The Laser Generation Threshold Characteristics of a Colloidal Solution of Gold and Platinum Nanoparticles with Rodamine 6G

Valeriy A. Donchenko[1,2], Mikhail M. Zinoviev[1], Alexey A. Zemlyanov[2],
Vladimir A. Kharenkov[1,2], Anna N. Panamaryova[3]
[1]National Research Tomsk State University, Tomsk, Russia
[2]Siberian Physical Technical Institute, Tomsk, Russia
[3] National Research Tomsk Polytechnic University, Tomsk, Russia

***Abstract* – In the work the spectral-energy characteristics of stochastic (non-resonator) laser generation of a thin layer of organic dye Rhodamine 6G solution with the addition of gold and platinum nanoparticles in the form of a colloidal solution in ethanol have been experimentally investigated. It has been experimentally established that the generation thresholds are reduced by two orders when adding nanoparticles to the active medium. It is shown that the use of nanoparticles having a plasmon absorption band in the region of the agitation radiation does not lead to a significant change of the active medium generation thresholds.**

***Index Terms* – Nanoparticles, resonatorless generation, plasmon resonance, generation thresholds.**

I. Introduction

Today the objects of nano-scale dimensions such as metal nanoparticles as well as their properties, particularly optical, are of great interest for scientists. With the help of such nanoparticles it is possible to generate laser radiation in strongly scattering reinforcing active media - organic laser dyes. Currently, there is a separate branch of physics devoted to the methods for laser radiation generation in such media which is referred to as random lasing [1]. For getting laser generation it is necessary to achieve the condition of the active medium intensification excess over losses in it. This condition is in such composite media is carried out at a much lower threshold agitations (one to two orders) and is more effective compared to the generation in the same media but without nanodispersion filling [2,3].

Currently it is accepted that increasing lasing efficiency in such composites is due to the use of plasmon resonance nanoparticles [4,5], which in the visible range are silver and gold nanoparticles having plasmon resonances at wavelengths of 420 nm for silver nanoparticles, 530 nm to 565 nm for gold and copper. Other metal nanoparticles have a plasmon absorption spectrum of the UV region. The phenomenon of plasmon resonance is well studied and is related to the resonant interaction of an external electromagnetic field with a metal nanoparticle causing collective oscillations of electrons in the conductivity band.

It causes the spatial redistribution of the incident field forming regions of increased radiation power density by two or more orders greater than the density of the incident wave power.

This increases the number of excited molecules within these regions. Due to the Purcell effect [6-8] it is also possible to increase the speed of active medium molecules conversions from the excited level into the primary. As a result, during the agitation action, a large number of stimulated emissions of photons appear. This should lead to a decrease in the generation and intensity of emission of the active medium thresholds.

II. Problem Definition

In our study we investigated the spectral-energy characteristics of the laser dye Rhodamine 6G with the addition of gold and platinum nanoparticles. Platinum nanoparticle plasmon resonance lies in the UV region (215 nm) while for the gold nanoparticles it is in the visible region at a wavelength of 532 nm [9]. Therefore, the comparison of the optical characteristics (such as the intensity of the active medium radiation and the generation threshold) with the addition of these nanoparticles can help to assess the true contribution of the plasmon resonance in the generation of the studied active medium.

III. Experimental Methods

Colloidal gold and platinum solutions were prepared by laser ablation [10] in ethyl alcohol. For the nanoparticles ablation the focused radiation of the second harmonic of Nd: YAG-laser LS-2134UTFs with a wavelength of 532 nm, 7 ns pulse duration and pulse repetition rate of 15 Hz was used. The volume gold target (Pt) was irradiated in ethanol at an initial peak power density on the target surface 2 GW/cm^2. While the particles stabilizing in the solution, the radiation power density was decreasing on the target surface due to clouding. The irradiation time was 20 min. The concentration of nanoparticles in the sample was determined by measuring the mass loss of the target sample, normalized to a volume of liquid, and was equal for gold 1.47 g/l for platinum, 0.61 g/l. Attenuation spectra of colloidal solutions were recorded with a spectrophotometer Shimadzu UV-3600 in the spectral range 250-700 nm. Fig. 1 shows an absorption spectrum of a colloidal gold solution.

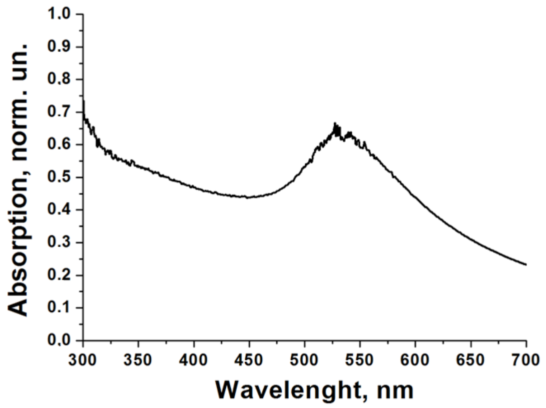


Fig. 1. The absorption spectrum of a colloidal solution of gold nanoparticles

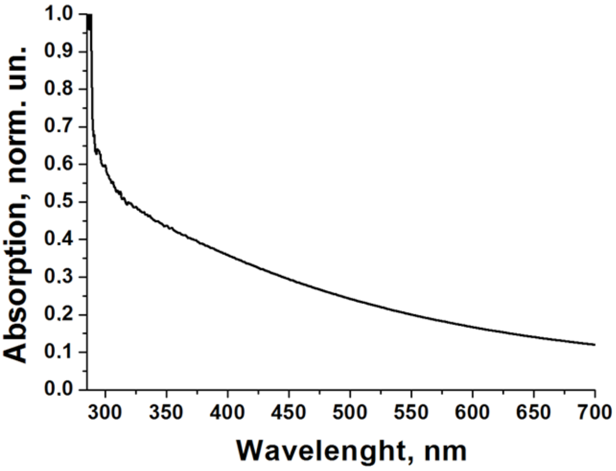


Fig. 2. The absorption spectrum of a colloidal solution of platinum nanoparticles

It is seen that the obtained absorption spectrum of gold nanoparticles has plasmon absorption peak at a wavelength of 530 nm. As in the experiment the radiation of the agitation at the wavelength of 532 nm was used, the conditions for manifestation of the plasmon resonance effect are performed. Fig. 2 shows the absorption spectrum of the colloidal platinum solution.

This absorption spectrum in the visible range does not have the plasma peaks. Indeed, platinum nanoparticles have a plasmon absorption band in the ultraviolet region of the spectrum at a wavelength of 215 nm what is also shown in the work [9]. Fig. 3 shows the obtained laser dye Rhodamine 6G absorption spectrum. It is seen that the maximum of the absorption spectrum lies in the vicinity of the agitation wavelength of 532 nm, therefore the dye will maximum efficiently convert agitation radiation energy into the energy of the active medium radiation.

On the basis of the ratio of 9 parts of colloidal alcohol solution to one portion of the laser dye Rhodamine 6G 10^{-2} m/l, we have obtained a concentration of the active dye solution 10^{-3} m/l and nanoparticles. This solution was placed between the slides, the thickness of the active layer was about 20 microns. Fig. 4 is a schematic diagram of the experimental setup in which the measurements were made.

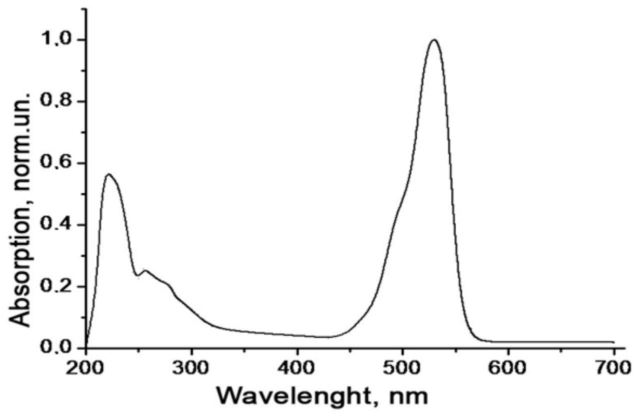


Fig. 3. The absorption spectrum of the laser dye Rhodamine 6G ethyl solution

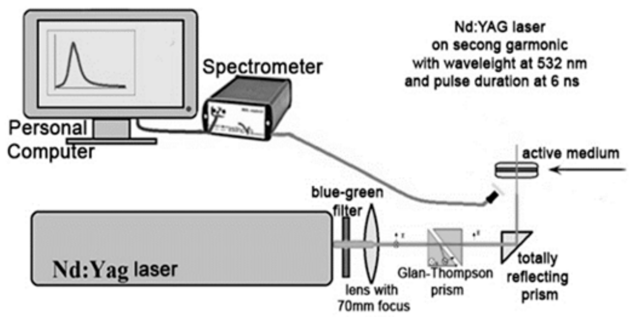


Fig. 4. Experimental setup

For excitation of the active solution Nd^{3+}:YAG-laser with the second harmonic generation with a wavelength $\lambda = 532$ nm was used. On the output laser window the filter Blue-green glass was installed to eliminate the first harmonic background radiation at the wavelength $\lambda = 1064$ nm. Continuous adjustment of the agitation power was carried out by a Glan-Thompson prism. The laser beam was focused to a diameter of approximately 2 mm with the help of the lens. The radiation receiver was a spectrometer AVASPEC ULS2048L-USB2, spectral range which ranges from 200 to 1100 nm with a resolution of 0.04 nm. The measurements were performed at the room temperature.

IV. Experimental Results

According to the experimental results, the dependences of the active medium radiation intensity and the agitation power threshold density on the volume fraction of nanoparticles have been obtained. They are presented in Fig. 5 and Fig. 6.

Fig. 5, 6 (curve 2) show the dependence of the agitation power threshold density on the concentration of nanoparticles in the active medium. It should be noted that the generation of pure dye Rhodamine 6G with the thickness of 20 microns is observed when the agitation power density of 10^8 W/cm^2. It is seen that the generation threshold in the case of adding the nanoparticles to the active medium is reduced by two orders. The difference in thresholds decrease in the case of nanoparticles of gold and platinum is 1.5 to 2 times, that is not significant in the background of total generation thresholds decrease by 100 times relatively pure dye.

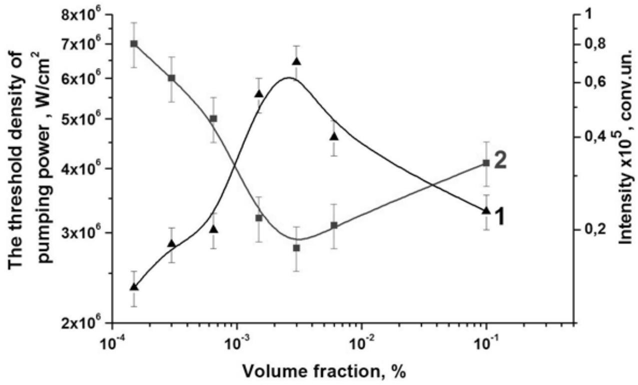


Fig. 5. Dependence of the active medium radiation intensity on the concentration of platinum nanoparticles (1); dependence of the agitation power threshold density on the concentration of platinum nanoparticles (2)

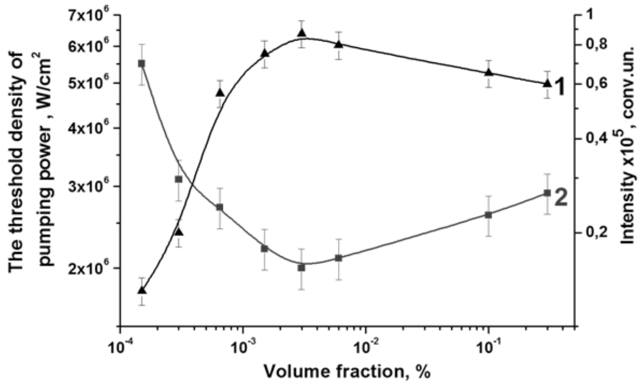


Fig. 6. Dependence of the active medium radiation intensity on the concentration of platinum nanoparticles (1); dependence of the agitation power threshold density on the concentration of platinum nanoparticles (2)

Also, Fig. 5, 6 (curves 1) show the dependence of the active medium radiation intensity on the concentration of nanoparticles in it at fixed agitation. It can also be noted that the difference of intensities is not essential in the case of platinum and gold nanoparticles. Thus, we can say that the gold nanoparticles having plasmon properties in agitation wavelength of 532 nm decrease laser generation thresholds not much more effectively than non-plasmon platinum nanoparticles.

Fig. 7 shows the dependence of the spectral width of the active medium generation on the concentration of the nanoparticles in it. This figure corresponds to Fig. 5, 6. The concentration range from 10^{-3} to 10^{-2} %, in which there is a maximum narrowing of the generation spectrum, coincides with the concentration range where minimum active medium generation thresholds and maximum intensity of its radiation are realized (also 10^{-3} up to 10^{-2} %).

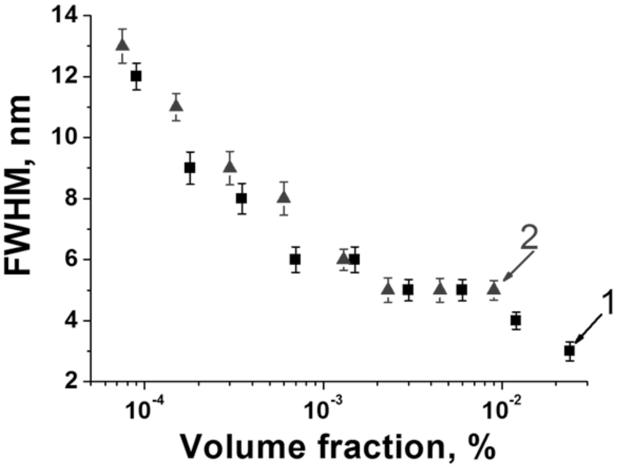


Fig. 7. Dependence of the laser generation spectrum width taken at a half-height on the concentration of gold nanoparticles (1) and platinum (2)

All this allows speaking about the efficiency of the generation in the range of gold and platinum nanoparticles concentrations from 10^{-3} to 10^{-2} % volume fraction.

V. Conclusion

This paper presents the results of the experiment on the determination of the active medium threshold characteristics - the dye Rhodamine 6G with the addition of colloidal solutions of platinum and gold nanoparticles. It is shown that in the spectrum of a colloidal solution of gold nanoparticle there is a plasmon absorption peak at an agitation wavelength of ~ 530 nm. Meanwhile, in the case of platinum nanoparticle, the plasmon absorption band lies in the ultraviolet region. It is shown that the use of plasmonic and non-plasmonic nanoparticles reduces the laser generation thresholds of the dye Rhodamine 6G more than two orders (100 times). It is shown that the difference in decrease of laser generation thresholds when using gold nanoparticles, having plasmon resonance at the agitation wavelength (532 nm), and platinum nanoparticles, that at a given wavelength don't have plasmon resonance, is not significant. The difference in the radiation intensities of the active medium at the same nanoparticles concentrations is also insignificant. In other words, the plasmon resonance effect makes a minor contribution to the picture of the generation of laser dye.

The work was performed as part of the Russian Ministry of the state task (task №2014 / 223, project code: 1347).

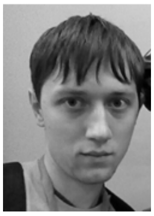
References

[1] V.S. Letokhov, «Generation of light in scattering medium with negative resonance absorption», ZETF, V. 53, No. 4, pp. 1442-1452, 1967.

[2] M.M. Zinovev, Al.A. Zemlyanov, A.V. Trifonova, V.A. Kharenkov, «The Lasing Thresholds Comparison in Active Medium Microlayers

with Metal and Dielectric Nanoparticles», EDM 2015, Erlagol, Altai 29 June - 3 July, pp. 282-284, 2015.
[3] D.S. Wiersma, A. Lagendijk, «Light diffusion with gain and random lasers», Phys. Rev.E., V.54, pp. 4256-4265, 1996.
[4] E. Fort, S. «Gresillon Surface enhanced fluorescence», Jpn. Appl. Phys. 2008. V. 45. № 17. P. 1265-1287.
[5] Armstrong R.L., Kim W.T., Shalaev V.M., and Safonov V.P. «Fractals in microcavities: giant coupled, multiplicative enhancement of optical responses», Phys. Rev. Lett., V.82, No. 24, pp. 4811-4814, 1999.
[6] E.M. Purcell «Spontaneous emission probabilities at radio frequencies», Phys.Rev. V.69, pp.681, 1946.
[7] V. Klimov, M. Dyuklua, V.S. Letokhov, «Spontaneous emission of an atom in the presence of nanobodies», Quantum. Electronics, V.31, No.7, pp. 569-586, 2001.
[8] D.V. Guzatov, V.V. Klimov, «Spontaneous emission of an atom located near a cluster of two spherical nanoparticles», Quantum Electronics, V.35, pp. 861-865, 2005.
[9] Yershov B.G. «Metal nanoparticles in aqueous solution: electronic, optical and catalytic properties», Rus. Chem. Journal, V. XLV, No. 3, pp. 20-30, 2001.
[10] V.A. Svetlichnyi, I.N. Lapin, «Structure and properties of nanoparticles fabricated by laser ablation of zn metal targets in water and ethanol», Russian Physics Journal, V. 56, No. 5, pp. 581-587, 2013.

Kharenkov Vladimir was born on October 24, 1988. Russian. In 2006 - 2010 he studied at the undergraduate, Tomsk State University, specialty “optical engineering”. In 2011-2012 studied at the magister, Tomsk State University, specialty “optical engineering”. From 2012, the graduate student at Tomsk State University, specialty “Optics”. In 2009 I was employed as a technician in the laboratory of optical waves propagation, the Siberian Physico-Technical Institute at the Tomsk State University. Since 2011, I hold rank of research engineer in the laboratory and take an active part in scientific researches. Winner of Presidential Scholarships for graduate students. In the summer of last year successfully completed his postgraduate TSU. Research interests: nanophotonics, nanoplasmonics, laser physics.



Zinoviev Mikhail was born on January 13, 1992. In 2010 entered the Radiophysics faculty of National Research Tomsk State University , he got Bachelor degree in 2014 and was admitted at the master`s program of the Optoelectronics System and Remote Sounding department of Radiophysics faculty. Currently he is the second year student in the master’s program in National Research Tomsk State University, Radiophysics faculty.