Thin films of organic dyes with silver nanoparticles: enhancement and spectral shifting of fluorescence due to excitation of localized surface plasmons

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Abstract

Organic dyes molecules are attractive objects of investigation due to their bright optical properties and wide range of applications in generation of coherent radiation, photodynamic cancer therapy, visualization etc. At the same time, optical properties of very thin dye layers that play an important role in the modern technogies, are studied insufficiently. In the layers of nanometer thickness dye molecules, often demonstrate such unwanted properties as reduced absorption, fluorescence quenching and changes of their spectra due to isomerization and aggregation [1].

In this contribution, we propose and demonstrate how silver nanoparticles may be used for enhancement of absorption and fluorescence of organic dye thin films. Our proposal is based on the fact that silver nanoparticles possess localized surface plasmon resonances that lead to the huge enhancement of the electric fields around them.

In the experiments, silver nanoparticles were vacuum-deposited on the quartz substrates and washed in the organic dye solvent for stabilization of their morphology. After that, optical density of nanoparticles in the vis-NIR spectral region was measured. The samples obtained in this way allow us to study interactions of silver nanoparticles with different organic thin films because they have wide absorption bands (400–900 nm). In this work we studied the influence of local fields of nanoparticles on three organic dyes with different maxima of absorption: malachite green with absorption peak at 618 nm in ethanol solution. rhodamine and coumarin with absorption peaks at 530 nm and 403 nm, correspondingly. Dyes were spin-coated on the surface and dried at ambient conditions.

It is known that the influence of metallic surfaces on the dye molecules is two-fold. On one hand, they contribute to the quenching of molecular excitation. On the other hand, the enhanced near fields at the metal surfaces and Purcell effect lead to the enhancement of the fluorescence. To get the most of the enhancement factors and at the same time to avoid quenching, we propose to use poly(methyl methacrylate) as a matrix that keeps the organic molecules at the optimum distance from the metal surface. Optical density spectra of organic dye doped PMMA films were enhanced in the presence of silver nanoparticles (fig. 1). Experimental investigations of the fluorescence demonstrated the 13-, 17-, and 20-fold enhancement for malachite green, rhodamine and coumarin in the presence of silver nanoparticles. Also, the fluorescence maximum is slightly shifted (about 10 nm) in the presence of silver nanoparticles (fig. 2).

References

[1] Toropov N.A., Parfenov P.S., Vartanyan T.A., J. Phys. Chem. C, **118** (2014) 18010–18014.

Figures

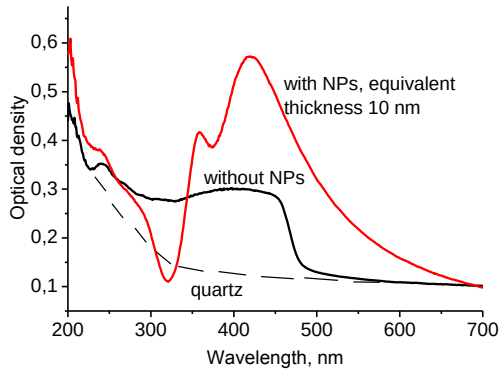

Fig. 1. Modification of optical density by silver nanoparticles (on example of coumarin in PMMA matrix)

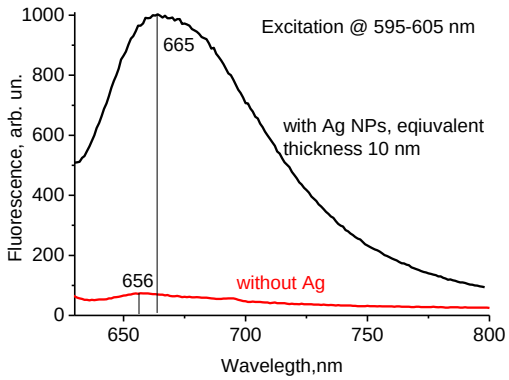

Fig. 2. Fluorescence enhancement and shifting by silver nanoparticles (on example of malachite green in PMMA matrix)