UDC 535.371:535.621:621.373:544.032

INFLUENCE Au NANOPARTICLES ON ABSORPTION AND LUMINESCENT PROPERTIES RHODAMIN C IN ETHANOL

Aimukhanov A.K., Esimbek A.M., Ibrayev N.Kh.

[1]Institute of Molecular Nanophotonics, E.A. Buketov Karaganda State University, Universitetskaya Str. 28, Karaganda, 100028, Republic of Kazakhstan Karaganda, Kazakhstan, ash_ok_94@mail.ru

*Au nanoparticles were obtained gold target ablation in ethanol second harmonic of solid state laser 215 LQ. The concentration of nanoparticles (NPs) Au was determined to change the target weight before and after ablation by duration of 30 minutes. Studies have shown that by adding Au nanoparticles by C = 5 * 10-6 mol / l solution of dye, the optical density at the absorption maximum is increased. Fluorescence intensity at the maximum increases 1.2 times. The provisions of maxima of the bands and their half-widths are not changed.*

***Keywords*:** laser ablation, gold nanoparticles, local plasmon resonance, absorption optical density, fluorescence intensit y, 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 gold on the low absorption and luminescence Rhodamin C.

1. Experimental part

Gold nanoparticles were obtained by ablation of a gold target in ethanol, the second harmonic of a solid-state laser Nd LQ - 215 (SOLAR). Au 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 Au 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 85 nm (Figure 1) in the test environment. Register absorption and fluorescence spectra of the samples was carried out by the Solar SM2203 spectrometer.

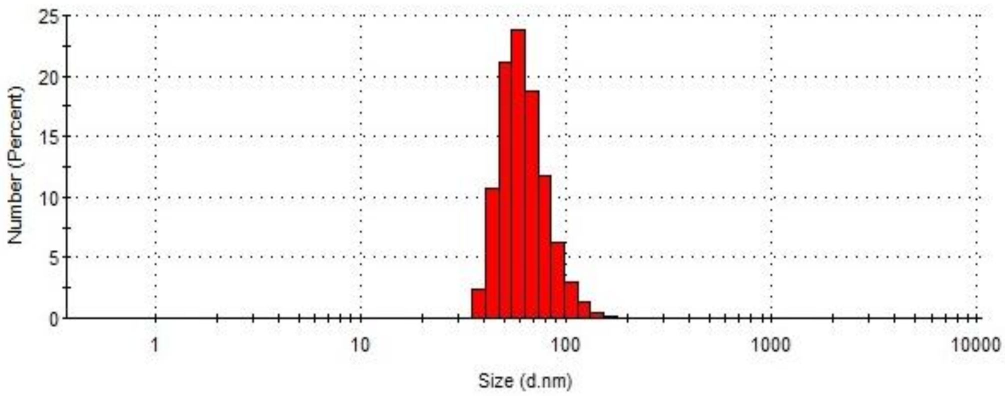

Fig. 1. The average sizes of Au nanoparticles

2. Results and discussion

The absorption spectrum of Au nanoparticles in ethanol (Figure 2) represents a broad band with a maximum at 535 nm. Rhodamin C absorption spectrum in ethanol has a maximum at λ_{abso}^{max} = 558 nm and a half width of the strip $\Delta\lambda_{1/2}^{abso}$ = 45 nm.

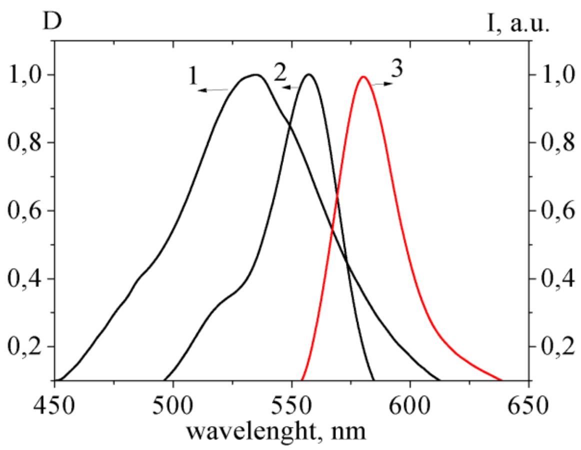

Fig. 2. The relative position of the absorption Gold nanoparticles (1) and fluorescence spectra of the Rhodamin C (2, 3)

Photoexcitation of the ethanol solution at λ_{exci} = 530 nm spontaneous fluorescence spectrum with a peak wavelength λ_{max}= 580 nm and a band-width $\Delta\lambda_{1/2}^{fluo}$ = 38 nm observed. Figure 2 shows that the absorption spectrum of Au NP overlaps with the absorption and fluorescence spectra of Rhodamin C, indicating that the performance of the plasmon resonance conditions are fulfilled.

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

Adding Au nanoparticles with concentration equal to $5*10^{-6}$ mol/l in a dye solution (C_{dye} = 10^{-5} mol/l) absorbance grows 1.2 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.

.

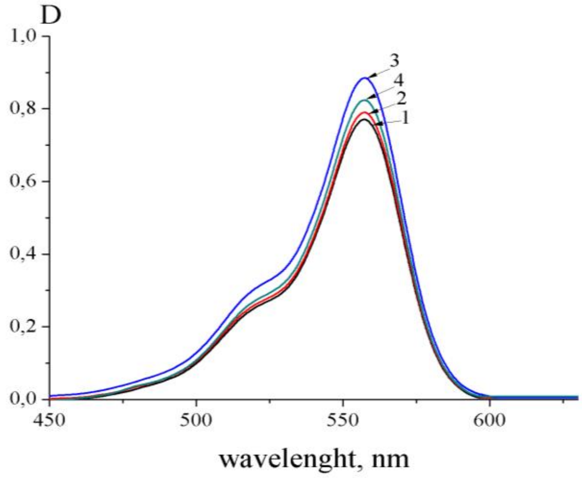

Fig.3. Influence of Au nanoparticles on the Rhodamin C absorption in ethanol:
1 – 0; 2 – $2\cdot10^{-6}$ mol/l; 3 – 5 10^{-6} mol/l; 4 – $5\cdot10^{-5}$ mol/l.

Reducing optical density of the dye in the presence of metal nanoparticles observed in [7]. 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 get 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 photoexcitation wavelength of an ethanol solution of the dye λ_{exci} = 530 nm and concentration equals 10^{-5} mol/l spontaneous fluorescence is observed (Figure 4). Adding gold NP in the alcoholic solution as a dye increases fluorescence intensity.

Rhodamin C, fluorescence intensity becomes 1.2 times stronger at the maximum. The intensity of the luminescence of the dye concentration increases until concentration will equal C_{Au} = $5*10^{-6}$ mol/l, and further increase C_{Au} 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 gold nanoparticles. At high concentrations of gold nanoparticles due to the decrease in the distance between the fluorophores and nanoparticles radiationless deactivation of the excited fluorescence state is dominating.

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

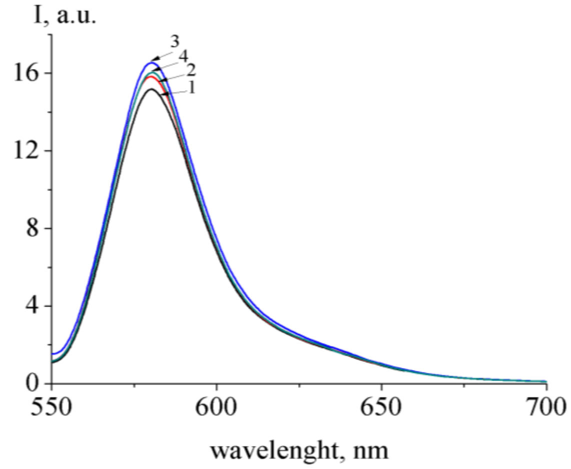

Fig.4. Effect of Au nanoparticles on Rhodamin C fluorescence in ethanol:
1 – 0; 2 – $2 \cdot 10^{-6}$ mol/l; 3 – $5\ 10^{-6}$ mol/l; 4 – $5 \cdot 10^{-5}$ mol/l.

Conclusion

Thus a result of the researches gold nanoparticles were obtained by ablation of a gold target in ethanol. It is shown, that by adding Au nanoparticles C = $5 * 10^{-6}$ mol/l in a solution of dye, optical density at the absorption maximum is increased 1.2 times and the fluorescence intensity at the maximum become 1.2 times bigger. At the high concentrations of nanoparticles observed drop in optical density at the absorption maximum and maximum of the spectra emission of the dye. Establishment, enhancement of absorption and emission 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.

ACKNOWLEDGEMENTS

The work was performed as part of the grant № 1124 / GF4 of the Ministry of Education and Science of the Republic of Kazakhstan

REFERENCES

1 Klimov V.V. *Nanoplasmonics*. Fizmatlit, Moscow, 2009, 480 p. [in Russian]

2 Tian Z.Q. Surface–enhanced raman spectroscopy: advancements and applications. *Spect*. 2005, Vol. 36, No. 6, pp. 466 – 470.

3 Lakowicz J.R. et al. Release of the self–quenching of fluorescence near silver metallic surfaces. *Analytical Biochemistry*. 2003, Vol. 320, pp. 13 – 20.

4 Homola J., Yee S.S., Gauglitz G. Surface plasmon resonance sensors: review. Sens *Actuators B* Chem., 1999, Vol. 54, pp. 3 – 15.

5 Oulton R.F. et al. Plasmon lasers at deep subwavelength scale. *Nature*, 2009, Vol. 461, pp. 629 – 632.

6 Kim W., Safonov V.P., Shalaev V.M., Armstrong R.L. Fractals in Microcavities: Giant coupled, multiplicative enhancement of optical responses. *Phys. Rev. Lett*., 1999, Vol. 82, No. 24, pp. 4811–4814.

7 Anger P., Bharadwaj P., Novotny L. Enhancement and quenching of single–molecule fluorescence. *Phys. Rev. Lett*., 2006, Vol. 96, pp. 113002 – 113005.

Article accepted for publication 25.11.2016

.