
PHYSICAL CHEMISTRY
OF NANOCCLUSERS AND NANOMATERIALS

Effect of Silver Nanoparticles on Luminescent and Generation Properties of Rhodamine 6G in Aqueous Alcohol Solutions

A. K. Zeinidenov, N. Kh. Ibrayev*, and V. K. Gladkova

Institute of Molecular Nanophotonics, Buketov Karaganda State University, Karaganda, 100028 Kazakhstan

**e-mail: niazibrayev@mail.ru*

Received December 14, 2015

Abstract—The plasmon effect that silver nanoparticles have on the luminiscent and generation properties of rhodamine 6G molecules in aqueous alcohol solutions is studied. It is found that the intensities of absorption and emission increase when silver nanoparticles are added to aqueous solutions of rhodamine 6G. It is shown that upon the laser photoexcitation of aqueous solutions of rhodamine 6G dye, spontaneous fluorescence occurs that is converted into stimulated laser emission as the pump power grows. It is found that an increase in intensity and a drop in the generation threshold of stimulated emission are observed when silver nanoparticles are added to a solution of rhodamine 6G. It is shown that the dependence of absorbance, the intensity of fluorescence, and the dye's generation of stimulated emission on the concentration of silver nanoparticles in solution falls as the proportion of alcohol grows.

Keywords: stimulated emission, fluorescence, silver nanoparticles, plasmon resonance, rhodamine 6G

DOI: 10.1134/S0036024416120359

INTRODUCTION

The interest in studying the optical properties of molecules of fluorophores in the near-field of metal nanoparticles (NPs) is growing steadily. The interest in this problem is due both to the need to clarify the fundamental aspects of radiation's interaction with matter and practical applications. The ability to monitor and control the optical properties of fluorophores is particularly relevant due to the problem of improving the sensitivity of molecular markers in diagnostic systems [1, 2].

Fluorophore molecules placed near the surfaces of metal NPs are subject to the action of local electromagnetic fields [3]. Depending on the distance between an NPs and a molecule, the fluorescence of the latter is either enhanced or quenched [4, 5]. At short distances and direct contact between NPs and fluorophores, the fluorescence is quenched due to the prevalence of nonradiative energy transfer from fluorescent molecules to NPs. Different kinds of intermediate dielectric layers that allow us to vary the distance from a fluorophore to the metal in a controlled manner are therefore used to study the dependence of fluorescence on the distance between a molecule and the metal [4, 6].

This problem can be solved by using metal NPs in aqueous alcohol solutions. Aqueous alcohol solutions are mixed associates whose properties depend nonlin-

early on the quantitative ratios of the components. Alcohol molecules (which are larger) disrupt the structure of the solvation shell of a fluorophore molecule when they are incorporated into the structure of water, while the incorporation of water molecules into the structure of alcohol does not appreciably change the latter. When dissolving small amounts of alcohol, the structure of water remains virtually unchanged, undergoing only minor deformation. A further increase in the concentration of alcohol leads to disruption of the water's structure [7]. Changing the structure of solvation shells in binary systems would allow us to control the distance between a molecule of fluorophore and a metal NPs.

In this work, we present the results from studying the impact the plasmon effect has on photoprocesses in dye molecules in aqueous alcohol solutions.

EXPERIMENTAL

Silver NPs were obtained via the reduction of AgNO₃ with citrate in aqueous solutions [8]. In preparing silver NPs colloidal solutions, we used deionized water obtained by means of multi-stage filtration on an AquaMax 360 Basic water purifier. The water's specific resistance was 18.2 MΩ/cm.

The size of the silver NPs in colloidal solutions was determined via dynamic light scattering on a submi-

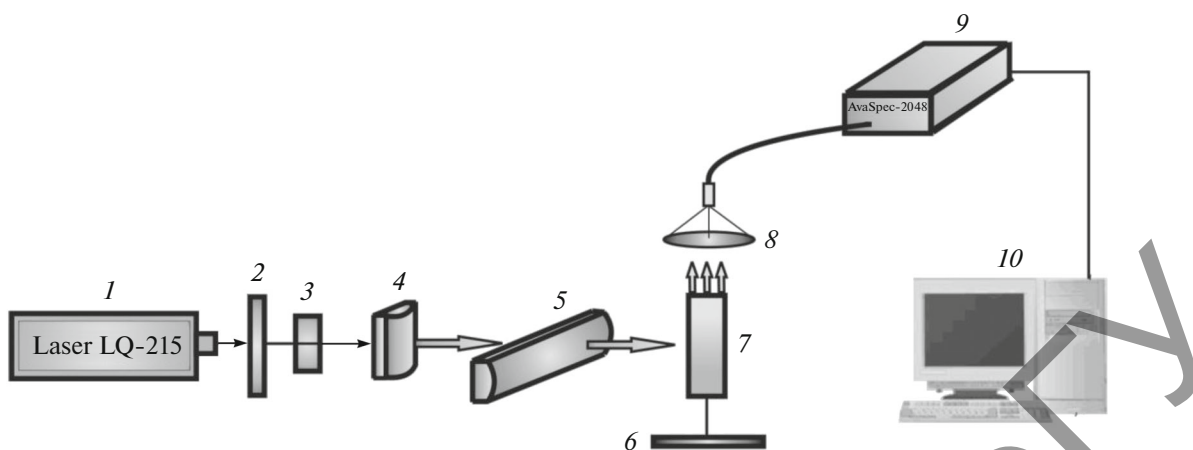


Fig. 1. Scheme of the experimental setup for studying the characteristics of molecular system generation: (1) laser LQ 215, (2) neutral density filters, (3) aperture, (4, 5) cylindrical lenses, (6) cavity end mirror, (7) sample, (8) collecting lens, (9) AvaSpec-2048 spectrometer, (10) PC.

ron particle size analyzer Zetasizer Nano ZS (Malvern). The average size of silver particles was 85 nm. The spread of the obtained values due to the dispersion of silver particles is minimal and lies in the range of 5 to 10 nm.

The shape of the silver NPs was determined using a scanning electron microscope (SEM) TESCAN Mira 3.

The absorption spectra of the samples were registered on a Cary 300 UV-Vis spectrophotometer. When the dependence of the dye's absorption spectra on the concentration of NPs was measured, the reference cell was filled with solutions of silver NPs with corresponding concentrations.

The spectral and energy characteristics of the stimulated luminescence of solutions of rhodamine 6G

(R6G) dye were measured upon excitation of the samples by a second harmonic Nd:YAG laser (Fig. 1, 1) (SOLAR LQ 215, $\lambda_{\text{gen}} = 532$ nm, $E_{\text{imp}} = 90$ mJ, $\tau = 10$ ns) in the transverse mode.

The characteristics of laser generation were measured with an optical resonator formed by cavity end mirror (6) and the front face of the cell with the solution of the dye (7). After passing through aperture (3), pumping radiation was focused on the side face of the cell on a strip with an area of 0.07 cm^2 using cylindrical lenses (4, 5). Radiation was generated in a narrow near wall region on the side of the inlet of the cell.

The power density of the pump was varied using neutral density filters (2), and was $0.005\text{--}0.2 \text{ MW/cm}^2$. The luminescence signal was focused on the input optical fiber of AvaSpec-2048 spectrometer (9) by converging lens (8). The relative accuracy of determining the spectral characteristics was 3%.

RESULTS AND DISCUSSION

Figure 2 shows SEM images of silver NPs. The sizes of the silver NPs, determined directly in a colloidal solution via dynamic light scattering and microscopy, agree with one another. Silver NPs are mostly spherical. The silver nanoparticles were 40–100 nm in size.

The absorption spectrum of a silver NPs in water (Fig. 3, curve 1) is a broad band with a maximum at 428 nm. It overlaps the absorption and fluorescence spectra of R6G (Fig. 3, curves 2, 3), indicating it meets the conditions of plasmon resonance.

Figure 4 shows the dependences of optical density of R6G on the concentrations of silver nanoparticles at different ratios of water and alcohol. In pure water, the dependence of optical density on C_{Ag} (curve 1) has its maximum at $C_{\text{Ag}} = 10^{-4} \text{ mol/L}$ when silver nanoparti-

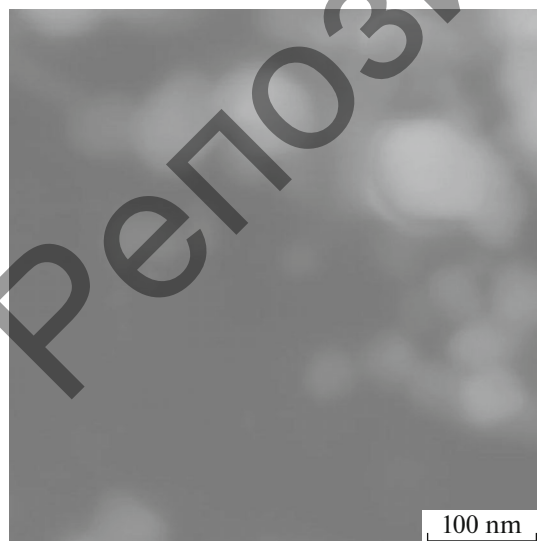


Fig. 2. SEM images of silver NPs.

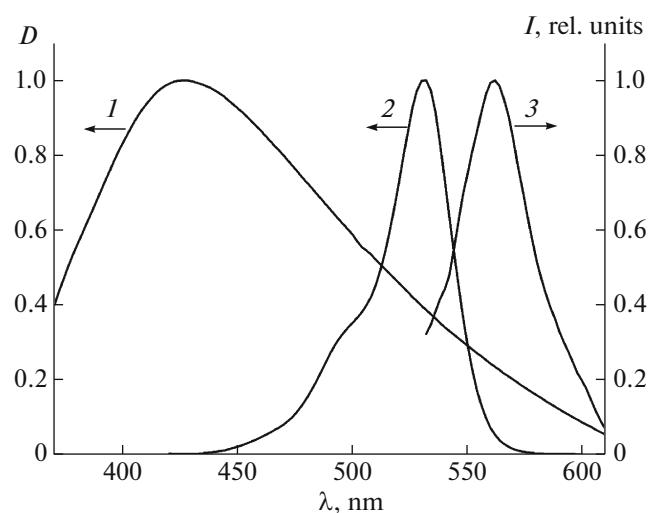


Fig. 3. Relative location of the absorption spectra of (1) silver NPs, (2) R6G, and (3) fluorescence of the dye in aqueous solution.

cles are added into the solution of the dye ($C = 10^{-5}$ mol/L). Similar dependences are observed for aqueous alcohol solutions (curves 2–5). They differ from aqueous solution and from one another in that the concentration of silver NPs at which the absorption maximum of the dye is observed is shifted toward lower values as the proportion of alcohol in the solution rises.

This increase of the optical density of the dye's absorption spectrum is due to the effect of the NPs electromagnetic field. The excitation of numerous plasmons in the particle results in efficient light scattering and the formation of an enhanced electromagnetic field near the surfaces of NPs. Scattered light can be reabsorbed by the molecules of R6G [9], and the overlap of the SPR absorption bands of silver NPs and R6G promote this reabsorption (Fig. 3), substantially increasing the amount of light absorbed by the system as a whole. A drop in the optical density of R6G in the presence of silver nanoparticles was also observed in [10].

The fluorescence of the dye undergoes similar changes upon changing the ratios of water and alcohol (Fig. 5): with an increase in the volume fraction of alcohol, the bend point is shifted toward lower concentrations of silver nanoparticles. According to [11, 12], the reason for the enhanced fluorescence of the molecules near metal NPs is an increase of the rate of fluorescence excitation due to localized plasmon resonance. At the same time, when the molecules are near the metal or in contact with it, nonradiative energy is transferred from the molecules to the NPs, reducing the probability of radiative decay of the excited molecules.

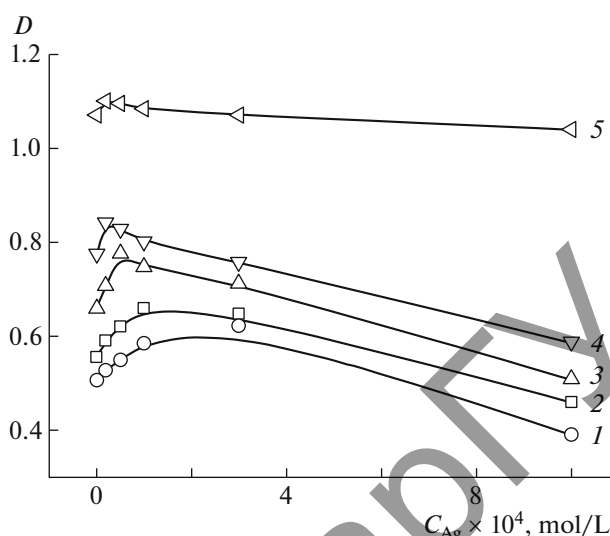


Fig. 4. Dependence of optical density of R6G on concentration of silver NPs in aqueous alcohol solution. Water/alcohol ratios, %: (1) 100 : 0, (2) 90 : 10, (3) 70 : 30, (4) 50 : 50, (5) 30 : 70.

The difference between the structures of water and aqueous alcohol solutions must be considered in order to explain the obtained dependences [13–18]. In contrast to a pure aqueous solution, in an aqueous solution diluted with alcohol, some of the dye molecules are surrounded by the solvation shells of alcohol molecules, which are weaker than those of water. This means the lifetime of an alcoholic solvation shell is shorter than those of the solvates of water molecules. In the periods between the collapse and formation of solvation shells, the molecules of the dye and NPs can

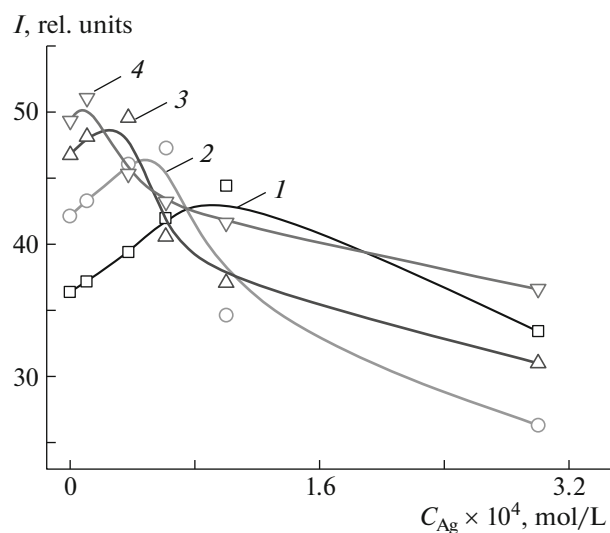


Fig. 5. Dependence of fluorescence spectra of R6G on concentration of silver NPs in an aqueous alcohol solution. Water/alcohol ratios, %: (1) 100 : 0, (2) 90 : 10, (3) 70 : 30, (4) 50 : 50.

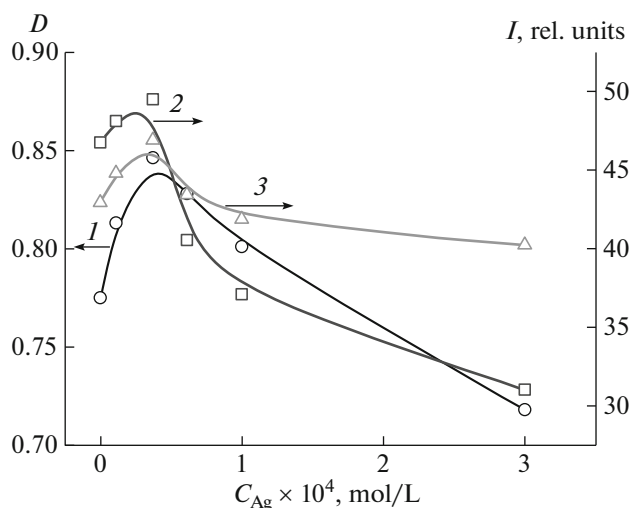


Fig. 6. Dependences of (1) optical density, (2, $\lambda = 564$ nm) intensity of fluorescence, and (3, $\lambda = 563$ nm) intensity of R6G generation in aqueous alcohol solution at a ratio of the components of 50 : 50% on the concentration of silver NPs.

close to the distances needed for interaction. Since the frequency of the rearrangement of solvates of alcohol molecules is higher than that of water, the probability of molecule–NPs pairs forming in an alcohol medium is higher than in water. This probably explains the drop in the concentration of silver NPs in order to obtain absorption and fluorescence maxima upon increasing the volume fraction of alcohol in binary solutions.

Measuring the properties of the stimulated emission of R6G dye in aqueous alcohol mixtures depending on the concentration of silver NPs revealed the same dependence as for absorption and fluorescence. Figure 6 shows curves for three processes at a water-to-alcohol ratio of 50 : 50%. For all curves, the bend maximum is observed at almost the same concentration. The relative increase in the values also remains approximately the same.

CONCLUSIONS

Our studies of the effect the plasmon resonance of silver NPs have on absorbance and the spontaneous and stimulated emission of dye molecules in aqueous alcohol solutions showed that the critical concentra-

tions of silver NPs at which absorption and emission maxima are observed fall as the volume fraction of alcohol rises in the mixture. This indicates that the probability of molecules and silver NPs converging is higher in alcoholic media than in water due to structural features of the solvation shells of the solvents.

REFERENCES

1. V. V. Klimov, *Nanoplasmonics* (Fizmatlit, Moscow, 2009; Pan Stanford, Singapore, 2011).
2. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Springer, Berlin, 2006).
3. L. Novotny and B. Hecht, *Principles of Nano-Optics* (Cambridge Univ. Press, Cambridge, 2006).
4. A. E. German and G. A. Gachko, *J. Appl. Spectrosc.* **68**, 987 (2001).
5. J. Homola, S. S. Yee, and G. Gauglitz, *Sens. Actuators B* **54**, 3 (1999).
6. F. R. Aussenegg, A. Leitner, and M. E. Lippitsch, *Surf. Sci.* **189–190**, 935 (1987).
7. N. Nishi, K. Koga, C. Ohshima, et al., *J. Am. Chem. Soc.* **110**, 5246 (1988).
8. R. S. Sheng, L. Zhu, and M. D. Morris, *Anal. Chem.* **58**, 1116 (1986).
9. Yu. A. Akimov, W. S. Koh, and K. Ostrikov, *Opt. Express* **17**, 10195 (2009).
10. A. Santhi, M. Umadevi, V. Ramakrishnan, et al., *Spectrochim. Acta, Part A* **60**, 1077 (2004).
11. S. A. Maier, *Plasmonics: Fundamentals and Applications* (Springer, Heidelberg, Berlin, 2007).
12. P. Anger, P. Bharadwaj, and L. Novotny, *Phys. Rev. Lett.* **96**, 113002 (2006).
13. K. P. Mishchenko and G. M. Poltoratskii, *The Structure of Aqueous and Nonaqueous Solutions of Electrolytes* (Khimiya, Leningrad, 1976) [in Russian].
14. V. A. Mikhailov, *J. Struct. Chem.* **2**, 625 (1961).
15. O. Ya. Samoilov and M. N. Buslaeva, *J. Struct. Chem.* **4**, 462 (1963).
16. O. Ya. Samoilov, *Structure of Aqueous Solutions of Electrolytes and Ion Hydration* (Akad. Nauk SSSR, Moscow, 1957) [in Russian].
17. V. A. Mikhailov and E. F. Grigor'eva, *J. Struct. Chem.* **16**, 374 (1975).
18. N. V. Chekalin and M. I. Shakhparonov, *Fiz. Fiz.-Khim. Zhidk.*, issue 1, 151 (1972).

Translated by L. Grineva