The Effect of Clustering of Gold Plasmonic Nanoparticle–Protein Complexes as a Factor in Increasing the Fluorescence Intensity



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ABSTRACT

The effect of clustering of gold plasmonic nanoparticle–protein complexes as a factor in increasing the fluorescence intensity has been studied. It has been shown that a change in the structure of the near field in the vicinity of complexes in clusters of various types leads to an increase in the integral excitation power of the fluorescent TagRFP protein. In our works, we theoretically studied the interaction of laser radiation with complexes of gold plasmon resonance nanospheres (GNS) with the TagRFP protein without taking into account the mutual near-field interaction of such complexes. The aim of this work is to evaluate the influence of this interaction on such characteristics as field amplification and absorption of laser radiation by clusters of GNS-TagRFP complexes. Naturally, these characteristics actually determine the intensity of the object's fluorescent response to photoexcitation. Therefore, for a comparative evaluation of the efficiency of GNS-TagRFP plasmonic protein complexes in clusters, the results of calculating the field distribution carried out for the wavelength λ of the protein photoexcitation maximum, namely λ =558 nm, are important. It is found that in each of the considered clusters, the field localization zones are redistributed: in the region of the closest approach of the complexes, they are characterized by an increase in the field maximum compared to the case of a solitary complex. Depending on the type and number of complexes in a cluster, the field maximum can increase up to 2 times. Accordingly, the non-uniformity of the specific absorption power also increases, which should be taken into account in the possible applications of the GNS-TagRFP complexes.

Purpose of the study

In our work [QUANTUM ELECTRON, 2021, **51** (1), 52-63, <u>https://doi.org/10.1070/QEL17492</u>], we theoretically studied the interaction of laser radiation with complexes of gold plasmon resonance nanospheres (GNS) with the TagRFP protein without taking into account the mutual near-field interaction of such complexes. The aim of this work is to evaluate the influence of this interaction on such characteristics as field amplification and absorption of laser radiation by clusters of GNS-TagRFP complexes. Naturally, these characteristics actually determine the intensity of the object's fluorescent response to photoexcitation.



Model

The structure of the GNS-TagRFP complexes analyzed by us is schematically shown in Fig. 1. Based on numerical

calculations performed by the finite element method in the COMSOL Multiphysics environment, we analyzed the distributions and averaged over the volume of the protein layer values of the field enhancement factor $\xi_E 2 = |E|^2 / |E_0|^2$ and volumetric radiation absorption density $Q = c(8\pi)^{-1} \operatorname{Im}(\varepsilon) |E|^2$, (E₀ and E are the complex amplitudes of the irradiating and induced fields, ε is the complex dielectric function).

Simulation results and discussion



Figure 2. Spectral dependences of the values spatially averaged over the volume of the complex protein layer: (a) - of field enhancement factor ξ_{E2avg} ; (b) – of specific radiation absorption power Q_{avg} . The distance between the complexes s is normalized to the diameter of the complex d=32.2 nm.

The found spectral dependences of the values of the spatially averaged field gain ξ_{E2avg} and the specific radiation absorption power Q_{avg} in the protein layer of the complex (a cluster of two complexes), as follows from those presented in Fig. 2a and Fig. 2b of the data differ significantly both in the character and in the position of the maxima.

The reason for this is the influence of the resonant nature of the spectral excitation curve of the protein on the absorbed power spectrum Q_{avg} . Therefore, for further comparative evaluation of the effectiveness of GNS-TagRFP plasmonic protein complexes in clusters, the results of calculating the field distribution carried out for the wavelength λ of the protein photoexcitation maximum, namely λ =558 nm, are important.



Figure 3. Topogram of the distribution of ξ_{E2} during cluster irradiation at a wavelength of λ =558 nm: (a) - a single complex; (b) - chains of two complexes; (c) - chains of three complexes; (d) - an infinite chain of complexes; (e) - two-dimensional array of complexes.

In each of the considered clusters, the localization zones of the field are redistributed: in the area of the closest approach of the complexes, they are characterized by an increase in the maximum ξ_{E2} compared to the case of a solitary complex. Depending on the type and number of complexes in a cluster, the maximum ξ_{E2} can increase up to 2 times. Accordingly, the non-uniformity of the specific absorption power also increases, which should be taken into account in the possible applications of the GNS-TagRFP complexes.

CONCLUSIONS

- 1. The clustering differential effect of the GNS-TagRFP complexes leads to the appearance of both the appearance of additional zones of field localization and a change in the field maxima/minimum compared to those that existed in solitary complexes.
- 2. The integral effect of the clustering of complexes manifests itself in an increase in absorption and, accordingly, plays the role of a factor in increasing the fluorescence intensity.

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