain media spectral intensity distribution, spot size (it represents the quantum yield of the random laser emitted towards the camera) and the spectral purity characteristics for the tested sample.

4. Conclusion

A new type of random gain media was synthesized via sol-gel method. The positions of TiO_2 nanoparticles within silica xerogel matrix were primarily determined by FTIR spectra, in which these particles cannot locate within the pores structure of such matrix because of the large size of these particles compared with the pores size (approximately 10 nm according to pH value of the solution). The influence of TiO_2 scatter on light emission was explored and the optimum concentrations of particle and dye were obtained. The results of random laser measurements show that the minimum band width at FWHM was 11 nm at 25 mJ and laser threshold at 3 mJ for a homogeneous silica xerogel sample doped with 10^{-4} mol/l of R610 dye and $4.5 \times 10^{13} \text{ cm}^{-3}$ of TiO_2 . This threshold was considered to be lower than that of organic hosts such as polymers [25]. It was also found that titanium particles contribute for small photodegradation of the dye molecules.

REFERENCES

- [1] D. S. Wiersma, "The Physics and Applications of Random Lasers," *Nature Physics*, Vol. 4, 2008, pp. 359-367. [doi:10.1038/nphys971](https://doi.org/10.1038/nphys971)
- [2] V. S. Letokhov, "Stimulated Emission of an Ensemble of Scattering Particles with Negative Absorption," *Journal of Experimental and Theoretical Physics Letters*, Vol. 5, 1967, pp. 212-215.
- [3] V. M. Markushev, V. F. Zolin and C. M. Briskina, "Luminescence and Stimulated Emission of Neodymium in Sodium Lanthanum Molybdate Powders," *Soviet Journal of Quantum Electronics*, Vol. 16, No. 2, 1986, pp. 281-283. [doi:10.1070/QE1986v016n02ABEH005792](https://doi.org/10.1070/QE1986v016n02ABEH005792)
- [4] N. M. Lawandy, R. M. Salachandran, A. S. L. Gomes and E. Sauvain, "Laser Action in Strongly Scattering Media," *Nature*, Vol. 368, 1994, pp. 436-438. [doi:10.1038/368436a0](https://doi.org/10.1038/368436a0)
- [5] H. Cao, Y. Zhao, S. T. Ho, E. W. Seelig, Q. H. Wang and R. P. H. Chang, "Random Laser Action in Semiconductor

- Powder," *Physical Review Letters*, Vol. 82, No. 11, 1999, pp. 2278-2281. [doi:10.1103/PhysRevLett.82.2278](https://doi.org/10.1103/PhysRevLett.82.2278)
- [6] G. Williams, S. C. Rand, T. Hinklin and R. M. Laine, "Blue and Infrared Laser Action in Strongly Scattering Nd: Alumina Nanopowders," *Conference on Lasers and Electro-Optics*, OSA Technical Digest, Optical Society of America, Washington DC, 1999.
- [7] D. Anglos, A. Stassinopoulos, R. N. Das, G. Zacharakis, M. Psyllaki, R. Jakubiak, R. A. Vaia, E. P. Giannelis and S. H. Anastasiadis, "Random Laser Action in Organic-Inorganic Nanocomposites," *Journal of the Optical Society of America B*, Vol. 21, 2004, pp. 208-213. [doi:10.1364/JOSAB.21.000208](https://doi.org/10.1364/JOSAB.21.000208)
- [8] M. A. Noginov, N. E. Noginova, H. J. Caulfield, P. Venkateswarl and M. Mahdi, "Line Narrowing in the Dye Solution with Scattering Centers," *Optics Communications*, Vol. 118, No. 3-4, 1995, pp. 430-437. [doi:10.1016/0030-4018\(95\)00177-A](https://doi.org/10.1016/0030-4018(95)00177-A)
- [9] E. Enciso, A. Costela, I. Garcia-Moreno, V. Martin and R. Sastre, "Conventional Unidirectional Laser Action Enhanced by Dye Confined in Nanoparticle Scatters," *Langmuir*, Vol. 26, No. 9, 2010, pp. 6154-6157. [doi:10.1021/la100813r](https://doi.org/10.1021/la100813r)
- [10] S. M. Morris, A. D. Ford, M. N. Pivnenko and H. J. Coles, "Efficient Random Laser Effect in a New Dye-Nematic Liquid Crystalline Composite," *Romanian Reports in Physics*, Vol. 62, No. 3, 2010, pp. 444-454.
- [11] R. C. Polson and Z. V. Vardeny, "Random Lasing in Human Tissues," *Applied Physics Letters*, Vol. 85, 2004, p. 1289. [doi:10.1063/1.1782259](https://doi.org/10.1063/1.1782259)
- [12] R. M. Balachandran, D. P. Pacheco and N. M. Lawandy, "Laser Action in Polymeric Gain Media Containing Scattering Particles," *Applied Optics*, Vol. 35, 1996, pp. 640-643. [doi:10.1364/AO.35.000640](https://doi.org/10.1364/AO.35.000640)
- [13] K. Yoshiko, S. Tatsuura, Y. Kawagishi, M. Ozaki, A. Zakhidov and Z. V. Vardeny, "Amplified Spontaneous Emission and Lasing in Conducting Polymers and Fluorescent Dyes in Opals as Photonic Crystals," *Applied Physics Letters*, Vol. 74, 1999, pp. 2590-2592. [doi:10.1063/1.123907](https://doi.org/10.1063/1.123907)
- [14] Y. Ling, H. Cao, A. L. Burin, M. A. Ratner, X. Liu and R. P. H. Chang, "Investigation of Random Lasers with 20 nm in an Active Medium," *Optics Communications*, Vol. 244, 2005, pp. 299-303. [doi:10.1016/j.optcom.2004.08.054](https://doi.org/10.1016/j.optcom.2004.08.054)
- [15] X.-H. Sun, X.-M. Tao, P. Xue, K.-C. Kwan and J.-G. Deng, "Low-Threshold Random Laser with One Mirror and Feedbacks in PMMA Nanocomposite Films," *Chinese Physics Letters*, Vol. 22, No. 10, 2005, p. 2568. [doi:10.1088/0256-307X/22/10/030](https://doi.org/10.1088/0256-307X/22/10/030)
- [16] S. García-Revilla, J. Fernández, M. A. Illarramendi, B. García-Ramiro, R. Balda, H. Cui, M. Zayat and D. Levy, "Ultrafast Random Laser Emission in a Dye Doped Silica Gel Powder," *Optics Express*, Vol. 16, No. 16, 2008, pp. 12251-12263. [doi:10.1364/OE.16.012251](https://doi.org/10.1364/OE.16.012251)
- [17] G. Zacharakis, N. A. Papadogiannis and T. G. Papazoglou, "Random Lasing Following Two-Photon Excitation of Highly Scattering Gain Media," *Applied Physics Letters*, Vol. 81, No. 14, 2002, pp. 2511-2513. [doi:10.1063/1.1511284](https://doi.org/10.1063/1.1511284)
- [18] G. S. He, T.-G. Lin, S.-J. Chung, Q. Zheng, C. Lu, Y. Cui and P. N. Prasad, "Two-, Three-, and Four-Photon-Pumped Stimulated Cavityless Lasing Properties of Ten Stilbazolium-Dyes Solutions," *Journal of the Optical Society of America B*, Vol. 22, No. 10, 2005, pp. 2219-2228. [doi:10.1364/JOSAB.22.002219](https://doi.org/10.1364/JOSAB.22.002219)
- [19] M. S. Ghamsari and M. Vafaei, "Sol-Gel Derived Zinc Oxide Buffer Layer for Use in Random Laser Media," *Materials Letters*, Vol. 62, 2008, pp. 1754-1756. [doi:10.1016/j.matlet.2007.09.081](https://doi.org/10.1016/j.matlet.2007.09.081)
- [20] D. Davazoglou and V. E. Vamvakas, "Arrangement of Si and O Atoms in Thermally Grown SiO₂ Films," *Journal of the Electrochemical Society*, Vol. 150, 2003, pp. 90-96. [doi:10.1149/1.1562601](https://doi.org/10.1149/1.1562601)
- [21] X. Song, N. Jiang, Y. Li, D. Xu and G. Qiu, "Synthesis of CeO₂-Coated SiO₂ Nanoparticle and Dispersion Stability of Its Suspension," *Materials Chemistry and Physics*, Vol. 110, 2008, pp. 128-135. [doi:10.1016/j.matchemphys.2008.01.042](https://doi.org/10.1016/j.matchemphys.2008.01.042)
- [22] W. A. W. Ibrahim, W. N. W. Ismail, A. S. A. Keyon and M. M. Sanagi, "Preparation and Characterization of a New Sol-Gel Hybrid Based Tetraethoxysilane-Polydimethylsiloxane as a Stir Bar Extraction Sorbent Materials," *Journal of Sol-Gel Science and Technology*, Vol. 58, 2011, pp. 602-611. [doi:10.1007/s10971-011-2434-7](https://doi.org/10.1007/s10971-011-2434-7)
- [23] A. Merouani and H. Amardjia-Adnani, "Spectroscopic FT-IR Study of TiO₂ Films Prepared by Sol-Gel Method," *International Scientific Journal for Alternative Energy and Ecology*, Vol. 6, No. 62, 2008, pp. 151-154.
- [24] Y.-G. Kwon, S.-Y. Choi, E.-S. Kang and S.-S. Baek, "Ambient-Dried Silica Aerogel Doped with TiO₂ Powder for Thermal Insulation," *Journal of Materials Science*, Vol. 35, 2000, pp. 6075-6079. [doi:10.1023/A:1026775632209](https://doi.org/10.1023/A:1026775632209)
- [25] B. T. Chiad, K. H. Latif, F. J. Kadhim and M. A. Hammed, "Random Laser of R6G Dye and TiO₂ Nanoparticles Doped in PMMA Polymer," *Advances in Materials Physics and Chemistry*, Vol. 1, 2011, pp. 20-25.