# Enhancing the Performance of Random Lasers
## *Effects of Localised Surface Plasmons and Resonance Energy Transfer*

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Abstract: We investigate the effect of different gain media and different scattering media in random lasers. We demonstrate an increase in the emission intensity and efficiency of random lasing by incorporating gold rather than dielectric alumina nanoparticles. There is a trade-off between enhancing the random laser performance due to the localised surface plasmon resonance field effects and reduction in performance due to fluorescence quenching by the gold nanoparticles. We use fluorescence resonant energy transfer between dye molecules to extend the wavelength range of emission.

## 1 INTRODUCTION

Random lasers offer interesting behaviour compared with standard (resonant cavity-based) lasers as they incorporate highly scattering materials combined with optical gain (Wiersma, 2008). Thus the laser output typically has reduced coherence, and broader linewidth than for a comparable standard cavity-based laser (Wan Ismail *et al.,* 2014). However, these lasers exhibit typical threshold behaviour and spatially distributed emission, with a relatively broad angular range of emission. The lasers can be used in a range of applications including as broadband – low coherence sources for Optical Coherence Tomography, and for probing the properties of the scattering materials themselves (such as in biosensing). Here, we describe methods to enhance the emission intensity or reduce the threshold of random lasers based on dye solutions with metal and dielectric scattering particles. We employ combinations of dyes to extend the available range of emission wavelengths from these systems.

## 2 EXPERIMENTS

The random laser solutions were prepared in methanol, using specified concentrations of titania nanoparticles (average diameter 200 nm, Sigma Aldrich), alumina nanoparticles (average size of 150 nm, Sigma Aldrich) and gold nanoparticles (average diameter 60 nm, Ted Pella) (Wan Ismail *et al.,* 2015). For the random lasers based on fluorescence resonance energy transfer, titania, (200 nm, $1\times10^{11}$ $cm^{-3}$) is added to a methanol solution of Rhodamine 6G ($5\times10^{-4}$ to $2\times10^{-3}$ M) and Oxazine 17 ($5\times10^{-4}$ M) (Sigma Aldrich). Random lasers based on localized surface plasmon effects incorporated gold nanoparticles at varying concentrations (from 3 x $10^{9}$ to 1 x $10^{12}$ $cm^{-3}$) with methanol solutions of rhodamine dyes ($10^{-3}$ M). The random laser suspensions were ultrasonically mixed to break up aggregates immediately before the laser experiments. For the laser experiments, the suspensions were placed in a 1 cm quartz cuvette containing a piece of teflon to suppress back-face reflections.

The pump source for the experiments was a Q-switched frequency-doubled Nd:YAG laser operating at 10 Hz pulse repetition rate with 4 ns pulse width. The front face of the random laser cuvette was irradiated at an incident angle of 30° to the normal to the front face with the pump light focussed using a 10 cm focal length lens to produce an excitation area of 1 mm diameter at the cuvette. The emission light at an angle of 45° to the cuvette's front face was collected by a lens and delivered to a fibre-coupled spectrometer (Ocean Optics USB2000 + UV-VS-ES



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with ~1 nm spectral resolution).

# 3 RESONANCE ENERGY TRANSFER

## 3.1 Extended Operating Wavelength Range of Random Dye Lasers

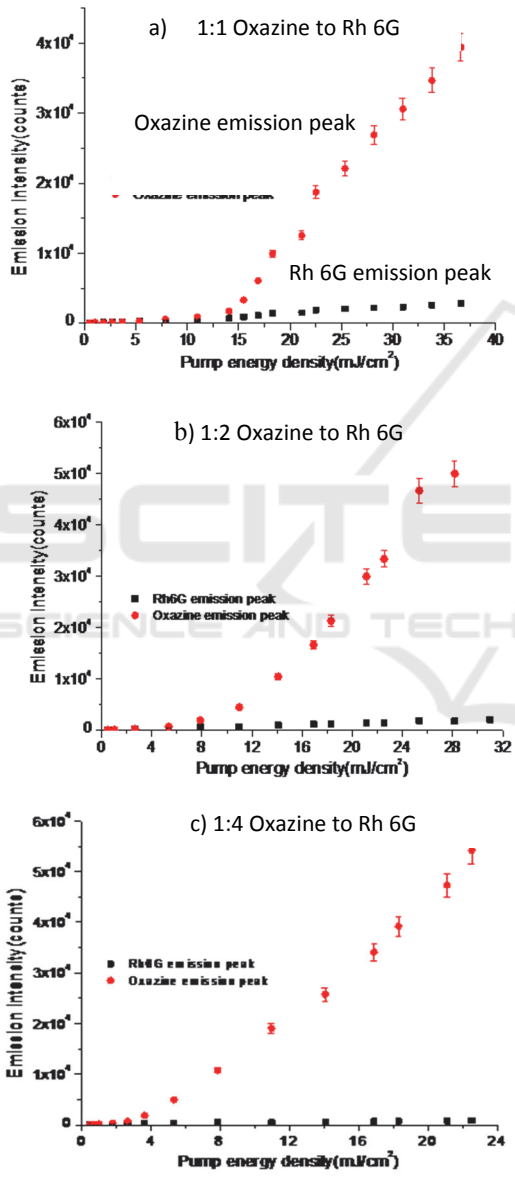


Figure 1: The peak emission intensity of Oxazine/ Rh6G/titania random lasers with different dye ratio combination; (a)1:1 (b)1:2 (c)1:4. The lasing threshold is observed for the oxazine emission peak when the emission intensity increases nonlinearly with the pump energy density.

Using combinations of fluorescent dyes, we can design effective energy transfer from a donor molecule to an emitter molecule by ensuring strong spectral overlap of the emitter absorption spectrum with the emission spectrum of the donor (Cerdan *et al.,* 2012). This can extend the operational wavelength of a laser for example (Alee *et al.,* 2013). We have investigated various dye combinations and concentrations to explore the efficiency of the energy transfer. Here we demonstrate near-IR emission beyond 700 nm from a 532 nm pump laser via resonant energy transfer from Rhodamine 6G to Oxazine dye, as an example.

Random lasing emission beyond 700 nm is achieved by combining two dyes with scatterers. Oxazine dye is a less efficient dye for random lasers excited with 532 nm green light but with the addition of Rhodamine 6G (Rh 6G), Oxazine can reach laser threshold. We obtain the most efficient transfer in the weakly scattering regime (with a scattering length of order 1 mm).

Figure 1 shows laser operation for a series of random lasers with Rhodamine 6G (5 x $10^{-4}$ to $2\times10^{-3}$ M) and oxazine ($5\times10^{-4}$ M) incorporating titania nanoparticles ($1\times10^{11}$ cm) as scatterers. The dye mixtures are in the ratios: 1:1, 1:2 and 1:4 for a mixture of Oxazine: Rh 6G. Figure 2 shows emission spectra from the lasers below and above laser threshold.

Figure 1 shows that the random laser threshold for Oxazine emission reduces gradually when the dye ratio increases. Increasing the concentration of Rh 6G increases the Oxazine lasing threshold due to the competition between Rh 6G emission and Oxazine emission. By providing high gain to the Rh 6G, the laser is driven to emit at the Rh 6G emission wavelength and this disrupts the energy transfer process to the Oxazine, leading to an increased lasing threshold.

# 4 LOCALISED SURFACE PLASMON RESONANCE

## 4.1 Random Lasers based on Rhodamine / Gold Compared with Rhodamine / Alumina

When metallic (gold) nanoparticles are added to random lasers incorporating Rhodamine 640 or Rhodamine 6G dyes, we observe a combination of resonance energy transfer with localized field enhancement which leads to increased emission

intensity and decreased laser threshold (Sen *et al.,* 2007). However if there is strong spectral overlap of the gold particles with the dye, excitation of the gold nanoparticles quenches the dye fluorescence, reducing the emission intensity. This may be overcome using specific nanoparticles or dye combinations (Xiaoyu *et al.,* 2013).

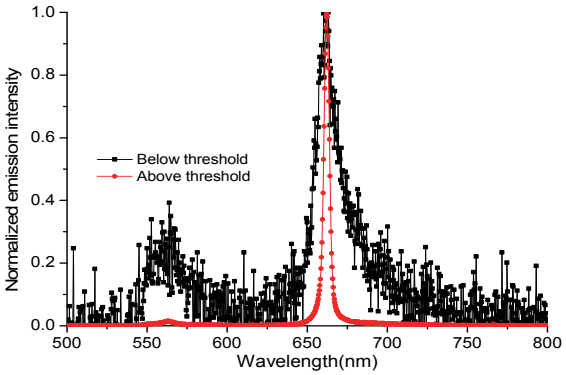


Figure 2: The emission spectra of Rh 6G ($2\times10^{-3}$M) with oxazine ($5\times10^{-4}$M) and titania ($1\times10^{11}$cm) random lasers below (3 mJ/cm$^2$) and above (8 mJ/cm$^2$) laser threshold.

Table 1 shows the lasing thresholds for Rh 640 / gold and Rh 6G / gold random lasers, indicating that the lowest lasing threshold occurs for $8\times10^{10}$ cm$^{-3}$ of gold nanoparticle concentration in both cases. The threshold increases in the weakly scattering regime for gold nanoparticle concentrations below this concentration, and also increases in the diffusive scattering regime above this concentration. For similar particle concentrations ($3\times10^{10}$ cm$^{-3}$), the lasing threshold of the Rh 640 / gold random lasers is ~18 mJ/cm$^2$, considerably lower than that for Rh 640 / alumina random lasers (~43 mJ/cm$^2$), shown in Table 2. Likewise, the lasing threshold of the Rh 6G / gold random lasers (~21 mJ/cm$^2$) is also considerably lower than that for Rh6G / alumina random lasers (~40 mJ/cm$^2$).

The decrease of the lasing threshold in these Rhodamine random lasers with the addition of gold nanoparticles is attributed to enhanced fluorescence from localised surface plasmon effects. Emission from both the Rhodamine dyes is absorbed by the gold nanoparticles. This leads to a concentration of the local electric field induced by excited surface plasmons at the gold nanoparticle surfaces. The excitation at the particle surface gives a concentrated local electric field with increased absorption by the dye and thus more amplification. The increase in the lasing threshold for higher gold nanoparticle concentrations is attributed to fluorescence quenching of the dye molecules due to non-radiative surface energy transfer from the excited dye to gold nanoparticles.

The scattering mean free path, $l_s$ at a pump wavelength of 530 nm for random dye lasers with alumina ranges from 0.35 mm, in the diffusive scattering regime (*sample size* > $l_s$ > $\lambda$) to 11.6 mm, in the weakly scattering regime ($l_s \geqslant$ *sample size*). The lasing threshold decreases when the scattering mean free path is decreased. In the Rh 640 / alumina and Rh 6G / alumina random lasers, the lasing threshold reduces with increasing alumina concentration and there is no additional loss for high alumina concentrations.

Table 1: Lasing threshold for Rh 640 and Rh 6G ($10^{-3}$ M) random lasers with various concentrations of gold nanoparticles.

| Gold nanoparticle concentration (cm$^{-3}$) | Rh 640 Laser threshold mJ/cm$^2$ | Rh 6G Laser threshold mJ/cm$^2$ |
|---|---|---|
| 3x $10^9$ | 27 | 28 |
| 3x$10^{10}$ | 18 | 21 |
| 8x$10^{10}$ | 13 | 15 |
| 3x$10^{11}$ | 21 | 28 |
| 1x$10^{12}$ | 26 | 32 |

Table 2: Lasing threshold for Rh 640 and Rh 6G ($10^{-3}$ M) random lasers with various concentrations of alumina nanoparticles.

| Alumina nanoparticle concentration (cm$^{-3}$) | Rh 640 Laser threshold mJ/cm$^2$ | Rh 6G Laser threshold mJ/cm$^2$ |
|---|---|---|
| 3x $10^9$ | No lasing | No lasing |
| 3x$10^{10}$ | 43 | 40 |
| 3x$10^{11}$ | 35 | 33 |
| 1x$10^{12}$ | 31 | 24 |

In the weakly scattering and diffusive scattering regimes, the scattering length $l_s$ for a wavelength of 530 nm for random dye lasers with gold nanoparticles varies from 0.42 mm to 111.1 mm, respectively. This is roughly as large as the size of the lasing region.

## 5 CONCLUSIONS

We demonstrate that random laser performance can be improved with addition of moderate concentrations of metallic nanoparticles (substituting for dielectric nanoparticle scatterers), and by selecting appropriate dyes for efficient radiative energy transfer. We examine the effect of localised surface plasmons and Fluorescence Resonance

Energy Transfer (FRET) on random laser performance incorporating Rhodamine dyes with alternative dyes and metallic nanoparticles.

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