

Plasmon-assisted aggregation and spectral modification of the layered rhodamine 6G molecules

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Abstract Rhodamine, a wide-used laser dye, is well-studied in the form of solution. Contrary to that, information on the properties of rhodamine in the thin film form is limited. Even less is known about modification of structural and optical properties of the rhodamine thin films in presence of the plasmonic nanoparticles. In this contribution we report on the results of experimental investigation of the rhodamine thin films doped with silver and gold nanoparticles supporting localized surface plasmon resonances. The nanoparticles were obtained on the quartz surfaces via physical vapor deposition. Then, part of the samples was covered up by the thin polymer film doped by rhodamine molecules using spin-coating technique. At the surfaces of other part of the samples the rhodamine thin films of different thicknesses were fabricated. In the near field of plasmonic nanoparticles, absorption and fluorescence spectra of the samples were enhanced and red-shifted. This enhancement was rationalized by the near fields effect and slight reduction of the decay time of the molecules. A new absorption and fluorescent band of rhodamine molecules which was red-shifted, is associated to J-aggregates formation and their fluorescence enhancement.

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1 Introduction

At present, one of the fastest developing areas of nanophotonics, called nanoplasmonics, exploit the plasmon effects in metal nanoparticles. However, the development of the element base for nanoplasmonics is hampered by the losses in metals, limited set of materials and poorly developed technology for their fabrication.

The main materials for nanoplasmonics are noble metal nanoparticles that possess the required optical properties in the visible range. This is due to excitation of the localized surface plasmon resonances, which in turn leads to the strong increase of local fields within the nanoparticles and on their surfaces. These near fields are able to significantly enhance Raman scattering, absorption, fluorescence, contribute to the emergence of the nonlinear response and other effects (Fleischmann and Hendra 1974) that have practical value in various areas of optical engineering, including the fabrication of ultra-fast optical switches, optical tweezers, solar cells, biological and chemical sensors, etc. (Haglund et al. 1993; Novotny et al. 1997; Lyon et al. 1999). Optical properties of the noble metal nanoparticles can be improved by coating of these structures by organic molecules. These structures are attractive for creating nanoscale coherent light sources including nanolasers (Bergman and Stockman 2003; Noginov et al. 2009).

Spectral and optical characteristics of the composites based on the metal nanoparticles and organic dyes can be controlled. It is achieved by the fact that the surface plasmon resonance of the metal nanoparticles is extremely sensitive to a particle shape and size, as well as composition and the dielectric permeability of environment, in particular organic dyes (Kelly et al. 2003; Rai et al. 2012; Kamaliev et al. 2016; Toropov et al. 2016).

Mostly for the nanophotonics devices fabrication solid-state structures are used (Popov et al. 2009; Martinez Martinez et al. 2005; Toropov et al. 2014; Ritchie and Burstein 1981). Rhodamine dyes have gained their wide-spread applications based on fluorescence signaling and encoding techniques due to their excellent fluorescence properties. Rhodamine 6G dye is one of the most exploited laser dye. Rhodamine 6G has a high fluorescence in diluted solution (Sasai et al. 2004). However, this fluorescence is drastically reduced in the solid state. Rhodamine forms molecular aggregates on solid surfaces in a similar manner as in concentrated solutions (Bujdak et al. 2003). However, the aggregation behavior of rhodamine 6G can be controlled. Rhodamine dye molecules and aggregates can be used as typical spectroscopic probes (Shinozaki and Nakato 2004). Solutions of organic dyes possess high fluorescence, what we cannot say about thin layers of the same dyes.

In this contribution we experimentally demonstrate how the presence of silver and gold nanoparticles modifies the fluorescence intensity and kinetics as well as the aggregation pattern of the rhodamine molecules in thin films.

2 Experimental section

Silver and gold were selected as materials for fabrication of nanoparticles because of plasmon resonance of its nanoparticles are in the visible range of the spectrum and partially coincide with absorption spectrum of the rhodamine thin films. The nanoparticles were

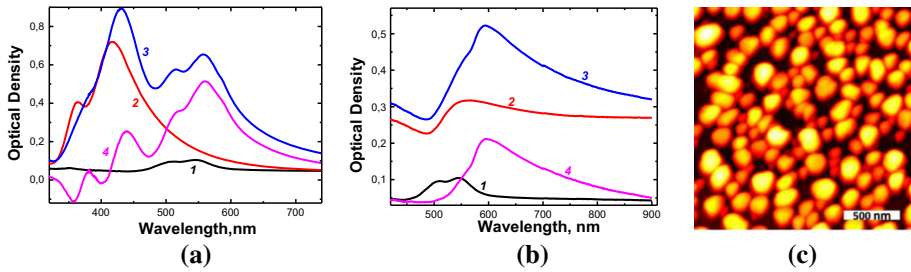


Fig. 1 **a, b** Optical density spectra of rhodamine + PMMA thin films (1); silver (a) and gold (b) nanoparticles (2); metallic nanoparticles covered with rhodamine + PMMA (3); and 4 is difference of spectra (3) and (2); **c** AFM image of the 10-nm Ag film

obtained in a form of the island films through physical vapor deposition on the quartz substrates in the vacuum chamber PVD 75 Kurt J. Lesker, at residual gas pressure of the order of 10^{-7} Torr. Both silver and gold nanoparticles growth follows to Volmer-Weber mechanism with occasionally formed islands on the defects of the quartz surface. The equivalent thickness of the metallic granular film was controlled by quartz microbalance and was set at 5 and 10 nm for different experiments. The samples of 10-nm thicknesses were additionally heated at 200 °C. Before covering the island by thin films, both types of the samples were kept in ethanol for 1 h to purify and removing the loosely bound particles from the surface.

The 5-nm samples were investigated by scanning electron microscopy (Fig. 1). Morphology of the film was a heterogeneous ensemble of the nanoislands. After that the rhodamine layers were made on the surface with the nanoparticles by spin-coating technique (3000 rpm, 60 s). The solutions of different concentrations were used for spin-coating that corresponded to the different thicknesses of rhodamine layers. The same solutions were applied on the bare quartz substrate to identify the effect of silver nanoparticles on the optical properties of rhodamine molecules. Thus, two sequences of layers, with 5-nm Ag nanoparticles and without them, was studied.

To investigate the influence of the near fields on aggregation and fluorescence enhancement, we used 10-nm Ag and Au nanoparticles isolated by polymethylmethacrylate (PMMA) layer. For this purpose, PMMA (4 mg) was dissolved in toluene (3 mL). The equivalent thickness of used PMMA was of a few nanometers, it was estimated using method described by (Walsh and Franses 2003). The samples of island films were covered by mixture of the PMMA and rhodamine, the concentration of the dye in the mixed solutions was set to 2.0 mmol/L.

At each step of the investigation, the samples were characterized through the optical density and fluorescence measurements using the spectrophotometer SF-56 (LOMO) and spectrofluorophotometer RF-5301PC (Shimadzu). The decay times of the rhodamine in PMMA matrix with 10-nm Ag and Au nanoparticles were measured by the laser scanning fluorescence microscope MicroTime 100 (PicoQuant).

3 Experimental results

Figure 1 plots the absorption spectra of the samples with silver (a) and gold (b) nanoparticles. Curves 1 in both pictures correspond to the thin rhodamine mixture with PMMA film on the bare quartz substrate and curve three corresponds to the Ag and Au

nanoparticles coated by the mixture film. Curves two correspond to the plasmonic absorption spectra of silver and gold island films on the quartz substrate with the equivalent thicknesses of 10 nm. An example of the image obtained with atomic-force microscopy of Ag ensembles is given also (Fig. 1c).

The amount of rhodamine molecules was identical in the samples with and without nanoparticles that was controlled by the concentration and volume of the coating solutions. To estimate the contribution of plasmonic nanostructures the spectra of nanoparticles were subtracted from the spectra of the obtained hybrids (curves 4 in Fig. 1a, b).

The absorption bands of the thin layer of rhodamine 6G molecules with PMMA are very close to plasmonic absorption of gold nanoparticles and red-shifted from the maximum of silver plasmonic absorption in their spectral positions, and have two maxima at wavelength of 511 and 545 nm.

For the samples with Ag nanoparticles three absorption maxima is resolved at the wavelengths of 432, 515, and 558 nm. Maximum at the wavelength of 432 nm is caused by the absorption of nanoparticles which red-shifted due to the increase of refraction index of surrounding medium. Two subsequent peaks are caused by absorption of rhodamine 6G molecules. The last two peaks are enhanced and shifted relative to organic thin films without silver nanoparticles. PMMA bands lie in UV-range (Zidan and Abu-Elnader 2005) and were not registered.

For the samples with Au nanoparticles one absorption peak with almost unresolved blue-shifted shoulder was observed (Fig. 1b). The shoulder in spectrum corresponds to well-known gold plasmonic absorption at the wavelength of 566 nm. At the same time the strong optical density enhancement which is not reduced to the sum of optical densities of the rhodamine + PMMA and Au nanoparticles taken separately was observed.

The observed changes are due to the shift of the resonance frequency of plasmon oscillations in Ag and Au nanoparticles and the formation of the aggregated forms of the dye because of the increase of optical density is occurred in the spectral region where rhodamine layer does not absorb at all.

For further interpretation, the spectral properties of thin films as a function of concentration were studied. The samples were prepared as the non-annealed silver island films of 5-nm equivalent thickness (Fig. 2c). Figure 2a plots the absorption spectra of the thin films of rhodamine 6G molecules without PMMA on the quartz substrate and on the island silver film (Fig. 2b). Rhodamine concentration in the solution was changed from 0.43 to 4.23 mmol/L. In Fig. 2 (in colors), curves of different colors correspond to the different concentrations.

In both cases, i.e. with and without silver nanoparticles, the linear dependence of absorption spectra on the dye concentration was observed. The optical density increased with the increase of the concentration of the used solution. Nonlinear dependence of the fluorescence spectra was observed for the thin film of dye molecules (Fig. 2d). At the maximum concentrations (more 2.96 mmol/L) for the thin organic film without nanoparticles (Fig. 2d) the quenching of fluorescence as well as a slight spectral shift were observed. Fluorescence quenching at increase the thickness is due to the formation of aggregates and slight re-absorption effect. In the case of the samples with silver nanoparticles an increase of the thickness of the organic film led to the faster increase of fluorescence intensity in red-shifted range (Fig. 2d). In addition, the shift of the spectra in the long-wavelength range and the formation of a new separate long-wavelength band were observed. The long-wavelength band is most pronounced in the case of the solution with maximum concentration.

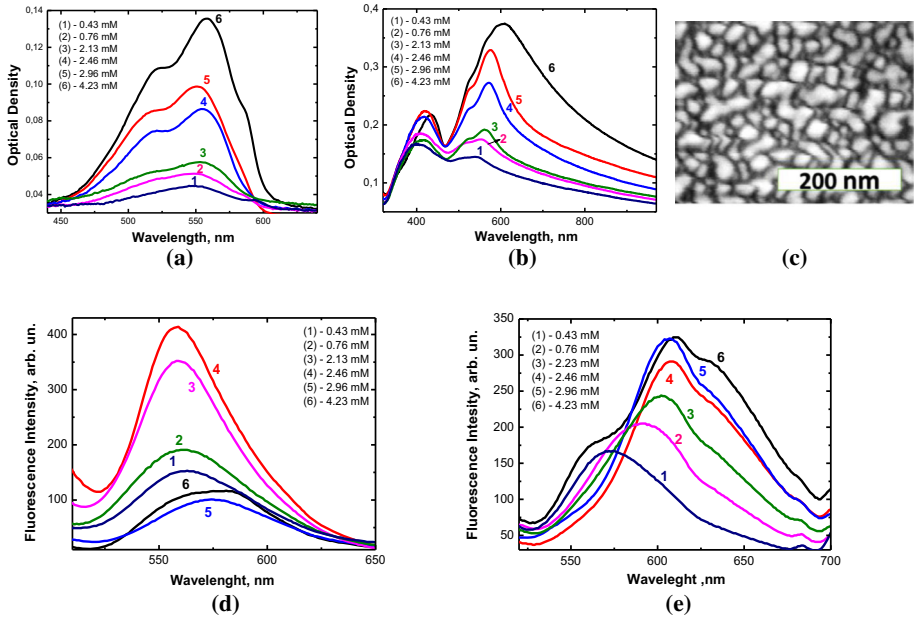


Fig. 2 Absorption spectra of rhodamine thin films depending on the concentration of coating solution **a** on the surface of the quartz substrate, **b** on the surface of the island silver film. **c** SEM image of the 5-nm silver island film. Fluorescence spectra of rhodamine thin films depending on the concentration of coating solution **d** on the surface of the quartz substrate, **e** on the surface with silver nanoparticles (excitation was at 500 nm)

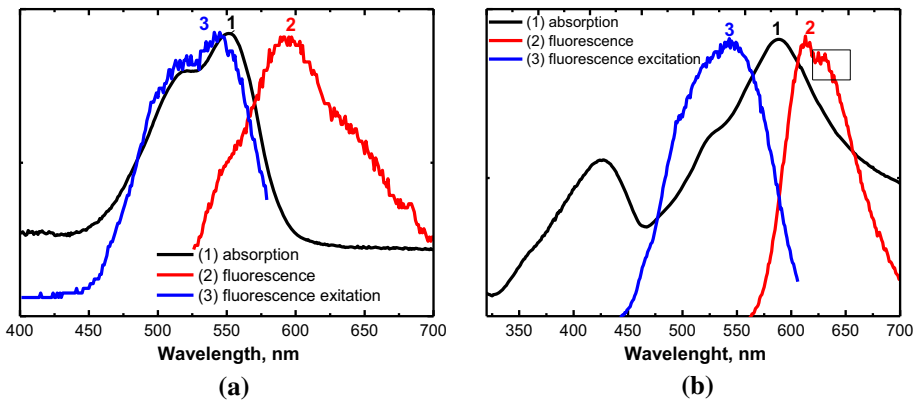


Fig. 3 Normalized spectra of rhodamine thin films (concentration—4.23 mmol/L): 1—absorption, 2—fluorescence, 3—fluorescence excitation spectrum **a** without nanoparticles, and **b** with nanoparticles

Figure 3 shows the normalized absorption, fluorescence and fluorescence excitation spectra of rhodamine film (Fig. 3a) and the same film with Ag nanoparticles. In the case of a thin film of the dye prepared from the solution with concentration of 4.23 mmol/L and with silver nanoparticles a second peak in the fluorescence spectrum at the wavelength of 630 nm was observed. This peak can be associated with the emission of aggregates. As

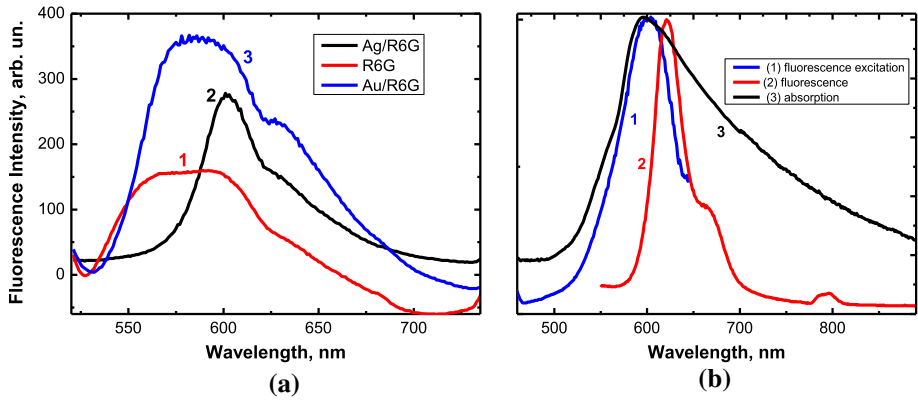
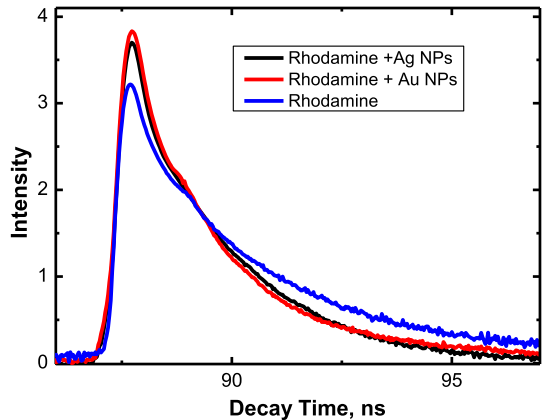


Fig. 4 **a** Fluorescence spectra of thin films: 1—rhodamine + PMMA, 2—rhodamine + PMMA with Ag nanoparticles, 3—rhodamine + PMMA with Au nanoparticles (excitation was at 500 nm). **b** Normalized spectra of rhodamine + PMMA thin films with Au nanoparticles: 1—fluorescence excitation spectrum, 2—fluorescence, 3—optical density

Fig. 5 Fluorescence kinetics of the rhodamine + PMMA thin film, and same with the silver and gold nanoparticles



without nanoparticles this peak was not clearly resolved, one can conclude that silver nanoparticles possibly change the radiation lifetime of the aggregates.

To prove that observed effect is associated with plasmonic excitation, the fluorescence spectra of rhodamine thin film with other, gold, 10-nm island film were also studied. The comparison of the fluorescence spectra of rhodamine with silver and gold nanoparticles is demonstrated in Fig. 4a. It is clearly seen that gold nanoparticles give the higher contribution to the fluorescence enhancement than silver nanoparticles because spectral coincidence of rhodamine and gold films is better.

At the same time, the spectral position of a new band both in the case of silver and gold nanoparticles was at 630 nm. We can conclude that this band corresponds to J-aggregates of rhodamine molecules.

To rationalize the observed enhancement, we measured the radiation lifetime of thin films of rhodamine and rhodamine thin films with Ag and Au nanoparticles (Fig. 5).

From the exponential fitting of measured decay kinetics we calculated the averaged lifetime for the samples. In the case of rhodamine film this time was of 3.8 ± 0.4 ns. While

in the case of rhodamine films with nanoparticles these times were shorter, 2.4 ± 0.2 ns for Au and 2.2 ± 0.2 ns for Ag nanoparticles. Thus, we can conclude that radiative decay is faster than the non-radiative decay, in generally. But used technique does not allow to estimate the decay time for each component of the layer separately.

4 Conclusion

In summary, optical properties of the solid-state composite structures based on silver and gold nanoparticles and organic layers formed of thin films of rhodamine 6G dye and rhodamine incorporated in PMMA were investigated. It is established, that the near field of nanoparticles exerts a strong influence on the dye molecules. In the presence of nanoparticles a modification of absorption and enhancement of fluorescence as well as spectral shifts of absorption and fluorescence bands were observed. The spectral shifts to longer wavelengths are due to the modification of the resonance frequencies of plasmon oscillations in plasmonic nanoparticles as well as to the dye molecules aggregation.

Thus, it has been found that the silver and gold nanoparticles contribute to the appearance of the aggregated forms of rhodamine with an increase in the thickness of rhodamine films. The direct proof of this fact is an observation of a long-wavelength shoulder in the fluorescence spectrum of rhodamine with silver nanoparticles and a clear peak in the samples with gold nanoparticles.

It was established that fluorescence decay time of rhodamine thin films with plasmonic nanoparticles is shorter than in the rhodamine films on the bare substrate. On the other hand, the quantum efficiency of rhodamine molecules and their aggregates is increased and fluorescence enhancement of the samples with metal nanoparticles is observed. Hence, one can conclude that the radiative decay is faster than the non-radiative decay.

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