UDC 535.371:535.621:621.373:544.032

INFLUENCE OF Cu NANOPARTICLES ON ABSORPTION AND LUMINESCENT PROPERTIES OF OXAZINE 1 IN ETHANOL

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*Researches have shown that by adding Cu NPs C = 5 * 10^{-6} mol/l in a solution of dye the optical density at the absorption maximum is increased in 1.14 times. Fluorescence intensity at the maximum becomes 1.1 times bigger. Position of maxima of the bands and their half-widths are not changed. Threshold of the stimulated emission reduced and equals 5/8 of its initial value. The duration of the laser pulse is reduced by 0.3 ns.*

Keywords: laser ablation, copper nanoparticles, local plasmon resonance, absorption optical density, fluorescence intensity, stimulated emission, the pulse width generation

Introduction

Many researches related to the excitation of local plasmon resonance (LPR) of metal nanoparticles (NP) [1] are actively conducting now. Among optical appearences of LPR of metal NP the most noble is gigantic Raman scattering [2]. Fluorescence dye molecules placed near the surface of metal nanoparticles are also affected by local electromagnetic fields. At the same time, depending on the distance between the nanoparticles and the molecule, fluorescence of latter either amplified or damped [3]. At close distances and direct contact of nanoparticles to fluorophores, a glow is extinguished due to the prevalence of nonradiative energy transfer from the fluorescent molecules to the nanoparticle.

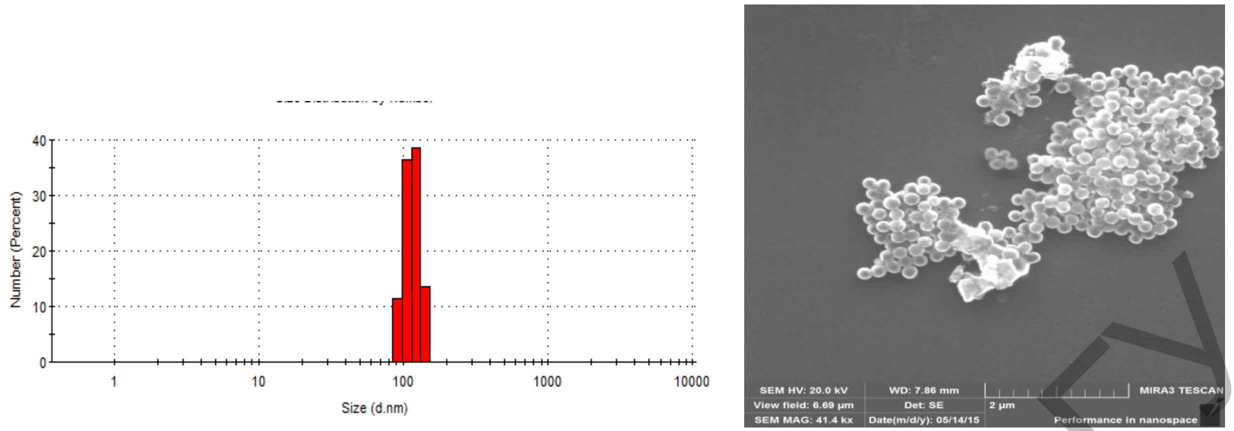
From a practical point of view, interest in plasmon effect is associated with the possibility to create a highly fluorescent sensors [4], optoelectronic devices [5], nanolasers, efficient photovoltaic cells], and others. One of the promising areas of modern laser physics is creating and investigating of composite media of the laser-active molecules and metal nanoclusters. Addition of metal NP in the active media of dye lasers leads to a decrease in the lasing threshold [6].

In this paper we conduct a study on the impact of metallic copper on the low absorption and luminescence oxazine 1.

1. Experimental part

Cu nanoparticles were obtained by ablation of a copper target in ethanol, the second harmonic of a solid-state laser Nd LQ - 215 (SOLAR). Cu nanoparticles concentration was determined by weight change of the target before and after the ablation and was 3.5*10^{-3} mol/l for 30 minutes ablation. The average size of Cu nanoparticles were determined by dynamic light scattering on the size analyzer of submicron particles Zetasizer Nano ZS.

Measurements showed that the average size of the nanoparticles is 115 nm (Figure 1, a) in the test environment. The morphology of the surface of the nanoparticles was studied with an electron microscope Tescan Mira 3MLU. It was found that in the test solvent is observed mainly spherical shaped nanoparticles, Figure 1, b.



a) б)

Fig.1. The average sizes (a) and microphotos (b) of Cu nanoparticles

2. Results and discussion

Register absorption and fluorescence spectra of the samples was carried out by the Solar SM2203 spectrometer. The absorption spectrum of Cu nanoparticles in ethanol (Figure 2) represents a broad band with a maximum at 586 nm. Oxazine 1 absorption spectrum in ethanol has a maximum at λ_{abso}^{max}= 650 nm and a half width of the strip $\Delta\lambda_{1/2}^{abso}$= 45 nm.

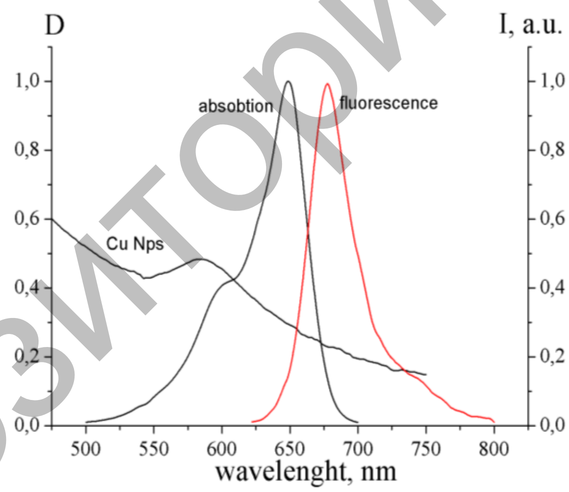
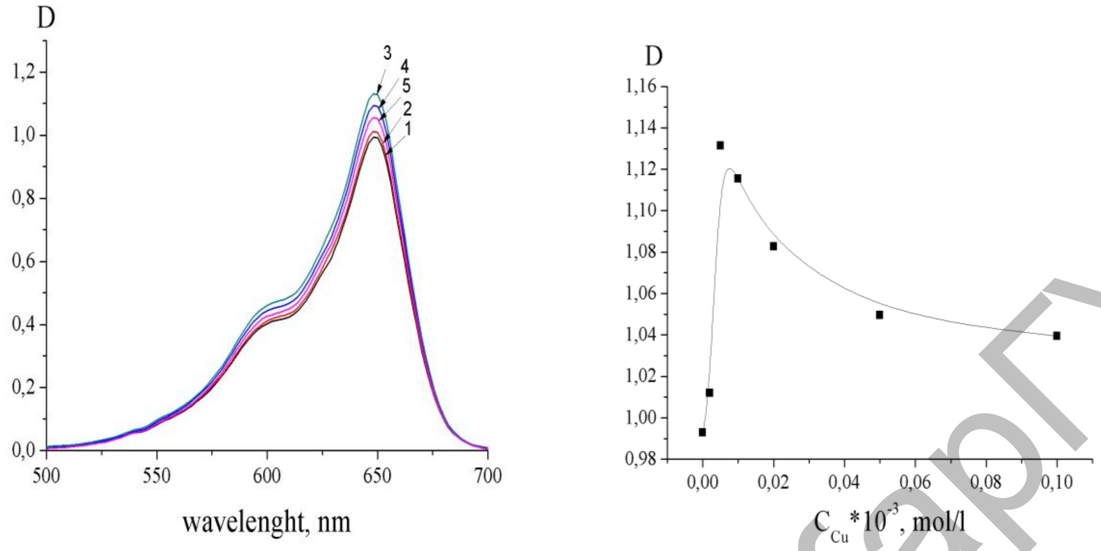


Fig.2. The relative position of the absorption and fluorescence spectra of the objects

Photoexcitation of the ethanol solution at λ_{exci} = 550 nm spontaneous fluorescence spectrum with a peak wavelength λ_{max}= 680 nm and a band-width $\Delta\lambda_{1/2}^{fluo}$ = 38 nm observed.

Figure 2 shows that the absorption spectrum of Cu NP overlaps with the absorption and fluorescence spectra of oxazine 1, indicating that the performance of the plasmon resonance conditions are fulfilled.

Figure 3 shows absorption spectra of dye molecules in the presence of Cu nanoparticles at different concentrations. At low concentrations of nanoparticles slight increase of absorbance of the dye solution in the maximum is observed.



1- 0 mol/l; 2-10^{-6} mol/l; 3- 5 * 10^{-6} mol/l; 4- 2 * 10^{-5} mol/l; 5- 5 * 10^{-5} mol/l.
Fig.3. Influence of Cu nanoparticles on the oxazine 1 absorption in ethanol

Adding copper nanoparticles with concentration equal to 5*10^{-6} mol/l in a dye solution (C_{dye} = 10^{-5} mol/l) absorbance grows 1.14 times at the maximum. Further concentration increase of the nanoparticles in a solution leads to a drop in optical density at the absorption maximum of the dye. The position of the maximum and its half-width do not change. Reducing optical density of the dye in the presence of metal nanoparticles observed in. Enhancement of absorption of the dye at low concentrations of the nanoparticles connected to the fact that the dye molecules are in the near field of metallic nanoparticles, plasmons in which are excited. Since the field near the nanoparticles significantly enhanced compared with the field of the incident light wave, the dye molecules in the near field absorb more than in the absence of nanoparticles in solution.

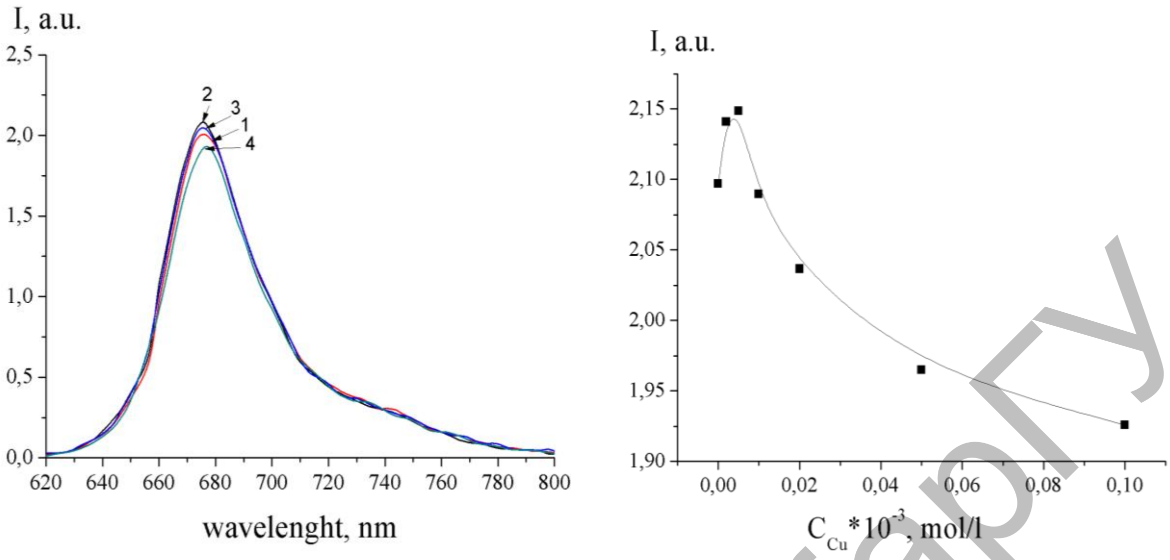
NP gets closer with each other as their number increases. This leads to increased interaction between them and NP clusters are organising when the distance is of the order of their size or less. Increasing of the size of the nanoparticles leads to an increase in the intensity of scattered light in the media. This may cause a decrease in the number of particles and excited plasmons and, as a result, decrease of absorption of the dye. In addition, strong light scattering can lead to the fact that photons incident on the solution cannot reach dye molecules and translucence will occur.

When photo excitation wavelength of an ethanol solution of the dye λ_{exci} = 550 nm and concentration equals 10^{-5} mol/l spontaneous fluorescence is observed (Figure 4). Adding copper NP in the alcoholic solution as a dye increases fluorescence instensity.

Oxazine 1 fluorescence intensity becomes 1.1 times stronger at the maximum. The intensity of the luminescence of the dye concentration increases until concentration will equal C_{Cu} = 5*10^{-6} mol/l, and further increase C_{Cu} leads to quenching of fluorescence (Figure 4). The position of the band maximum and its half-width does not change.

According to [7], greater fluorescence of the molecules near the metal nanoparticles is an increase in the fluorescence excitation rate due to local plasmon resonance. At the same time, the arrangement of molecules near the metal surface or in contact with it, nonradiative energy transfer from the molecules to the nanoparticles occurs, resulting in reduced probability of radiative decay of the excited molecules.

At low concentrations of nanoparticles, when they are far from dye's molecules, increase in fluorescence due to plasmon resonance occurs because of copper nanoparticles. At high concentrations of copper nanoparticles due to the decrease in the distance between the fluorophores and nanoparticles radiation less deactivation of the excited fluorescence state is dominating.

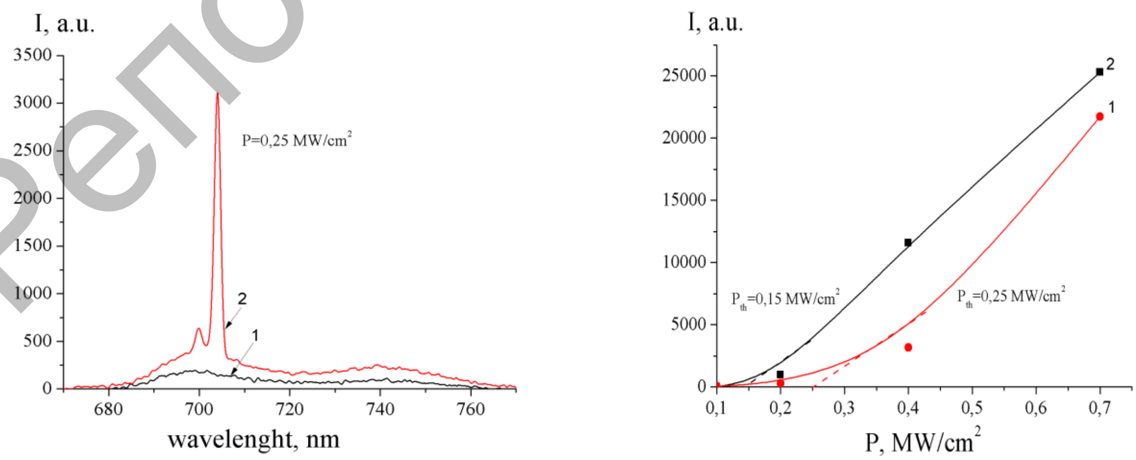


1-0 mol/l; 2-5*10^{-6} mol/l; 3-2*10^{-5} mol/l; 4-5*10^{-5} mol/l.

Fig.4. Effect of Cu nanoparticles on oxazine 1 fluorescence in ethanol

The intensity of fluorescence in solution with silver nanoparticles can be increased due to additional absorption of exciting emission, scattered by silver nanoparticles. However, at high concentrations of nanoparticles non-radiative decay channel of excited molecules is apparently determining.

The effect of the concentration of the nanoparticles on the lasing characteristics of the alcohol oxazine 1 solution with a concentration of 10^{-3} mol/l was investigated. Samples have been exciting by the second harmonic of SOLAR LQ 215 in (λ_{gen} = 532 nm, 90 mJ, T = 10 ns) laser in a glass cell of a cross form. If the value of the pump power density excesses the threshold generation, stimulated emission of two bands (λ_{gen1} = 700 nm, λ_{gen2} = 705 nm) is observed in the long-wavelength fluorescence band. A further increasing of the pump source power results in increased intensities of emission bands and in narrowing of generation band. Adding copper nanoparticles in the solution of investigating dyes leads to a decrease of the stimulated emission threshold and it becomes 1.6 times lower (Figure 5).

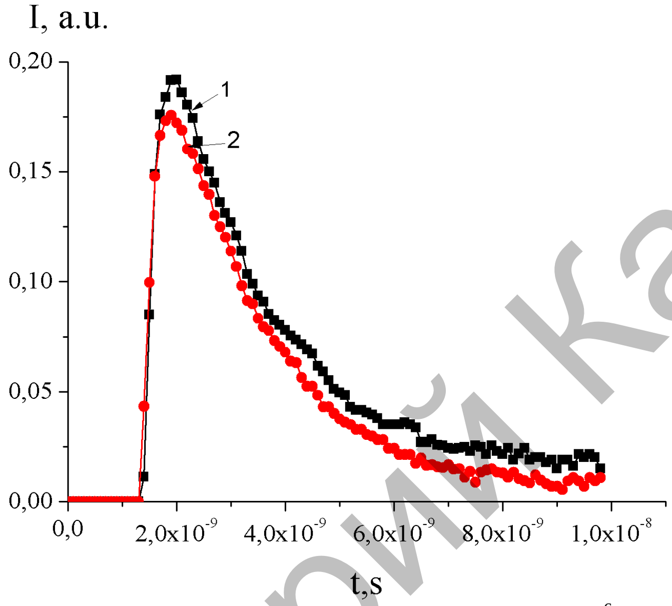


1- without nanoparticles; 2 nanoparticles

Fig.5. Influence of Cu nanoparticles on the threshold of a forced luminescence oxazine 1 in ethanol

Concentration values of Cu NPs corresponding to maximum fall of the lasing threshold, present themselves as concentrations of maximal fluorescence efficiency. Concentrations of Cu NPs, at which the maximum fall of the lasing threshold corresponding to a concentration of maximum fluorescence yield.

The time characteristics of solutions pulse emission were measured using picosecond DET025A (Thorlabs) receiver and DSO-X-3102A (Agilent Technologies) oscilloscope. The width of the time of the instrumental function of the measuring system at half maximum was equal 0.3 nanoseconds.



1- without nanoparticles; 2- with nanoparticles (P = 5 * 10^{-6} mol / l)

Fig.6. Influence of Cu nanoparticles on the kinetics of forced luminescence of oxazine 1 in ethanol

Figure 6 shows the kinetics of the luminescence of solutions oxazine 1 in ethanol. Generation impulse duration does not exceed the duration of the pump pulse and it is about τ_{gen}~8 ns (Figure 4, curve 1). When Cu nanoparticles C_{Cu} = 5*10^{-6} mol/l are added to a solution, observed decline in the duration of the laser pulse is about τ_{gen}~7.3 ns.

Conclusion

Thus, studies have shown that the addition of copper nanoparticles with concentration eqaul 5*10^{-6} mol/l to a dye solution, the optical density at the absorption maximum increases 1.14 times. Further increase of nanoparticles concentration in the solution leads to a decrease in the maximum optical density of the dye. Fluorescence intensity becomes 1.1 times bigger at the maximum. Position of maxima of the bands and their half-widths are not changed. Threshold of the stimulated emission is reduced 1.6 times. The duration of the laser pulse is reduced by 0.3 ns. Concentrations of Cu NPs, at which the maximum fall of the lasing threshold corresponding to a concentration of maximum fluorescence yield.

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Article accepted for publication 13.05.2016