Model of fluorescence and quenching of a protein molecule in a plasmonic complex

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ABSTRACT

A mathematical model of fluorescence and quenching of a protein molecule in the "TagRFP-nanosphere" plasmonic complex is proposed and described, depending on the material and size of the nanoparticle, and the size of the gap. The point dipole approximation is used to model the radiation source. The model includes a sequential solution to the following two problems. Firstly, the electromagnetic field enhancement in the near-field of the metallic nanosphere is determined, which influences the excitation of the fluorescent molecule. Secondly, from the solution of the electrodynamic problem, radiative and non-radiative losses are estimated to determine the quantum yield of the fluorescent protein molecule-plasmonic nanoparticle complex. The solution of the formulated problems is carried out using the finite element method. Numerical results have been obtained that make it possible to determine the conditions for constructing an effective fluorescent plasmonic complex.

Object of research and features of models

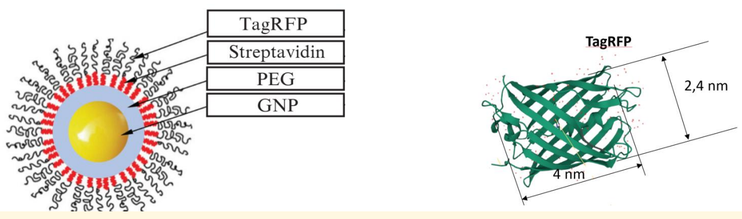


Figure 1. Structure of "plasmonic nanoparticle-fluorescent protein" complexe (left) and structure of TagRFP molecule (right).

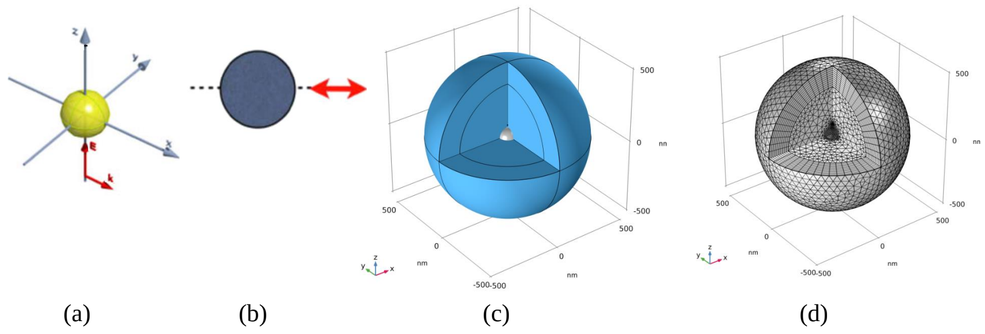


Figure 2. Schematic representation of: two schemes for calculating the irradiation of a nanoparticle by a plane polarized wave (a) and the radiation of a dipole near the nanoparticle (b); example of the computational domain(c) and the finite-element mesh (d).

Set of parameters for modeling

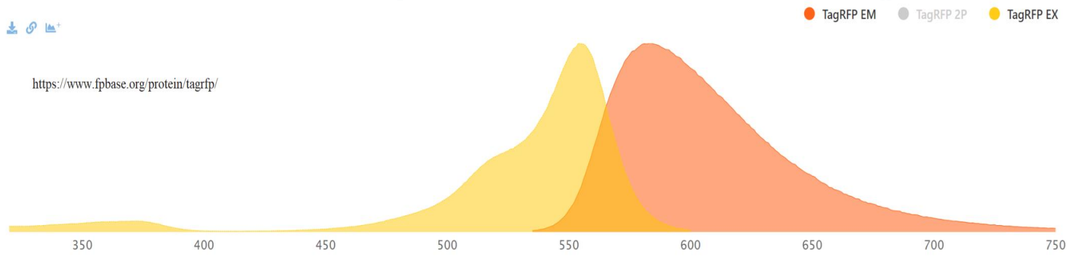


Figure 3. Exciation (TagRFP EX) and emission (TagRFP EM) spectra of TagRFP.

- The intrinsic quantum yield of the isolated molecule TagRFP – **QY_0=0.48**
- Nanoparticle material – **Au, Cu, Ag**
- Nanoparticle diameter – **D=20; 60, 120 nm**

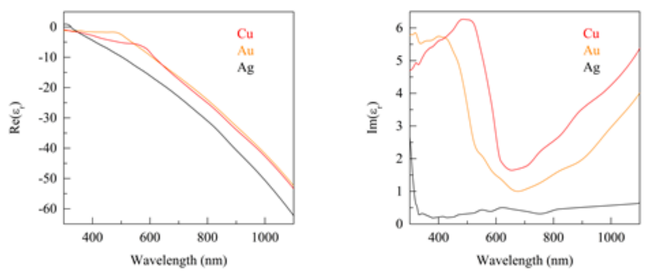


Figure 4. Spectral dependences of the real (left) and imaginary (right) parts of the dielectric function of nanoparticle materals

Simulation results and discussion

Results of solving the problem 1 - On localization of the near-field of a nanoparticle, absorption of radiation of a plane polarized wave

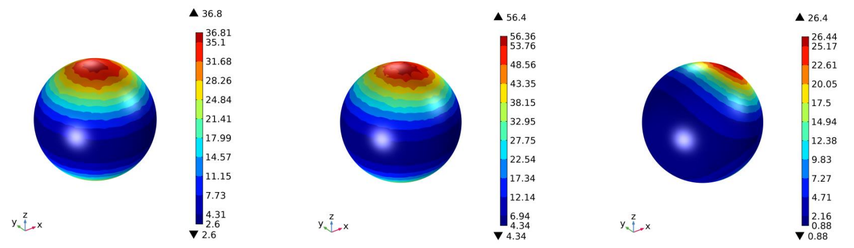


Figure 5. Topograms of the distribution of the E-field enhancement on the surface of gold nanoparticles of various sizes at the excitation wavelength of the TagRFP λ=555 nm.

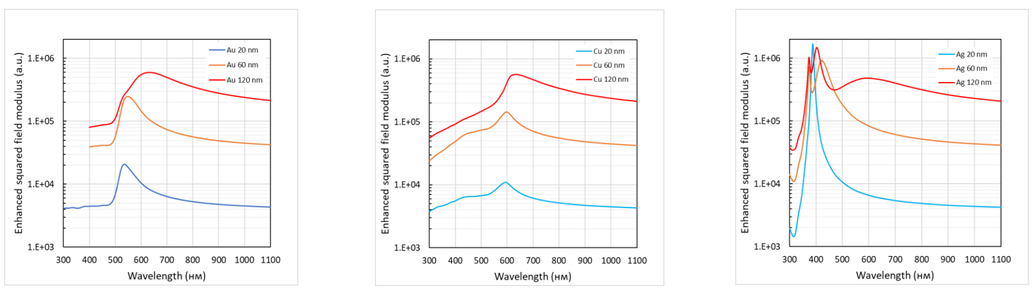


Figure 6. Spectral dependences of the E-field enhancement on the surface of **Au** (left fragment), **Cu** (middle fragment) and **Ag** (right fragment) nanoparticles of various diameter.

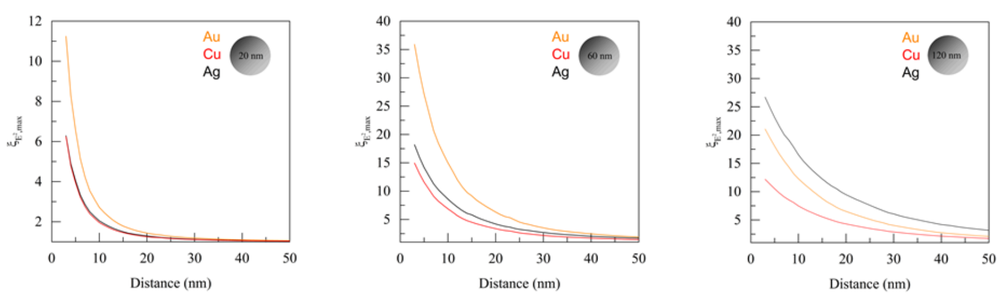
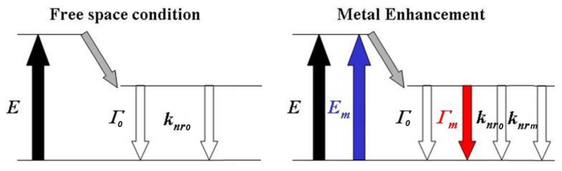


Figure 7. Dependence of the maximum of E-field enhancement coefficient vs distance to the nanoparticle when irradiated with a plane wave at the excitation wavelength of the TagRFP λ=555 nm.

Results of solving the problem 2 - On the emission of a fluorophore molecule and the calculation of the ratio of radiation losses to non-radiation losses



Modified Yablonsky diagram for the case of radiation of a solitary molecule in free space (fragment on the left) and in the presence of metal (fragment on the right). E и E_m represent the rate of excitation without metal and excitation rate with metal amplification; Γ_0 is the emission rate; Γ_m represents the rate of radiation due to the proximity of metal; k_{nr} is the rate without radiation. Presented on the basis of the provisions of works [L. Novotny and B. Hecht 2012, ISBN 978-1-107-00546-4] and [W. Deng et al. Physical Chemistry Chemical Physics 2013, doi:10.1039/C3CP50206F]. Then for the quantum yield of a solitary molecule QY0 and near a metal nanoparticle QY we can write: $QY_0 = \frac{\Gamma_0}{\Gamma_0 + k_{nr0}}$, $QY = \frac{\Gamma_0 + \Gamma_m}{\Gamma_0 + \Gamma_m + k_{nr} + k_{nrm}}$.

And for the fluorescence enhancement factor: $K_{flu}=P_{\text{fluorophore}}/P_0 = |E_{ex}|^2 QY_0$, where $P_{\text{fluorophore}}$ and P_0 are the number of photons in the presence and without a nanoparticle; E_{ex} is the intensity of the enhanced field at the excitation wavelength of the protein; k_T is the coefficient of linear change in fluorophore activity upon heating; T_{in} is the initial temperature of the protein molecule; QY_{em} is quantum yield of a molecule near a nanoparticle at the emission wavelength; ΔT – the amount of heating of the protein molecule; QY_0 is the quantum yield of the fluorophore molecule, determined at a certain reference temperature T_0

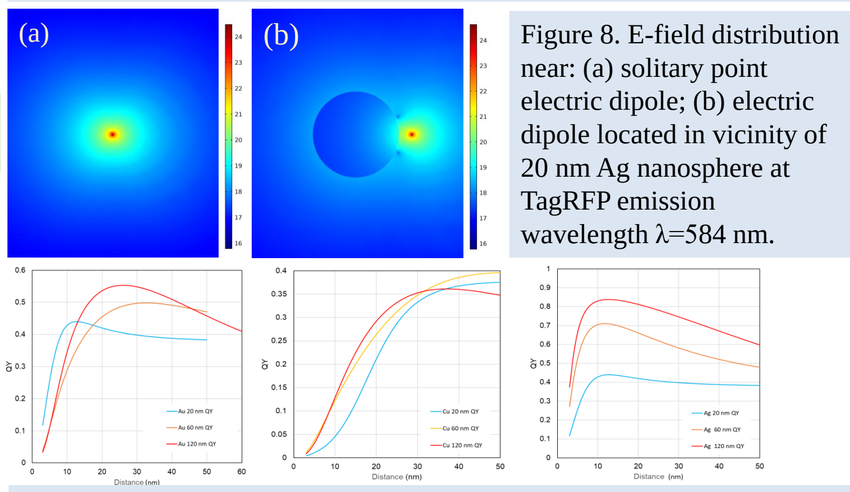


Figure 8. E-field distribution near: (a) solitary point electric dipole; (b) electric dipole located in vicinity of 20 nm Ag nanosphere at TagRFP emission wavelength λ=584 nm.

Figure 9. Dependence of the of the quantum yield of the TagRFP fluorophore molecule vs distance to the nanoparticle when emits at emission wavelength of the TagRFP protein λ_{em}=584 nm.

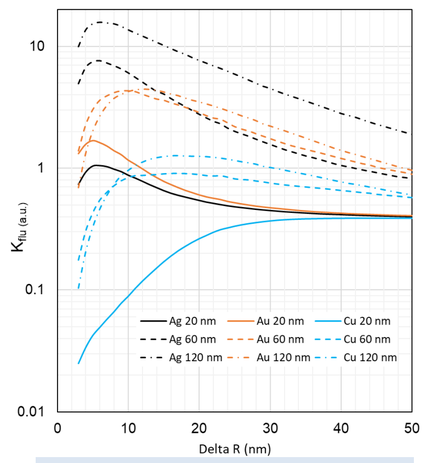


Figure 10. Fluorescence enhancement factor vs distance to the nanoparticle when emits at emission wavelength.

CONCLUSIONS

1. **Model software has been developed that expands the possibilities for solving practical problems of creating more effective fluorescent complexes for bioimaging systems.**
2. **The maxima of metal-enhancement factor noticeably shift to smaller gaps in comparison with similar dependences of the quantum yield maxima. It was found that the optimum gap lies in the range of 6-10 nm.**
3. **Competitive solutions appear to be fluorescent complexes based on large-sized silver and gold nanoparticles. Nanoparticles with a diameter of 20 nm have a significantly lower fluorescence enhancement factor. Copper nanoparticles do not create conditions for a satisfactory increase in fluorescence; in most cases, they even contribute to fluorescence quenching.**

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