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Investigation of the influence of gold nanoparticles on stimulated luminescence of phenylamine 160 in ethanol

Investigations of the influence nanoparticles of gold on the properties of stimulated emission of phenylamine 160 in ethanol were carried out. Au nanoparticle ablation gold targets were obtained in standard second harmonic solid laser ND. The concentration of the nanoparticles Au was deyermined to change yhe mass of the target before and after ablation and amounted to 5*10-3 mol/l within 30 minutes ablation. The average size Au nanoparticles were determined by dynamic light scattering in sub-micron particles size analyzer Zetasizer Nano ZS. Measurements showed that the investigated wednesday the average size of nanoparticles is 80 nm. Nanoparticles of gold were obtained by laser ablation of a gold target in ethanol. The concentration of nanoparticles was determined from the change in the mass of the target before and after ablation. It is established that when 160 nanoparticles of gold are added to the phenylamine solution, an increase in laser radiation intensity of 1.4 times and a narrowing of the lasing band is observed 1.5 times. The generation intensity reaches a maximum value at a concentration of gold nanoparticles CAu = 10-4 mol/l. Given the kinetics of the luminescence of solutions F160 in ethanol in the presence of gold nanoparticles. It is shown that pulse generation does not exceed the duration of the pump pulse and is τген~of 7.4 NS. When added to a solution of gold nanoparticles SAI = 10-4 mol/l there is a reduction of the pulse duration generating τ~6.7 NS. The threshold for the onset of stimulated emission is reduced by a factor of 2.2. The duration of the generation pulse decreases 1.1 times.

Keywords: Gold nanoparticulars, dyes molecules, stimulated emission, plasmon effect, laser generation.

1. Introduction

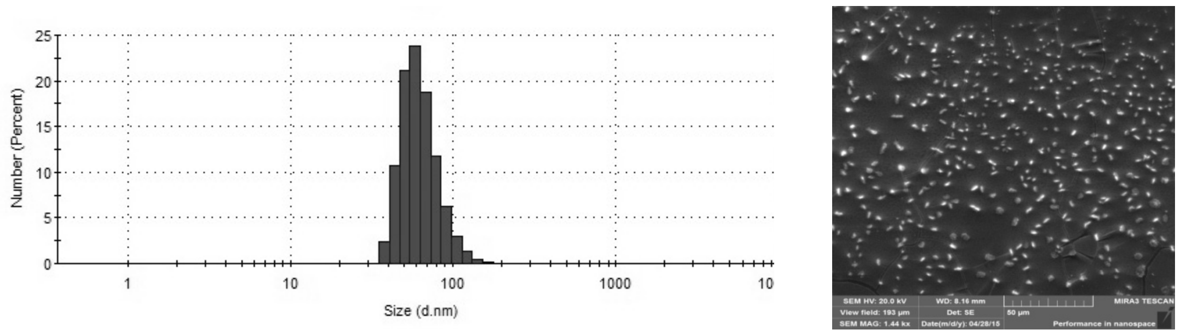
At the present time, studies are actively carried out related to the excitation of localized plasmon resonance (LPR) [1, 2]. Among the optical manifestations of LPR of nanoparticles (NP) metals, the most famous is the giant Raman scattering of light [3]. Luminophore molecules placed near the surface nanoparticles of metals also experience the effect of local electromagnetic fields. In this case, depending on the distance between the NP and the molecule, the fluorescence of the latter either increases or is quenched [4, 5]. At close distances and direct contact between NP and fluorophores, the luminescence is extinguished due to the predominance of nonradiative energy transfer from fluorescing molecules to NPs.

From a practical point of view, interest in the plasmon effect is associated with the possibility of creating highly sensitive luminescent sensors [6], optoelectronic devices [7], nanolazers [8], effective photovoltaic cells [9], etc. One of the modern promising directions of laser physics is the creation and study of composite media from laser-active molecules and metallic nanoclusters. There is evidence that the addition nanoparticles of metals to the active medium of dye lasers leads to a decrease in the lasing threshold [10].

2. Experimental

In this paper, we present the results of a study of the effect of metallic nanoparticles of gold (Au) NP on the generation properties of phenylamine 160 (Ph160) in ethanol.

Au nanoparticles were obtained by ablation of the gold target in ethanol with the second harmonic of the solid-state Nd laser LQ 215 (SOLAR). The concentration of Au nanoparticles was determined from the change in the mass of the target before and after ablation and amounted to $5*10^{-3}$ mol/l for 30 minutes of ablation. The average sizes of the Au nanoparticles were determined by dynamic light scattering using a Zetasizer Nano ZS submicron particle size analyzer. The measurements showed that the average nanoparticle size in the investigated medium is 80 nm (Fig. 1 a).



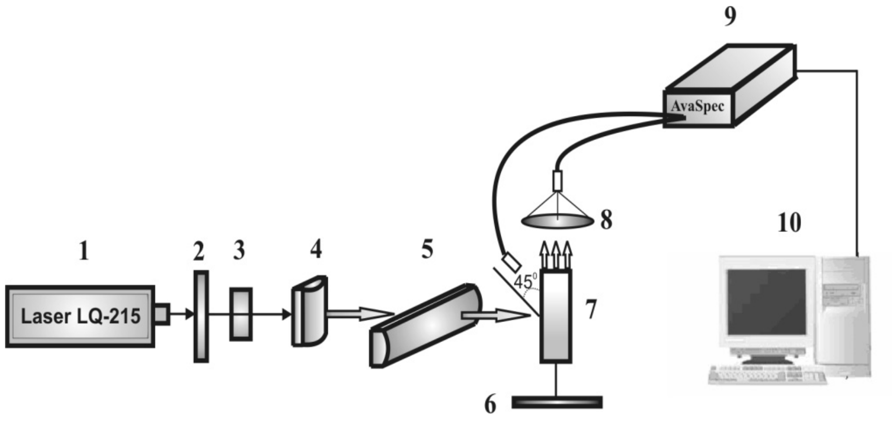
a b

Figure 1. Distribution of gold nanoparticles sizes in ethanol (a) and microscopic images of gold nanoparticles (b)

The morphology of the surface of nanoparticles was studied in the Tescan Mira 3MLU electron microscope. It was found that the predominantly spherical shape of the nanoparticles is observed in the investigated solvent (Fig. 1 b).

Measurement of the spectral characteristics of the stimulated emission of the samples was carried out in an installation whose block diagram is shown in Figure 2. Measurements of the spectral and energy characteristics of the stimulated luminescence were carried out by excitation of the samples with the second harmonic of the Nd: YAG laser (1) (SOLAR LQ 215, λ_{gen} = 532 nm, E_{imp} = 90 mJ, τ = 10 ns).

When measuring the characteristics of laser generation, an optical resonator was used, which was formed by a blind mirror (6) and the front face of the cuvette with the dye solution (7). The pump radiation passing through the diaphragm (3) with the help of cylindrical lenses (4, 5) was focused on the side face of the cuvette in a strip with an area of 0.07 cm^2. The radiation was generated in a narrow near-wall region from the side of the entrance wall of the cuvette.



1 — LQ 215; 2 — neutral density filters; 3 — diaphragm; 4.6 — lens; 5 — sample;
7 — AvaSpec-2048; 8 — computer

Figure 2. Diagram of an experimental setup for investigating the generation characteristics of molecular systems

The pump power density was varied with the help of neutral filters (2) and was 0.005-0.2 MW/cm^2. The luminescence signal with the help of a collecting lens (8) was focused on the optical fiber input of the AvaSpec-2048 spectrometer (9). The relative error in determining the spectral characteristics was 3%.

3. Results and discussion

Measurement of the absorption spectra of the films was carried out on a Cary UV-VIS (Agilent Technologies) spectrophotometer and Cary Eclipse fluorescence (Agilent Technologies). The absorption spectrum of nanoparticles of gold in ethanol (Fig. 3, curve 1) is a broad band with a maximum at 535 nm and overlaps well with the fluorescence and absorption spectra of phenylamine 160 (Ph160) (Fig. 3, curves 2, 3), which indicates the fulfillment of conditions plasmon resonance.

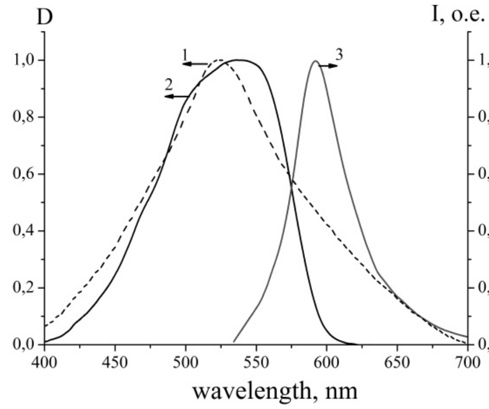
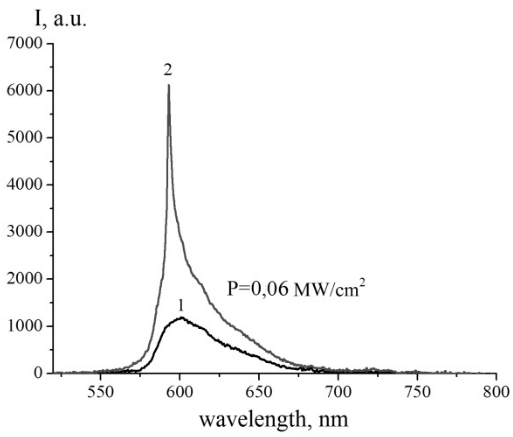


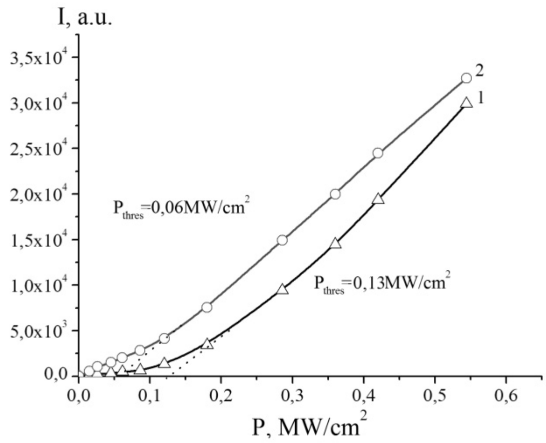
Figure 3. Relative location of the absorption spectra of Au nanoparticles (1), Ph160 (2) and dye fluorescence (3)

To study the generation characteristics Ph160) in ethanol with a concentration of 10^{-3} mol/l were used. Generation of the band of stimulated emission of the dye was obtained at the maximum of the band of the fluorescence spectrum. Figure 4 shows the spectrum of generation of laser radiation Ph160) in ethanol at a constant pumping power.



1 — pure dye; 2 — dye with gold nanoparticles

Figure 4. Spectra of radiation Ph160 in ethanol



1 — pure dye; 2 — Ph160 with 10^{-4} mol/l Au nanoparticles

Figure 5. Dependence of radiation intensity on pump energy

At low pump power densities, a fluorescence spectrum with spectrum characteristics is observed as for stationary excitation. With increasing pump power, the intensity of the maximum of the band increases with a simultaneous narrowing of the spectrum. With a power density of the pump source exceeding the value $P = 0.13$ MW/cm^2, laser dye radiation is generated with a maximum of the spectrum at a wavelength of 592 nm and a half-width of 11.8 nm.

When gold is added to the solution, an increase in the radiation intensity, a lowering of the laser radiation generation threshold, and narrowing of the lasing band (Fig. 5) occur. The maximum intensity of generation is observed at a concentration of nanoparticles $C_{Au} = 10^{-4}$ mol/l.

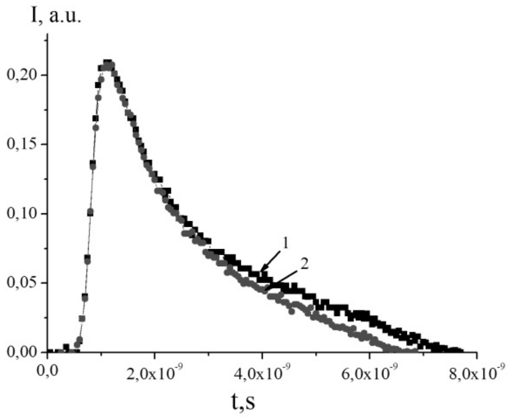
The influence of nanoparticles of Au on the generation properties of Ph160 in ethanol is presented in Table. It can be seen from Table 1 that at an optimum concentration of gold nanoparticles in solution, the half-width of the dye generation band decreases almost twofold. It was found that the dependence of the lasing intensity on the concentration of nanoparticles of gold correlates with the data on spontaneous fluorescence. This is an indication that stimulated emission is generated from spontaneous fluorescence.

T a b l e

Effect of Au nanoparticles on the generation properties of Ph160 in ethanol

C_{Au}, mol/l	$I_{\max}^{gen}$, a.u.	$\lambda_{\max}^{gen}$, nm	$\Delta\lambda_{1/2}$, nm
0	4254	592	11.8
10^{-6}	4550	592	9.3
10^{-5}	5156	593	8.6
$2*10^{-5}$	5648	592	8.1
10^{-4}	6145	592	7.8
$2*10^{-4}$	5185	591	8.4
$5*10^{-4}$	4354	592	9.7
10^{-3}	4158	592	12.3
$3*10^{-3}$	3979	592	14.5

A further increase in the power of the pump source leads to an increase in the radiation intensities and a narrowing of the lasing bands. The addition of gold nanoparticles to the solution of the investigated dyes leads to a reduction in the threshold for the onset of stimulated emission by 2.16 times (Fig. 4). Figure 6 shows the luminescence kinetics of solutions of Ph160 in ethanol in the presence of gold nanoparticles.



1 — without nanoparticles; 2 — with nanoparticles ($C_{Au} = 10^{-4}$ mol/l)

Figure 6. Effect of gold nanoparticles on the kinetics of generation of Ph160 in ethanol

The duration of the generation pulse does not exceed the duration of the pump pulse and amounts to t_{gen} ~ 7.4 ns (Fig. 5, curve 1). When gold nanoparticles $C_{Au} = 10^{-4}$ mol/l are added to the solution, the pulse duration of the generation pulse is reduced to ~6.7 ns (Fig. 6, curve 2).

4. Conclusion

The carried out researches have shown, that at addition in a solution of phenylamine of 160 nanoparticles of gold is growth of intensity of laser radiation, decrease in a threshold and narrowing of a lasing band is observed. The generation intensity reaches a maximum value at a concentration of gold nanoparticles $C_{Au} = 10^{-4}$ mol/l. The threshold of stimulated emission is reduced by 2.16 times. The duration of the generation pulse decreases 1.1 times.

Acknowledgements

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Этанолдағы фениламин 160 бояғышының еріксіз люминесценциясына алтын нанобөлшектердің әсерін зерттеу

Алтынның нанобөлшектер қасиеті еріксіз сәуле шығару фениламин 160 этанолдағы әсеріне зерттеулер жүргізілді. Алтын нанобөлшектері этанолдағы алтын нысан екінші гармоникалық қаттыденелі Nd лазерлік абляция арқылы алынды. Au нанобөлшектердің концентрациясы анықталып, массасы нысанаға дейін және кейін сейілуінің өзгерту бойынша және ішінде аблирлеу арқылы 5*10-3 моль/л-30 мин құрады. Au нанобөлшектерінің орташа мөлшері субмикронды бөлшектер Zetasizer Nano ZS динамикалық шашырау әдісімен жарық анализаторда белгілі болды. Өлшеу көрсеткендей, зерттелетін ортада нанобөлшектердің орташа мөлшері 80 нм. Фениламиннің ерітіндісіне 160 алтынның нанобөлшектерінің қосу кезінде лазерлік қарқындылығы сәуле шығару 1,4 есеге, жолақтың тарылу қарқыны 1,5 есеге өсті. Алтын нанобөлшектері концентрациясы C_{Au} = 10-4 моль/л кезінде генерациялау қарқындылығы максималды мәнге жетеді. Кинетика жарығы ерітінділердің Ф160 этанолдағы алтын нанобөлшектердің қатысуымен берілген. Көрсетілгендей, бұл импульстің ұзақтығы генерациялаудан аспайды, импульстің ұзақтығы τ~7,4 нс құрайды. Алтын нанобөлшектерін C_{Au} = 10-4 моль/л ерітіндіге қосқан кезінде генерация импульсінің ұзақтығы қысқарады $\tau_{ген}$~6,7 нс. Шегі туындаған мәжбүрлі сәулелену 2,2 есеге, генерация импульсінің ұзақтығы 1,1 есеге азаяды.

Кілт сөздер: алтын нанобөлшектері, молекула бояғыштары, еріксіз сәулелену, плазмондық эффект, лазерлік генерация.

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Исследование влияния наночастиц золота на вынужденную люминесценцию фениламина 160 в этаноле

Проведены исследования влияния наночастиц золота на свойства вынужденного излучения фениламина 160 в этаноле. Наночастицы Au были получены абляцией золотой мишени в этаноле второй гармоникой твердотельного Nd лазера. Концентрация наночастиц Au определялась по изменению массы мишени до и после абляции и составила $5*10^{-3}$ моль/л в течение 30 минут аблирования. Средние размеры наночастиц Au были определены методом динамического рассеяния света на анализаторе размера субмикронных частиц Zetasizer Nano ZS. Измерения показали, что в исследуемой среде средний размер наночастиц составляет 80 нм. Установлено, что при добавлении в раствор фениламина 160 наночастиц золота наблюдается рост интенсивности лазерного излучения в 1,4 раза и сужение полосы генерации в 1,5 раза. Интенсивность генерации достигает максимального значения при концентрации наночастиц золота $C_{Au} = 10^{-4}$ моль/л. Приведены кинетики свечения растворов Ф160 в этаноле в присутствии наночастиц золота. Показано, что длительность импульса генерации не превышает длительность импульса накачки и составляет $\tau_{ген}$~7,4 нс. При добавлении в раствор наночастиц золота $C_{Au} = 10^{-4}$ моль/л наблюдается сокращение длительности импульса генерации $\tau_{ген}$~6,7 нс. Порог возникновения вынужденного излучения сокращается в 2,2 раза. Длительность импульса генерации уменьшается в 1,1 раза.

Ключевые слова: наночастицы золота, молекулы красителя, вынужденное излучение, плазмонный эффект, лазерная генерация.

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