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E.P. Menshova[1*], N.Kh. Ibrayev[1], N.D. Strekal[2]

[1]*Institute of Molecular Nanophotonics, Karaganda Buketov University, Karaganda, Kazakhstan;*
[2]*Yanka Kupala State University of Grodno, Grodno, Belarus*
[*]*(Corresponding author's e-mail: menshovayevgeniya @gmail.ru)*

Plasmon-enhanced sensitization of singlet oxygen on silver island films

The influence of the plasmonic effect of silver island films on the absorption, fluorescence and long-term luminescence of rose bengal in polyvinyl butyral films has been studied. Under the plasmon effect, the optical density of the dye increased by 3.3 times, the fluorescence intensity by 8.5 times, and the long-lived fluorescence and phosphorescence by 7.08 times and 10.21, respectively. It is shown that in the plasmon field of metal nanoparticles, both an increase in the excitation rate and an increase in the rates of radiative decay of excited singlet and triplet states occur. Phosphorescence of singlet oxygen with a lifetime of 86.46 μs was observed when excited in the absorption band of rose bengal. Based on the calculation of the quenching constants of rose bengal phosphorescence by molecular oxygen molecules, it is shown that the plasmonic effect enhances the energy transfer from dye triplets to oxygen molecules in collision complexes $[T_{PS}...^3\Sigma_g^-]$ as a result of heteroannihilation. Subsequently, the triplet pair decomposes to form a singlet oxygen molecule and a photosensitizer molecule in the ground state. The plasmonic effect of silver nanoparticles leads to an increase in the generation of singlet oxygen by 4.8 times.

Keywords: singlet oxygen generation, silver island films, plasmon effect, phosphorescence, long-lived fluorescence, photosensitizer, photodynamic therapy, molecular oxygen.

Introduction

Oncological diseases are a pressing problem both for Kazakhstan and the whole world. Over the past 20 years, the incidence of cancer has increased by 25% in our country. But the development of methods for diagnosing and treating the disease in the early stages reduced mortality by 33%.

One of the modern methods of cancer treatment is photodynamic therapy (PDT). The mechanism of PDT is complex and not fully understood. There are two processes occurring in tumor tissue: the photodynamic effect, sometimes called the photodynamic reaction, and the processes occurring in the tumor after its completion, that is the process of destruction of cancer cells [1].

Three main components are involved in PDT: light, a photosensitizing drug (photosensitizer - PS) and singlet oxygen $O_2(^1\Delta_g)$ [2]. The effectiveness of PDT is determined mainly by the level of PS accumulation, its localization in the cell and photochemical activity. This is due to the fact that in biosystems $O_2(^1\Delta_g)$ is quickly intercepted by amino acids and proteins and its lifetime is about 170–320 ns in the cytoplasm and 24–30 ns in the lipid phase of biomembranes. In cells containing many quenchers, the diffusion length of $O_2(^1\Delta_g)$ does not exceed 10–20 nm [3]. Consequently, $O_2(^1\Delta_g)$ can only damage biological structures in the immediate vicinity of photosensitizer molecules. Fluorescent microscopic studies have shown that PS mainly accumulates in membrane structures (plasma membrane, mitochondrial membranes), therefore they are considered the most likely primary targets, the defeat of which leads to cell damage and death [4–7].

Under the influence of a light quantum, O2(1Δg) is formed in the molecules of lipids, cell membrane proteins and intracellular organelles, which breaks the atomic bonds in the molecule and begins translational motion, moving in 1 μs to a distance of 50 Å [8]. The chain of the molecule is broken and destroyed with the formation of free radicals, which leads to damage to cell membranes. This process occurs within a few minutes after the start of laser irradiation [9, 10].

When a photosensitizer molecule absorbs a light quantum, it transforms into an excited singlet state (S_{1PS}) and then into a long-lived triplet state (T_{PS}) (reaction (1)). The transfer of energy from the PS in the triplet state to the oxygen molecule $O_2(^3\Sigma_g^-)$ transforms it into the singlet state $O_2(^1\Delta_g)$ (reaction (2)). Excited oxygen and photosensitizer molecules return to their original state and are able to enter into chemical reactions. The entire cycle can be restarted after the arrival of a new quantum of light energy. After several cycles, the photosensitizer "burns out" [11].

$$S_{0\,PS} + h\upsilon \rightarrow S_{1\,PS} \rightarrow T_{PS} \quad (1)$$

$$T_{PS} + {}^3\Sigma_g^- \rightarrow [T_{PS} \quad {}^3\Sigma_g^-] \rightarrow S_{0\,PS} + {}^1\Delta_g. \quad (2)$$

Intensive development of PDT requires the development of new generations of PS based on nanomaterials with better photostability and higher efficiency of $O_2(^1\Delta_g)$ generation, as well as ways to improve the efficiency of existing ones [12–15]. For this purpose, the use of various types of metal nanoparticles and the creation of metal-PS composites are being considered [13, 16–19].

For the first time, Geddes et al. [20] observed and investigated possible mechanisms of $O_2(^1\Delta_g)$ generation under the influence of metal nanoparticles (NPs). Since then, many attempts have been made to explain this process. Many authors agree that a possible reason is an increase in the excitation rate as a result of an increase in the electric field around metal nanostructures [17, 21]. Consequently, the rate of intersystem crossing conversion ($S_{1PS} \rightarrow T_{PS}$) can be increased, which leads to increased energy transfer from PS molecules in the excited triplet state to the surrounding oxygen molecules with the formation of $O_2(^1\Delta_g)$. Also, the size and shape of silver clusters affect the performance of silver-enhanced $O_2(^1\Delta_g)$ generation [22].

The first fundamental studies were carried out on planar metal-photosensitizer systems [20]. Planar plasmonic nanostructures for studying plasmon-enhanced $O_2(^1\Delta_g)$ generation are usually fabricated by creating metal islands on a silicon or glass substrate. Metal islands can be synthesized using various approaches.

Reference [16] reported that by changing the plasmonic coupling parameters, such as nanoparticle size and shape, fluorophore/particle, and excitation wavelength of the coupling photosensitizer, the $O_2(^1\Delta_g)$ output can be easily tuned.

Various approaches to control the distance between PS molecules and the surface of a metal substrate on a nanometer scale made it possible to increase the generation of $O_2(^1\Delta_g)$ [23–25]. Firstly, this is due to the nonlinear propagation of the electric field in the environment, where the maximum electric field is observed at the surface of the metal and decreases exponentially with increasing distance from the surface. Secondly, nonlinear nonradiative energy transfer from excited PS molecules to the metal surface has an inverse relationship with the distance between the PS molecule and the metal surface [26].

For practical application of the planar metal- PS system, rigid glass and quartz substrates were replaced with flexible silicone ones. NPs were first incorporated into silicone polymers, and then PS molecules were sorbed on them. Silicone nanocomposites with NPs of various sizes have shown very effective antibacterial properties [27–30].

One of the important requirements for PCs for their practical use in PDT is their water solubility [31]. In this case, an important factor in the study is the interaction between colloidal metal NPs and PS molecules in solutions. PS molecules can be attached directly to the surface of metal NPs with their stabilizing substance through either electrostatic interaction or covalent bonding. Methods for attaching various PS molecules to metal NPs contained in various surfactant stabilizing substances, such as cetyltrimethylammonium bromide [32-33], poly(ethylene glycol) [34], tetraoctylammonium bromide [35-36], adenosine triphosphate [37], polyethyleneimine [38-39], was studied.

Metal NPs are mainly spherical gold and silver (AuNPs and AgNPs). But it is worth noting that the shape of NPs is another key factor influencing on the generation of $O_2(^1\Delta_g)$, because it determines the enhanced electric field as well as the amount of energy transferred. For example, Mthethwa and Nyokong [40] showed that Au nanobipyramids and Au nanorods (NRs) can enhance $O_2(^1\Delta_g)$ generation by 2-fold and 1.96-fold, respectively. It is assumed that the asymmetric shape and anisotropy in the enhanced electric field

around the metal NPs play a large role in the metal-enhanced $O_2(^1\Delta_g)$ generation [41]. Other studies have also shown that Au nanorods have better $O_2(^1\Delta_g)$ enhancement performance compared to spherical AuNPs [42]. Macia et al. [43] reported that silver nanocubes enhanced $O_2(^1\Delta_g)$ generation by rose bengal by 4 times. They concluded that the higher gain is due to the enhanced electric field at the sharp corners and edges of the nanocube.

As in planar metal-PS systems, plasmon-enhanced generation of singlet oxygen in colloidal systems is also distance dependent. To control the distance between PS molecules and metal NPs, silica and polymer shells are synthesized. PS molecules can be attached to the surface of the dielectric electrostatically [44], covalently [43, 45] and/or embedded inside the dielectric [46, 47]. When photosensitizer molecules are incorporated inside a dielectric layer such as silica, the final nanostructure becomes more biocompatible (due to the inertness of the dielectric layer) and has more potential for further modification (e.g. mesoporous silica shell structure) for in vivo applications with less dark cytotoxicity, because the PS molecules are not directly affected [48, 49]. When the PS molecules are attached to the surface of the dielectric layer through electrostatic interaction or covalent bonding, the distance between the PS and the metal nanoparticles is relatively easier to control [50, 51].

Fundamental research by our group showed the influence of Ag and Au NPs on the spectral and luminescent properties of xanthene [52], polymethine [52, 53], indopolycarbocyanine [21] and other dyes. The influence of the plasmonic effect of Ag nanoparticles (NPs) on singlet-singlet (S–S) and triplet-singlet (T–S) energy transfer in the same donor-acceptor pair of organic molecules was studied [52, 54]. A mathematical model was proposed that takes into account the influence of plasmonic nanoparticles on the deactivation of excited states of molecules [21, 52–55]. The distance dependence of plasmon-enhanced fluorescence and delayed luminescence of molecular planar nanostructures was also studied [55].

The purpose of this work is to study the process of enhancing the generation of singlet oxygen by dye molecules adsorbed on silver island films (SIFs).

Experimental

To study the plasmonic effect on $O_2(^1\Delta_g)$ generation, SIFs substrates were prepared using the chemical deposition method described in [52]. Then the films were annealed at 240^0C for 30 min. According to scanning electron microscope data (Mira 3LMU, Tescan), spherical islands with a size of 30–150 nm are uniformly distributed on the surface of the films (Fig. 1a). The broadened absorption spectra also indicate a large scatter in the sizes of islands in films obtained by chemical deposition (Fig. 1b).

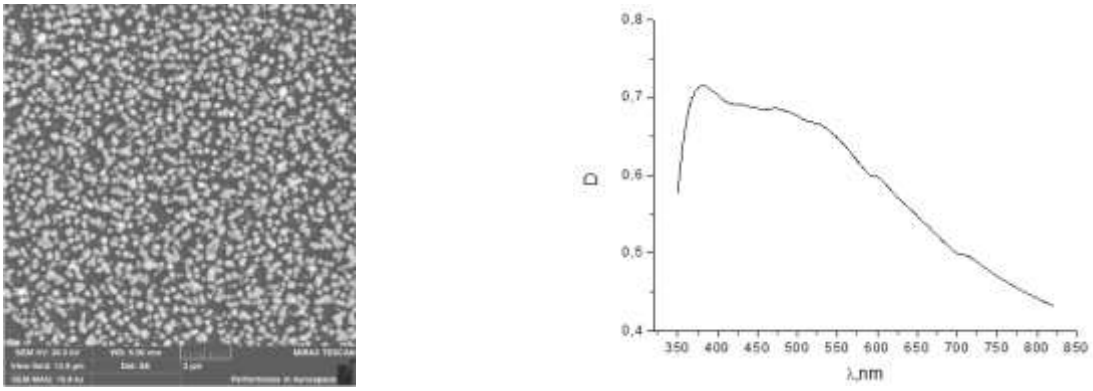

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Figure 1. SEM image (a) and absorption spectrum (b) of SIFs obtained by chemical deposition onto a cover glass

Rose Bengal (BR) dye was chosen as a PS [56]. Films of polyvinyl butyral (PVB, Sigma Aldrich) with a dye concentration of $5 * 10^{-5}$ M were obtained on the surface of clean cover glasses and SIFs using the spin-coating method.

Absorption, fast and long-lived luminescence spectra were recorded using Cary 300 and Eclipse spectrometers (Agilent Technologies). Measurements of delayed fluorescence (DF) and phosphorescence (Phos) of BR films were carried out using an Optistat DN vacuum cryostat (Oxford Instruments). The measurements were carried out with changes in pressure in the cryostat.

The decay kinetics of long-lived luminescence was recorded with an FLS1000 spectrometer (Edinburgh Instr.) with UV, Vis-PMT and NIR-PMT (Hamamatsu). Photoexcitation of the samples was carried out with an LQ529 Nd:YAG laser (SolarLS) with an excitation wavelength of 532 nm.

Results and Discussion

Figure 2 shows the absorption, fluorescence, and long-lived emission spectra of BR on pure glass and on SIFs. Optical density increased by 3.3 times on SIFs. The fluorescence intensity on SIFs increased by 8.5 times (Fig. 2a).

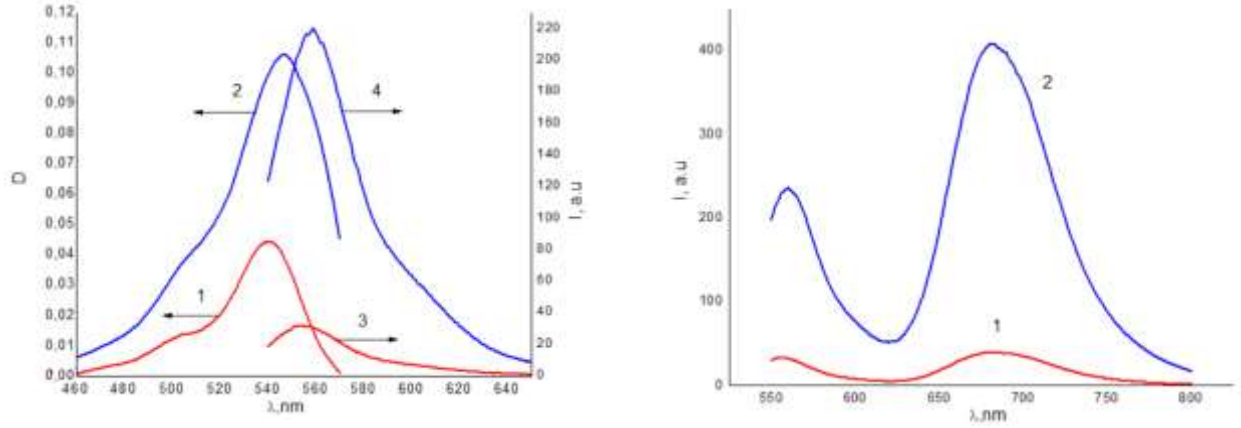

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Figure 2. (a) Absorption (1,2) and fluorescence (3,4) spectra of BR in a PVB film on glass (1,3) and on SIFs (2,4); (b) Long-lived emission spectra of BR on glass (1) and on SIFs (2) (λ_{ex} = 530 nm)

In the long-lived luminescence spectra of BR (Fig. 2b), two bands are observed: DF and Phos. The maximum of DF is at 560 nm, and Phos is at 685 nm. In the presence of Ag NPs, the intensity of DF increases by 7.08 times, and the intensity of Phos – by 10.21 (Table 1).

The Phos decay kinetics of BR on glass and on SIFs in air (curves 1) and in a degassed state at a pressure in a cryostat of 10^{-3} mBar (curves 2) are presented in Figure 3. The lifetime of long-lived emission in the presence of a plasmon decreases slightly for DF and Phos (Table 1). The observed increase in luminescence intensity with a simultaneous reduction in the duration of long-lived luminescence of BR on SIFs is a consequence of an increase in the rate of radiative decay [21, 55].

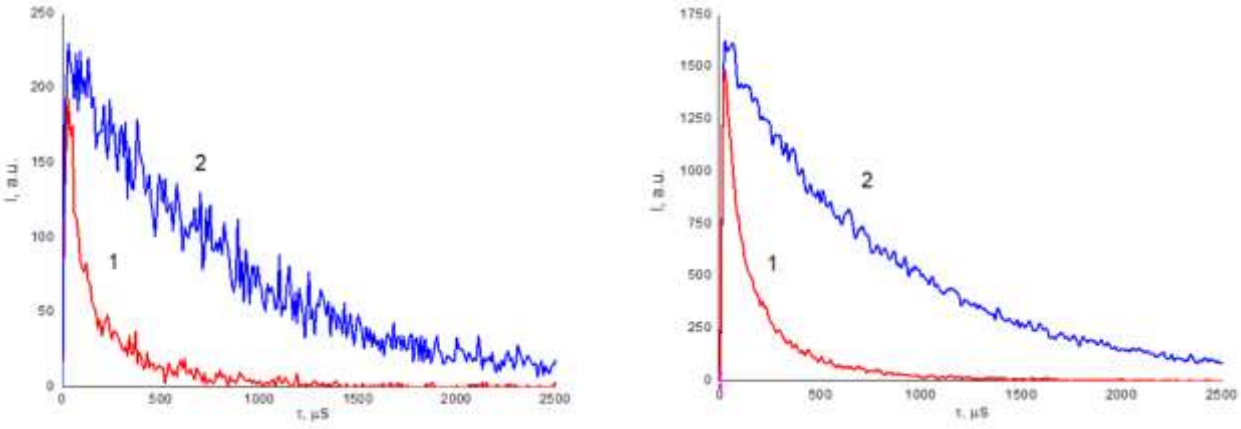

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Figure 3. Decay kinetics of BR Phos on glass (a) and on SIFs (b) with (1) oxygen and (2) without it (λ_{ex} = 530nm)

Table 1

Intensity, lifetime of DF and Phos of BR at an air pressure in a cryostat of 10^{-3} mBar on glass and SIFs (λ_{ex} = 530 nm)

	On glass		On SIFs		I/I_0	τ/τ_0
	I_0, o.e.	τ_0, ms	I, o.e.	τ, ms		
DF	33.41	0.85±0,1	236.49	0.81±0.1	7.08	0.95
Phos	40.06	0.80±0,1	408.82	0.78±0.1	10.21	0.98

The effect of oxygen concentration on DF and Phos in plasmon presence and without it was studied. Figure 4 shows the dependences of the intensity of DF and Phos on the pressure in the cryostat. For DF (curves 1, 2) on glass and on SIFs, an increase of the emission intensity up to 5 mBar is observed and then a decrease. While the intensity of phosphorescence (curves 3, 4) decreases monotonically.

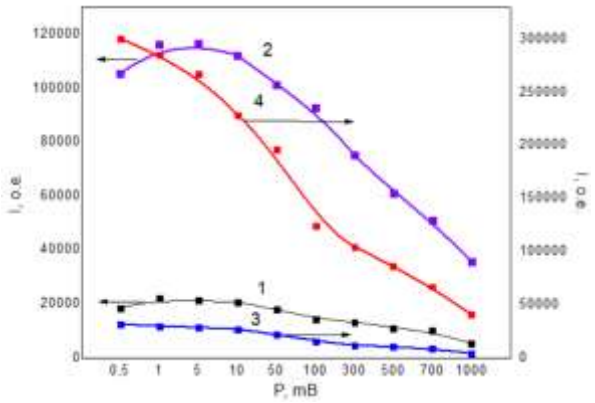

Figure 4. Dependence of the intensity of DF (1.2) and Phos (3.4) of BR on glass (2, 4) and on SIFs (1.3) on the pressure in the cryostat (λ_{ex} = 530 nm, λ_{reg} = 560 nm for DF and λ_{reg} = 690nm for Phos)

The dependence of the DF intensity on the $O_2\left({}^3\Sigma_g^-\right)$ concentration (Fig. 4) is the result of singlet-triplet annihilation (reaction (4)) between triplet-excited PS molecules and singlet oxygen molecules formed after its sensitization by the PS (reaction (3)):

$$T_{PS} + {}^3\Sigma_g^- \rightarrow [T_{PS}\ldots {}^3\Sigma_g^-] \rightarrow S_{0PS} + {}^1\Delta_g \quad (3)$$

$$T_{PS} + {}^1\Delta_g \rightarrow [T_{PS}\ldots {}^1\Delta_g]^3 \rightarrow S_{1\,PS} + {}^3\Sigma_g^- \rightarrow S_{0\,PS} + {}^3\Sigma_g^- + h\upsilon_{DF} \quad (4)$$

$${}^1\Delta_g \rightarrow {}^3\Sigma_g^- + h\upsilon_{Phos}\,, \quad (5)$$

where (3) is the reaction of singlet oxygen sensitization; (4) — singlet-triplet annihilation reaction; (5) — singlet oxygen phosphorescence reaction.

At low oxygen concentrations, the number of triplet PSs is still sufficient for the formation of $[T_{PS}\ldots {}^3\Sigma_g^-]$ pairs, which, decaying with the formation of S_1 states of the PS, additionally generate its DF [57–59]. This leads to an increase in DF intensity. With increasing oxygen concentration, stronger quenching of PS triplets occurs. As a result, the efficiency of both singlet–triplet (4) and intrinsic (1) annihilation processes decreases, which leads to a decrease in the intensity of PS luminescence.

Let's consider the effect of Ag NPs on the generation of singlet oxygen. Upon photoexcitation, phosphorescence of singlet oxygen was observed in the absorption band of the dye. $O_2({}^1\Delta_g)$ phosphorescence kinetic curves have two phases — rise and fall (Fig. 5) and can be approximated in accordance with the two-exponential equation:

$$I(t) = I_0\left[\exp\left(-\frac{t}{\tau_{decay}}\right) - \exp\left(-\frac{t}{\tau_{rise}}\right)\right],$$

where $I(t)$ — $O_2(^1\Delta_g)$ phosphorescence intensity per second, I_0 — pre-exponential factor, and τ_{decay} и τ_{rise} — the time constants of the decay and rise phases [60].

The rise phase is determined by the rate of formation of singlet oxygen as a result of energy transfer from BR triplets to $O_2\left(^3\Sigma_g^-\right)$, the decay phase is determined by the process of singlet oxygen deactivation.

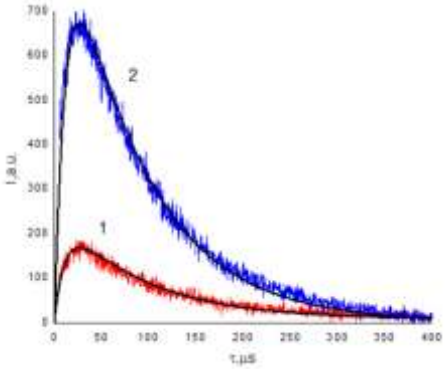

Figure 5. Decay kinetics of singlet oxygen phosphorescence (λ_{reg} = 1270 nm), sensitized with BR, on glass (1) and on SIFs (2) at atmospheric pressure (λ_{ex} = 530 nm)

Under the influence of the plasmon effect, the generation of singlet oxygen increases by 4.8 times (Fig. 5, Table 2). Under the influence of plasmon, the duration of the rise and decay phases of $O_2(^1\Delta_g)$ phosphorescence decreased by 14% and 3%, respectively. The decrease of the lifetime of $O_2(^1\Delta_g)$ phosphorescence is associated with an increase in the radiative transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$.

Table 2

Effect of SIFs on the integral intensities and lifetime of singlet oxygen (λ_{reg} = 1270 nm) at atmospheric pressure (λ_{ex} = 530 nm)

	$S \bullet 10^4$, o.e.	τ_{rise}, μs	τ_{decay}, μs	S/S_0	$\tau_{rise}/\tau_{rise\ 0}$	$\tau_{decay}/\tau_{decay\ 0}$
$O_2(^1\Delta_g)$ on glass	7.77	12.40±0.93	86.46±1.1	-	-	-
$O_2(^1\Delta_g)$ on SIFs	1.63	10.61±2.31	84.23±2.44	4.8	0.86	0.97

From the data on the effect of oxygen concentration above the sample surface on the intensity of phosphorescence, the quenching constants were determined from the Stern-Volmer equation [61; 75]:

$$\frac{I_{ph}^0}{I_{ph}} = 1 + k_q \tau_0 \cdot [Q],$$

where I_{ph}^0 — intensity of Phos in the absence of O_2, I_{ph} — intensity of Phos in the presence of O_2, k_q — the quenching coefficient, τ_0 — the lifetime of Phos in the absence of O_2, and $[Q]$ — the concentration of O_2.

Based on the Stern-Volmer graphs, the quenching constants of BR phosphorescence by oxygen molecules were calculated (Fig. 6). k_q =4,99 • 10^2 c^{-1} for dye films on glass, and k_q =6,48 • 10^2 c^{-1} on SIFs.

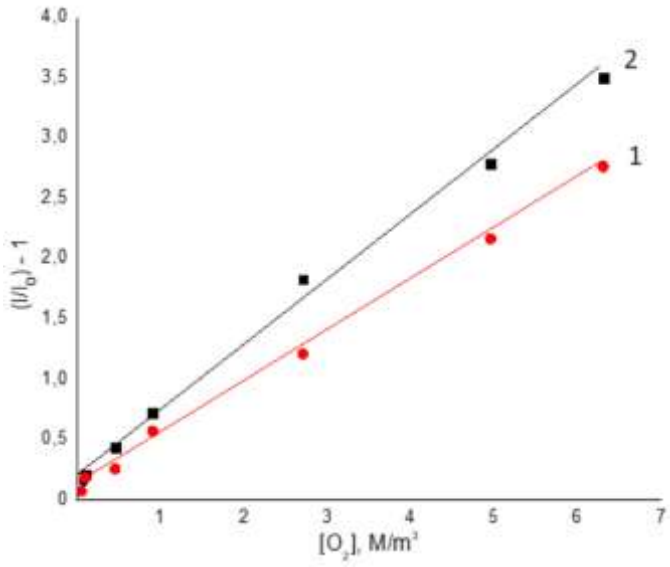

Figure 6. Stern-Volmer quenching constants of BR phosphorescence by O_2 molecules on glass (1) and on SIFs (2)

The obtained data indicate that the quenching of triplet BR molecules by molecular oxygen is enhanced in the plasmon field. The plasmonic effect promotes the transfer of energy from dye triplets to oxygen molecules in collision complexes $[T_{PS}...^3\Sigma_g^-]$ as a result of heteroannihilation. Subsequently, the triplet pair decomposes to form a singlet oxygen molecule $^1\Delta_g$ and $S_{0\,PS}$.

Conclusions

The influence of the plasmonic effect of silver nanoparticles on the absorption, fluorescence and long-term luminescence of BR in polyvinyl butyral films was studied. It was shown that in the plasmon field of metal nanoparticles, both an increase in the excitation rate and an increase in the rates of radiative decay of excited singlet and triplet states occur.

Phosphorescence of singlet oxygen with a lifetime of 86.46 μs was observed upon excitation in the absorption band of the dye. It was shown that the plasmonic effect promotes the quenching of triplet dye molecules by molecular oxygen. The intensity of the oxygen emission increased under the influence of the plasmon effect.

Acknowledgements

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Е.П. Меньшова, Н.Х. Ибраев, Н.Д. Стрекаль

Күміс аралдық қабыршақтардағы синглетті оттегінің плазмонмен күшейтілген сенсибилизациясы

Күміс аралдық қабыршақтардың плазмондық әсерінің поливинилбутирал қабыршақтарындағы бенгал раушанының жұтылуына, флуоресценциясына және ұзақ мерзімді люминесценциясына әсері зерттелді. Плазмонның әсерінен бояғыштың оптикалық тығыздығы 3,3 есе, флуоресценция қарқындылығы 8,5 есе, ал баяу флуоресценция мен фосфоресценция сәйкесінше 7,08 және 10,21 есе өсті. Металл нанобөлшектерінің плазмондық өрісінде қозу жылдамдығының жоғарылауы да, қозған синглет пен триплет күйлерінің радиациялық ыдырау жылдамдығының да жоғарылауы анықталды. Бенгал раушанының жұтылу жолағында қозған кезде өмір сүру уақыты 86,46 мкс болатын синглетті оттегінің фосфоресценциясы байқалды. Бенгал раушанының фосфоресценциясын молекулалық оттегі молекулаларымен сөндіру константаларын есептеу негізінде, плазмондық әсер гетероаннигиляция нәтижесінде соқтығысу кешендеріндегі $[T_{ФС}...^3\Sigma_g^-]$ бояғыш триплеттерінен оттегі молекулаларына энергияның берілуін күшейтуге ықпал ететіндігі көрсетілген. Кейіннен триплет жұбы ыдырап, синглетті оттегі молекуласын және негізгі күйдегі фотосенсибилизатор молекуласын түзеді. Күміс нанобөлшектерінің плазмондық әсері синглетті оттегінің 4,8 есе көбеюіне әкеледі.

Кілт сөздер: синглетті оттегінің генерациясы, күміс аралдық қабыршақ, плазмондық әсер, фосфоресценция, баяу флуоресценция, фотосенсибилизатор, фотодинамикалық терапия, молекулалық оттегі.

Е.П. Меньшова, Н.Х. Ибраев, Н.Д. Стрекаль

Плазмон-усиленная сенсибилизация синглетного кислорода на островковых пленках серебра

Исследовано влияние плазмонного эффекта островковых пленок серебра на поглощение, флуоресценцию и длительную люминесценцию бенгальской розы в пленках поливинилбутираля. Под воздействием плазмона оптическая плотность красителя возросла в 3,3 раза, интенсивность флуоресценции — в 8,5, а замедленной флуоресценции и фосфоресценции — в 7,08 и в 10,21 раз, соответственно. Показано, что в плазмонном поле металлических наночастиц происходит как увеличение скорости возбуждения, так и рост скоростей радиационного распада возбужденных синглетных и триплетных состояний. При возбуждении в полосе поглощения бенгальской розы наблюдалась фосфоресценция синглетного кислорода со временем жизни 86.46 мкс. На основе расчета констант тушения фосфоресценции бенгальской розы молекулами молекулярного кислорода показано, что плазмонный эффект способствует усилению передачи энергии от триплетов красителя к молекулам кислорода в комплексах столкновения $[T_{ФС}...^3\Sigma_g^-]$ в результате гетероаннигиляции. В последующем триплетная пара распадается с образованием молекулы синглетного кислорода и молекулы фотосенсибилизатора в основном состоянии. Плазмонный эффект наночастиц серебра приводит к увеличению генерации синглетного кислорода в 4,8 раза.

Ключевые слова: генерация синглетного кислорода, островковые пленки серебра, плазмонный эффект, фосфоресценция, замедленная флуоресценция, фотосенсибилизатор, фотодинамическая терапия, молекулярный кислород.

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Information about authors

Menshova, Evgeniya — Junior Research Fellow, Institute of Molecular Nanophotonics, Karaganda Buketov University, Karaganda, Kazakhstan; e-mail: menshovayevgeniya@gmail.com; ORCID ID: https://orcid.org/0000-0003-3646-3763;

Ibrayev, Niyazbek — Doctor of physical and mathematical sciences, Professor, Director, Institute of Molecular Nanophotonics, Karaganda Buketov University, Karaganda, Kazakhstan; e-mail: niazibrayev@mail.ru; ORCID ID: https://orcid.org/0000-0002-5156-5015;

Strekal, Natalia — Doctor of physical and mathematical sciences, Professor, Department of General Physics, Yanka Kupala State University of Grodno, Grodno, Belarus; e-mail: nat@grsu.by; ORCID ID: https://orcid.org/0000-0001-6560-3679.