ANNOTATION

of the dissertation for the degree of Doctor of Philosophy (PhD)
6D060400-Physics

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Influence of plasmon effect of metal nanoparticles on the spectral-luminescent and lasing characteristics of polymethine dyes

Topic relevance. The study of photophysical processes in organic dyes and molecular ensembles passing near the surface of plasmon nanoparticles (NPs) is one of the urgent problems of modern optical spectroscopy and luminescence. Organic dye molecules placed near the surface of metal NPs are exposed to local electromagnetic fields. In this case, the rates of radiative and nonradiative intramolecular electronic transitions either increase or decrease depending on the distance between NPs and organic molecules. These effects can be used in optical nanotechnology to create media with desired properties, as well as highly sensitive luminescent sensors, optoelectronic devices, nanolasers, etc. The addition of NPs of metals to the active medium of dye lasers leads to a decrease in the lasing threshold. However, despite the practical importance of these effects and the fact that they were observed for different types of dyes, the regularities of the influence of plasmons of metallic NPs on the spectral-luminescent properties of dyes, depending on their structure, have not yet been studied.

The use of the plasmon effect for improving the efficiency of photophysical processes in polymethine dyes (PD) is especially attractive. Polymethines are widely used as active and passive media for lasers, since they have the largest range of spectral-luminescent and nonlinear-optical properties among organic dyes. For example, ultrashort light pulses and lasing in the long-wavelength region of the spectrum were obtained using cationic dyes. It was also found that by using localized plasmon resonance (LPR) of NPs of noble metals, it is possible to lower the threshold and improve the quality of generation of laser radiation from cationic polymethines. It was shown that NPs are also capable of significantly influencing the photophysical properties of electrically neutral representatives of polymethines - merocyanine dyes.

In addition, PD, due to the fact that they have high extinction coefficients and tunable absorption spectra in the entire visible and near infrared region, are very promising objects for photovoltaics. In particular, in dye-sensitized solar cells, the interest in which is due to low production costs, stability, transparency and flexibility compared to other photovoltaic cells.

To increase the efficiency of solar cells, the LPR phenomenon of metal NPs and its effect both on photoprocesses inside dye molecules and to improve the electrophysical parameters of a semiconductor can be used. In particular, metal NPs

and nanostructures can be placed both inside and outside the working electrode to increase the concentration and light collection of light by the solar cell, as well as to use the effect of light scattering from metal NPs. In addition, the LPR phenomenon of metal NPs leads to an improvement in the spectral sensitivity of solar cells, and also affects the efficiency of injection and transport of charge carriers inside a semiconductor.

The dissertation novelty lies in the study of plasmon-activated processes of generation and deactivation of electronically excited states of PD of various structures. The results obtained can serve as a scientific basis for the development of new methods of plasmon modulation of characteristics and signals in devices of molecular photonics, photovoltaics, photocatalysis and detectors. The ability to control the conditions of such interaction will make it possible to form a large number of new nanostructures, to study new phenomena and properties characteristic of nanoobjects, and, on this basis, to create new functional materials and devices.

The results can be used to develop scientific foundations for obtaining optical devices, highly efficient luminescent light sources, nanosensors, functional elements of molecular electronics, photovoltaic devices, and in biophysics.

The dissertation aim is to study the influence of the features of the plasmon effect of metal nanoparticles on the spectral-luminescent, generation and photovoltaic characteristics of polymethine dyes of various chemical structures.

The study objects are cationic indopolycarbocyanines, PD with functional sulfo groups, merocyanine and cationic electronically asymmetric PD, plasmonic Ag and Au nanoparticles, Ag/TiO_2 «core/shell» nanostructures, TiO_2 films, dye sensitized solar cells, films of porous aluminum oxide Al_2O_3.

Scientific novelty includes the following:

1) The dependence of the plasmon enhancement of the fluorescence of dyes on the structure of the dye and the spectral overlap of absorption and fluorescence bands of PDs and Ag NPs was investigated by the example of the vinyllogical series of cationic symmetric indopolycarbocyanines. A mathematical model is proposed that takes into account the effect of plasmonic NPs on the deactivation of the excited state of organic dye molecules and correlates well with experimental data;

2) «Core/shell» NPs of Ag/TiO_2 and PDs with and without sulfo groups were doped in titanium oxide films. The greatest plasmon effect on the spectral-luminescent and photovoltaic properties of these films have been observed for functionalized dyes;

3) The effect of silver NPs on the spectral-luminescent and lasing properties of the merocyanine dye in ethanol solution has been studied. It has been demonstrated that stimulated emission of a merocyanine solution at a concentration of 10^{-4} mol/L can be achieved only in the presence of Ag NPs;

The structure and scope of the dissertation. The structure of the dissertation work is determined by the tasks set and consists of an introduction, 5 sections, a

conclusion, a bibliography. It is presented on 97 pages of typewritten text, illustrated with 45 figures, 11 tables, contains a list of cited literature of 161 titles.

Key findings include the following:

1. The coefficient of plasmon enhancement of the fluorescence intensity in the vinylogical series of cationic symmetric indopolycarbocyanines increases with lengthening of the polymethine chain. The main reason for the increase in fluorescence intensity is an increase in the fluorescence rate of dye molecules in the presence of metal NPs. Förster energy transfer from dyes to Ag NPs is a competing process with respect to plasmon-enhanced fluorescence.

2. The efficiency of dye-sensitized solar cells increases in the presence of Ag/TiO_2 nanostructures due to an increase in the spectral sensitivity of the cells and upon sensitization of semiconductor with PDs with functional groups.

3. In the presence of plasmonic metal NPs, an increase in the absorption cross section and an increase in the fluorescence quantum yield of the PDs are observed and electron-asymmetric PD in solutions and porous films of aluminum oxide are observed, which is the reason for a decrease in the generation threshold of stimulated emission of the dye.

Scientific and practical significance of dissertation:

1. A comprehensive theoretical and experimental study of the effect of plasmonic NPs on the photonics of PD of various structures makes it possible to predict the physicochemical properties of synthesized nanostructures, that is important when creating new materials with desired properties.

2. Experimental data on the effect of plasmonic nanostructures on the efficiency of solar cells sensitization by PD will be used to increase the efficiency of solar radiation conversion by organic photovoltaic devices.

3. The data on the effect of metal NPs on the stimulated luminescence of organic dyes can be used to create active elements of tunable lasers based on localized surface resonances.

Approbation of work and publication. The main results of the work were reported and discussed at conferences: XIV International Scientific Conference dedicated to the 80th anniversary of the founder of the conference, Professor T.A. Kuketaeva "Solid State Physics, Functional Materials and New Technologies (SSPh-2018)" (2018, Bishkek-Karaganda); Republican scientific and practical conference dedicated to the 80th anniversary of Professor Zh.S. Akylbaeva "Actual problems of heat power engineering and applied thermal physics" (2018, Karaganda); X International Conference "Fundamental Problems of Optics - 2018" (2018, St. Petersburg); The 7th International Conference on nanomaterials and advanced energy storage systems "INESS-2019" (2019, Almaty); 11th International Scientific Conference “Chaos and Structures in Nonlinear Systems. Theory and Experiment "(2018, Karaganda); The 8th International Conference on nanomaterials and advanced energy storage systems "INESS-2020" (2020, Nur-Sultan); IX International Conference on Photonics and Information Optics (2020, Moscow); Republican

scientific and practical online conference dedicated to K.M. Aryngazin "Actual problems of modern physics and semantic pedagogy" (2021, Karaganda).

Publications. Based on the results of the dissertation, 17 publications were published: 4 articles in journals included in the Thomson Reuters and Scopus databases: Journal of Luminescence (IF – 3.28, Q1); Optics and Spectroscopy (IF– 0.748, Q4); Engineered Science (Scopus, percentile – 98); Materials Today: Proceedings (Scopus, percentile 38); 2 articles included in the RSCI database, 2 articles in journals recommended by the Committee for Control in Education and Science of Kazakhstan ESM and 9 publications in the materials of international conferences.