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Two-photon pumping of random lasers by picosecond and nanosecond lasers

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ABSTRACT We experimentally demonstrated two-photon pumping of random lasers using picosecond and nanosecond pump lasers. The picosecond laser pumping experiment was performed with 400 ps laser pulses at 770 nm, and the gain media was a Coumarin 480D dye solution doped with TiO_2 nanoparticles. Onset of laser action was observed at a pump laser pulse energy below 500 μJ. The nanosecond laser pumping experiment was performed with 7 ns laser pulses at 1064 nm, and the gain media was a Rhodamine 640 dye solution doped with TiO_2 nanoparticles. Onset of laser action was observed at a pump laser energy ~ 18 mJ. Our results suggest that there exists an optimal pulse duration of the pumping laser in two-photon pumped random lasing that leads to minimum photodamage of the gain media and still keeps a high pumping efficiency.

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1 Introduction

Since the first experimental demonstration of laser action in an optically pumped solution of Rhodamine 640 perchlorate doped with TiO_2 scatters [1], random lasing has been observed in a series of disordered media, including semiconductor powder [2], dye-doped gelatin containing scattering particles [3], dye infiltrated animal tissues [4], and dye infiltrated human tissues [5]. Until now, most of random lasing experiments were performed using one-photon excitation. However, a random laser based on two-photon excitation is very attractive to medical application due to the fact that the use of near infrared light usually provides better penetration depth into highly scattering media than visible light [6]; thus, it can potentially become a three-dimensional imaging tool for diagnostic of tumors beneath skin [5]. Although G. Zacharakis et al. have reported a two-photon pumped random laser in dye-doped gelatin cubes containing TiO_2 nanoparticles using a 200 fs Ti:sapphire laser at 800 nm as pump source [7], we are skeptical whether this technique can really be applied on diagnostic of human tissue because of the high peak intensity ($\sim 2 \times 10^{11}$ W/cm^2) required for their lasing threshold. For example, König et al. reported that a 50% cloning efficiency of CHO cells (50% of cells failed normal cell division) occurred at a peak intensity of approximate 3.5×10^{11} W/cm^2 for 240 fs pulses at 780 nm wavelength [8]. Therefore, in order to apply two-photon pumped random lasing in medical applications, it is necessary to optimize the excitation pulse condition so that both the high pump efficiency and the low tissue damage can simultaneously be attained.

Althoughh femtosecond (fs) lasers of pulse durations below 500 fs are widely used as light sources for multiphoton excitation of fluorescent dyes in scanning laser microscopy due to their high excitation efficiency [9], such short laser pulses may not be the optimal sources for the two-photon pumping of random lasers. In multiphoton microscopy, the high excitation efficiency of fs laser pulse comes from its high peak intensity, which is a result of a constructive superposition of a series of waves within the bandwidth of the fs laser pulse. For example, the bandwidth of a 200 fs laser pulse with its central wavelength at 800 nm is approximately 5 nm. When the 200 fs pulse propagates in a disordered media, strong scattering will occur which destroys the phase correlation between the waves of different wavelengths, causing elongation of the pulse duration. In fact, D. Oron et al. have suggested that an ultrashort pulse impinging on a scattering plate, such as a piece of ground glass, will not only spatially but also temporally disperse after passing through the plate [10]. Similarly, in the case of the two-photon pumping of random laser, the temporal dispersion of the fs laser pulse will also occur, which reduces the peak intensity, and in turn, the two-photon pump efficiency. To compensate for this loss of pump efficiency, high pump fluence becomes necessary when ultrashort pulses with wide bandwidth are used. It is interesting that until now the change of the temporal pulse shape during the fs laser pumping of random laser has not been discussed. Nevertheless, based on this consideration, we carried out two-photon pumped random lasing experiments, using relatively long pulse durations, such as picosecond (ps) and nanosecond (ns) laser pulses. Additionally, if the central wavelength of the pump laser is near 800 nm, the use of the long pulses in the two-photon pumped random lasing might provide another advantage – reducing the phototoxicity effect caused by the three-photon absorption of Tryptophan, because Tryptophan has a strong one-photon absorption peak in the wavelength range of 260–280 nm (approximately one-

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third of the 800 nm excitation wavelength) and is abundant in bio-tissue [11]. As the pump laser pulse duration becomes longer, the three-photon absorption efficiency of Tryptophan will decrease faster than the two-photon pump efficiency of dye due to its higher nonlinearity.

2 Experiments and results

We prepared two types of random media for our experiments. The one used in the ps laser pumping experiment was Coumarin 480D dye dissolved in ethanol and doped with TiO_2 nanoparticles, and the other one used in the ns laser pumping experiment was Rhodamine 640 (Rh640) dye dissolved in ethanol and doped with TiO_2 nanoparticles. We prepared the Coumarin 480D dye solutions with different concentrations in the range of 10 mM to 40 mM; and the Rh640 dye solutions with different concentrations in the range of 9 mM to 26 mM. The TiO_2 nanoparticles had a diameter of approximate 400 nm. The TiO_2 nanoparticles were first dissolved in distilled water at various concentrations in the range of 10 mg/mL to 300 mg/mL, and then the dye solution and the TiO_2 solution were mixed with each other at a ratio of 1 : 1. The mixture was immediately used in the experiment. We performed two-photon pumping of random lasers with either a home-built Ti:sapphire laser (770 nm, 400 ps, 10 Hz) or a commercial Nd:YAG laser (1064 nm, 7 ns, 10 Hz, Continuum, Minilite II). In both experiments, the laser beams were first passed through an aperture of 5 mm diameter, and then focused onto a cuvette containing the random media by a lens with a focal length of 600 mm. The emission spectra were recorded by a spectrometer (USB2000, Ocean Optics Inc.).

First, we performed the two-photon pumping of random laser using the ns laser. The concentrations of the Rh640 dye solution and the TiO_2 nanoparticles solution were 18 mM and 150 mg/mL, respectively. Then the two solutions were mixed with each other at a ratio of 1 : 1 and were immediately used in the experiment. Shown in Fig. 1a are the spectra recorded at different pump pulse energies. Clearly, the fluorescence spectrum became narrow when the pump pulse energy increased. The narrowest spectrum width we obtained was ~ 13 nm at the highest pump pulse energy of 26 mJ. Even narrower spectrum width could be expected if higher pump pulse energy were used; however, the pump pulse energy was limited by the output power of our Nd:YAG laser. Figure 1b shows the spectrum width of the two-photon pumped random laser as a function of the pump pulse energy. As one can see, when the pump pulse energy was raised above the threshold energy (~ 18 mJ), the fluorescence spectrum width decreased at a higher rate with the increasing pump pulse energy. Based on the focal spot size of our pump laser beam, the calculated threshold intensity is $\sim 3 \times 10^9$ W/cm^2.

Another interesting finding in the ns laser pumped two-photon random laser is a red-shifted spectrum peak. Figure 2 shows both the fluorescence spectra from a solution of Rh640 dye dissolved in ethanol (18 mM) without doping of nanoparticles and from the Rh640 dye solution doped with TiO_2 nanoparticles (same as the mixture mentioned above) pumped by the 1064 nm Nd:YAG laser. The pump pulse energy was 8.4 mJ in both measurements, which is significantly lower than the pump pulse threshold energy of random laser. Interestingly, the two spectra are significantly different from each other. The fluorescence spectrum of the dye solution doped with TiO_2 nanoparticles was broader than that from the pure dye solution, and its peak was red-shifted. In fact, as also can be seen in Fig. 1, the peak of the spectrum of the fluorescence emission from the TiO_2 nanoparticle-doped dye solution kept on shifting to red part of the spectrum when the pump pulse energy was increasing. The peak of the two-photon pumped random laser spectrum was, therefore, near 650 nm. Although it should be further investigated, we conjecture that the red-shifting of the laser spectrum peak in the two-photon pumped

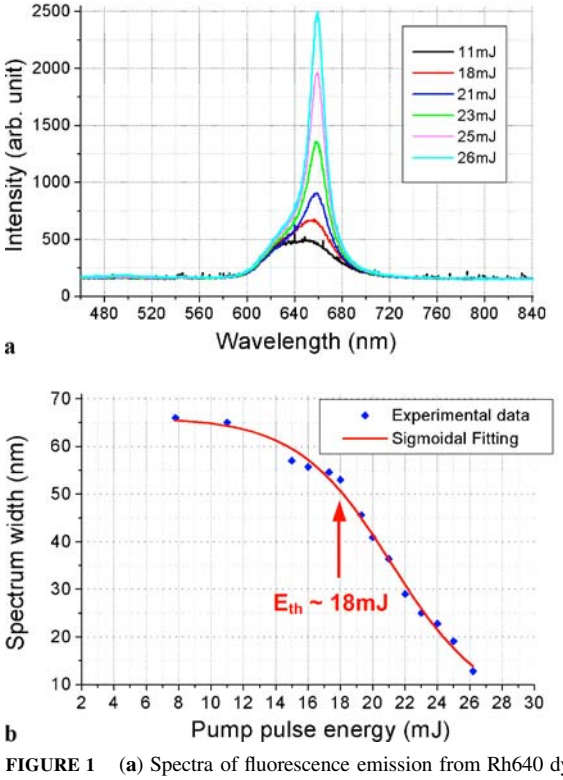

FIGURE 1 (**a**) Spectra of fluorescence emission from Rh640 dye solution doped with TiO_2 nanoparticles and pumped by 1064 nm Nd:YAG laser at different pulse energies; (**b**) spectrum width of ns laser pumped two-photon random laser as a function of pump pulse energy

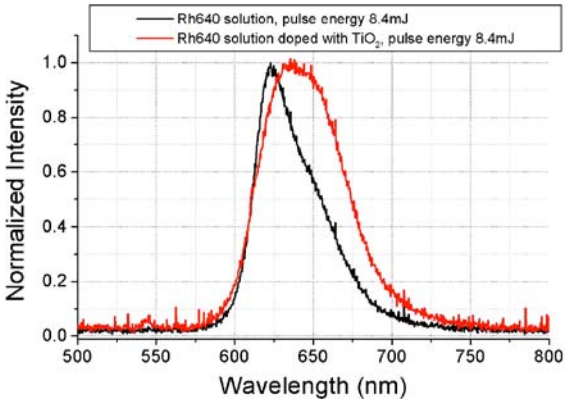

FIGURE 2 Spectra of fluorescence emission from pure Rh640 dye solution and dye solution doped with TiO_2 nanoparticles. In both cases, the pump pulse energies of the 1064 nm Nd:YAG laser were 8.4 mJ

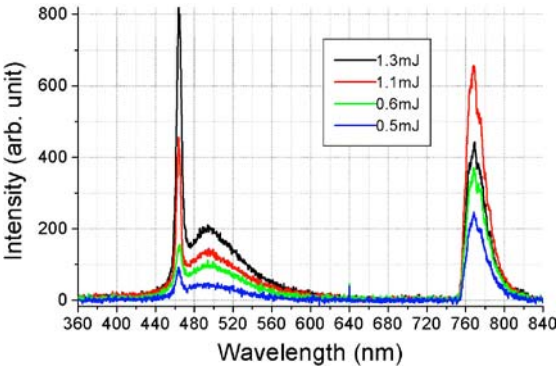

FIGURE 3 Spectra of fluorescence emission from Coumarin 480D dye solution doped with TiO_2 nanoparticles and pumped by 770 nm Ti:sapphire laser of 400 ps pulse duration at difference pulse energies

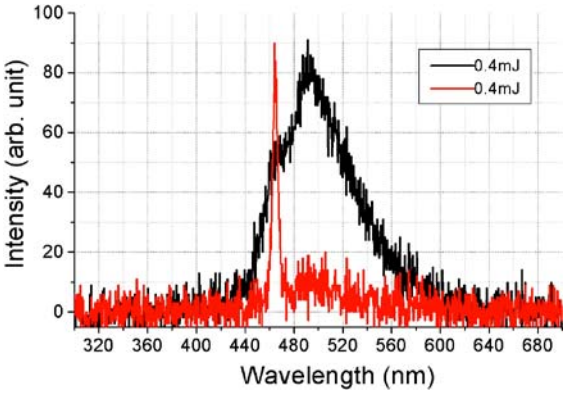

FIGURE 4 Different spectra of fluorescence emissions from Coumarin 480D dye solution doped with TiO_2 nanoparticles and pumped by 770 nm Ti:sapphire laser at a same pulse energy of 0.4 mJ

random laser is a result of the re-absorption of the fluorescence emission in the blue part of the spectrum. Actually, we also carried out one-photon pumped random lasing experiment using a frequency-doubled Nd:YAG laser at 532 nm to pump the above random medium, and the observed peak of laser spectrum was near 610 nm (data not shown here). An essential difference between the two-photon pumped and the one-photon pumped random lasers is that, in the former case, the excitation volume could be expanded in the longitudinal direction because of the greater penetration depth of the longer wavelength, leading to increased scattering times in colloidal solution and consequently, the longer propagation distance of the fluorescence photons in the random media. Namely, the two-photon pumping scheme produces a three-dimensional excitation volume rather than a two-dimensional one. Therefore, the fluorescence in the blue part of the spectrum could be more easily re-absorbed in the two-photon pumped random media, pushing the peak of laser spectrum toward longer wavelength.

Since the pump pulse threshold energy of the ns laser pumped two-photon random laser was too high, we then carried out the ps laser pumped two-photon random lasing experiment. Shown in Fig. 3 are the random laser spectra from the Coumarin 480D dye solution ($\sim$ 30 mM) mixed with TiO_2 nanoparticles (100 mg/mL) and pumped by the 770 nm Ti:sapphire laser of 400 ps pulse duration at difference pulse energies. A spectrum width of 5.8 nm was observed with a pump pulse energy of 1.3 mJ. However, unlike the repeatable spectral shape observed in the ns laser pumped two-photon random lasing experiment, the spectra of the ps laser pumped two-photon random laser were somewhat unstable when low pump pulse energies were used. In fact, in our experiments, we found that there was no spectrum narrowing effect that could be observed for all the ps pump pulse energies under 250 μJ. After the pump pulse energy was raised to 300 μJ, a narrowed spectrum could be observed at a low frequency when the pump pulses continuously impinged onto the cuvette. The possibility of the occurrence of random lasing increases with the pump pulse energy. After the pump pulse energy was further increased to above 500 μJ, stable narrow emission spectra were observed. For example, the two different fluorescence spectra in Fig. 4 were measured under the same experimental conditions, with one showing laser-like emission spectrum but the other one only spontaneous emission spectrum. If we assume a threshold pulse energy of 400 μJ in the ps laser-pumped two-photon random lasing, then the calculated threshold intensity is $\sim 2 \times 10^9$ W/cm^2, which is two orders of magnitude lower than the threshold pump intensity of the 200 fs laser shown in [7]. The cause of the instability of the ps laser pumped random laser at low pump pulse energies is still unclear yet. One possibility is that there could be a fluctuation of the output power of our ps laser. Another possibility is the instability of the dye solution doped with TiO_2 nanoparticles. Since our experiments were carried out using a dye solution doped with TiO_2 nanoparticle, the nanoparticles could be moving around in the dye solution via Brownian motion, and they would also gradually sink into the bottom of the cuvette due to gravity; therefore, the distribution and the density of the TiO_2 particles in the solution were changing all the time. Nevertheless, compared to the ns laser pumped two-photon random laser, the ps laser pumped random laser is much more sensitive to the experimental conditions. This difference also implies that the mechanisms behind the ps laser and ns laser pumped two-photon random lasers might be completely different. Namely, the ns laser pumped random laser could be an amplified spontaneous emission (ASE), which is also referred as to random lasing with nonresonant feedback; and the ps laser pumped random laser could be a "true" random laser or a random laser with coherent feedback [12].

3 Discussions and conclusion

In order to understand the advantage of using a ps laser as the light source in two-photon pumping of random laser, we now compare our result with the fs laser pumped random laser in [7]. Generally speaking, the realization of random laser requires a certain quantity of the dye molecules to be pumped to the excited state so that the optical gain in the disordered media can be higher than the optical loss. If the pump pulses are significantly shorter than the decay time of dye fluorescence, then spontaneous emission from the dye can be neglected in the pump pulse duration. Furthermore, we assume that the two-photon excitation in either of our experiments or in [7] is in the linear regime where saturation doesn't occur, because the two-photon absorption cross-sections of most fluorescent dyes are only at a level of

2×10^{-50}–2×10^{-49} cm^4 s/photon [13] with which both the fs and the ps pump pulses can only excite a small part of dye molecules. Based on these assumptions, the quantity of the excited dyes can be easily determined as $N_E \propto I^2\tau$, where N_E is the population of excited dyes, I is the peak intensity of pump laser pulse, and τ is the pulse duration. From this equation, it is easy to theoretically predict that in order to obtain the same population of the excited dyes for initiating random lasing, the threshold intensity of the 400 ps pump laser pulse used in our experiment should be $1/\sqrt{2000} \approx 1/45$ of that of the 200 fs laser pulse, provided that all the other experimental conditions (such as focal spot sizes, scattering media, dye types, dye concentrations, density of TiO_2 nanoparticles, and so on) are close to each other in both experiments. However, we experimentally showed a 100-fold reduced pump intensity for the 400 ps pulse to reach the random lasing threshold, as compared with the fs laser pumped two-photon random laser in [7]. We speculate that the temporal elongation of the 200 fs laser pulse in the random media might be an important factor which makes the fs laser less efficient than the ps laser in the two-photon pumping of random lasing. Nevertheless, since it has been reported that the threshold fluence for ablation of bio-tissues could be dramatically higher with a ps laser than with a fs laser [14], it is reasonable to expect that ps lasers could be better sources than fs lasers to achieve two-photon pumped random lasing in bio-tissues.

We also found that the threshold pump intensity in two-photon random lasing cannot be further reduced by simply extending the pulse duration, such as shown in our ns laser pumping experiment. Since most laser dyes have a lifetime of a few ns, spontaneous emission during the ns pump pulses will significantly reduce the population of the excited dyes. This means a reduction of pump efficiency. Besides, the high pulse energy ($\sim$ 18 mJ) carried by the ns pulses will deposit much heat in the focal spot area, causing severe thermal effect. For these reasons, we consider that ns pump lasers might not be good candidates for two-photon pumping of random laser in medical applications. However, from a scientific point of view, the different behaviors between the ns laser pumped one-photon and two-photon random lasers may present a clue of the enhanced penetration depth for the two-photon pumping scheme. In fact, the bichromatic emission from one-photon pumped scattering media has been intensively investigated, and different models were proposed for explaining this phenomenon [15–17]. To date, the observation of dichromatic emission from one-photon and two-photon pumped scattering media has not been reported; thus, it deserves more investigation.

To summarize, we demonstrated the two-photon pumped random lasers using either ps or ns laser pulses. Our results suggest that it is necessary to select a proper pulse duration in the two-photon pumped random lasers for minimize the photodamage of working media, which is extremely important for the potential application of random lasing as a three-dimensional imaging tool for diagnostic of tumors beneath the skin.

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