Plasmon-Exciton Interaction in AuNP - Phthalocyanine Core/Shell Nanostructures.

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Abstract. We report results of theoretical modeling of photophysical properties of hybrid gold-core nanoparticles (AuNP) covered with the chlor-aluminium phthalocyanine (CAP) shell. The extinction spectra, the near field distribution and the CAP fluorescence quantum yield (QY) changing due to the vicinity to the AuNP were theoretically calculated for different values of the core/shell ratio parameter and compared to experimental data obtained for the structures under consideration.

1. Introduction

Noble metallic nanoparticles are promising building-block materials for various applications due to their tunable optical properties which depend on the size, shape and environment. Such particles support localized surface plasmon resonances, collective oscillations of surface electrons leading to the generation of a locally enhanced field. Placing chromophore molecules near to the metal surface, in the strong local field, can lead to the manifestation of such phenomena as modification of scattering and absorption spectra of the chromophore/metal structure in comparison with those of the constituents individually \cite{1,2}; modification of the chromophore’s fluorescent properties \cite{3}; surface enhancement of Raman scattering (SERS) \cite{4}; considerable enhancement and modification of nonlinear-optical properties and, in some cases, lasing in multilayer structures \cite{5}. Recently, considerable interest has been focused on plasmonic nanoparticles covered with a shell of phthalocyanine (Pc) molecules. Such hybrid particles are considered as perspective structures for biology and medicine applications (e.g. photodynamic therapy of oncologic diseases), optoelectronics and photovoltaics, various gas sensors and etc. In spite of the great interest displayed by researchers to the hybrid plasmonic nanostructures \cite{6, 7} little attention is paid to the explanation and modeling of the photophysical mechanisms occurring in such systems.

2. Theoretical model

The scheme of the model of the interaction between AuNP and CAP is presented in Fig.1. In order to explain linear optical properties of AuNP-CAP particles such as absorption, scattering and luminescence we used the joint solution approach of the following two problems. The first one is the problem of the light scattering by a multilayer spherical particle represented in Ref. 8. Applying this approach one can consider the AuNP-CAP particle as a two-layer spherical particle and calculate its near field distribution. At this step it is necessary to evaluate correct values of complex dielectric permittivity of each layer, the AuNP core and the CAP shell. The values of the AuNP dielectric permittivity were evaluated with the following analytical expression \cite{10}. 


\[ e_m(\omega, r) = e_{\text{bulk}}(\omega) + \omega_p^2 \left( \frac{1}{\omega^2 + i \omega \gamma_{\text{bulk}}^{\text{int,ra}}} - \frac{1}{\omega^2 + i \omega \gamma_{\text{int,ra}}^{(r)}} \right). \]  

(1)

where \( e_{\text{bulk}}(\omega) \) is a dielectric constant of the bulk metal, \( \omega_p \) is a plasmon frequency for bulk metal, \( \gamma_{\text{int,ra}}^{(r)} \) is an effective damping constant (related to the frequency of electron - metal/chromophore interface scattering), \( \gamma_{\text{int,ra}}^{\text{bulk}} \) is a bulk metal damping constant (related to the frequency of electron scattering in the bulk metal), \( \xi \) is a parameter which is dependent on the details of the scattering process (e.g. isotropic or diffuse scattering, \( \xi = 1 \) in our case), \( v_F \) is the velocity of the electrons at the Fermi energy, \( r \) is the radius of metal particle. The expression (1) includes the size adjusted Drude term and the interband transitions term describing the electron transitions from d – valence band to SP – conduction band in the short wavelength region. The average size of the AuNP core was equal to 18 nm, as was obtained by a scanning electron microscope. The permittivity of the CAP shell was taken equal to that of zinc Pe [11] due to nearly identical optical properties of these two compounds. CAP layer thickness was taken to be equal to 2.5.

The second step is to determine relative changes in the relaxation rates of the CAP molecule in the previously calculated near-field. In our procedure the outer shell of CAP molecules was considered as the layer of two-level quantum systems. It is known, that intensity of luminescence is proportional to rate of luminescence \( \gamma_{\text{em}} \). Thus, the equation for the luminescence intensity of CAP placed near to the AuNP was confronted to the luminescence intensity of CAP in free space determined by the following expression [9]

\[ \frac{\gamma_{\text{em}}}{\gamma_{\text{em}}^0} = \frac{\gamma_{\text{exc}}[\gamma_{r}/\gamma]}{\gamma_{\text{exc}}^0[\gamma_{r}^0/\gamma^0]} = \frac{\gamma_{\text{exc}}}{\gamma_{\text{exc}}^0} \frac{QY}{QY^0} \]

(2)

where \( \gamma_{\text{em}}, \gamma_{\text{exc}}, \gamma_r \) are rates of luminescence, excitation, spontaneous emission, respectively, \( \gamma \) is the total decay rate and \( QY \) is the quantum yield of CAP molecules. The upper index “0” relates to the values of mentioned parameters in free space, whereas its absence relates to the parameters in the vicinity of the AuNP. Then the problem of changes in the rate of spontaneous decay of these systems in the self-consistent near-field was solved. This near-field was determined by solving the problem of the light scattering by the multilayer structure.

Figure 1. Scheme of the theoretical treatment (Model).
3. Results and discussion

Using the described above theoretical approaches, the extinction cross-sections for uncoated AuNP and AuNP-CAP core/shell nanostructures were determined. We also calculated the contributions of the scattering and absorption processes to the entire extinction. Below are the results of the calculated extinction spectra for AuNP with the average diameter equal to 18 nm (figure 2a), and the scattering/absorption ratio as the function of a wavelength (figure 2b). Similar curves for the particles coated with phthalocyanine molecules are shown at the figure 2 c,d.

As can be seen from Fig.2 the extinction spectrum of the hybrid structure (Fig. 2b) is broadened with a not large increase in magnitude in comparison with the spectrum of the pure AuNP colloid. The extinction cross section also increases in a long-wavelength range of the spectrum, which is the consequence of the presence of intensive absorption band in the Pc layer due to the exciton excitation. It should be mentioned that the spectrum changing character during the formation of an outer Pc layer is not of an additive nature. This indicates to the influence of the outer layer on the AuNP field mode structure, which is dictated by free electron oscillations, i.e. LSP.

The determination of near field distributions is one of the major result of the first step calculation. The near field distributions of coated and “pure” AuNP are represented in Fig. 3.
Figure 3. The intensity of near field distribution generated by coated (a,b,c) and “pure” (d,e,f) AuNp, for $\lambda_{Exc}^{(1,2,3)} = 488; 532; 650$ nm respectively.

Fig. 3a and 3b shows that the field in the core/shell structure is strongly localized in the Pc shell. The intensity enhancement reaches a 20-fold increase in comparison with the intensity of the incident field. Unlike the similar distributions of the “pure” uncoated AuNp (Fig. 3 d, e, f), a non-monotonic character of the field distribution along the radial direction is observed. In order to investigate the influence of the structure’s components on optical properties of the entire system we chose the wavelength of the incident field that it could coincide with a spectral position of the exciton resonance in the Pc and the position of LSP resonance.

Figure 4. Relative luminescence, quantum yield and the rate of excitation as dependences on the distance from chromophore to particle.
As can be seen, the luminescence increases with the distance from the surface of the gold core. There is the strengthening coupling between the relaxation rate of the entire “particle-chromophore” system and higher order modes of the free electron oscillations when the distance decreases. It can be explained by the exciton-plasmon coupling. In our calculations we took into account the higher order modes which are up to 110.

4. Experimental section

The quenching of luminescence was also observed, which is related to the processes of energy transfer between AuNP and CAP molecules and to the subsequent Ohmic losses of energy in the AuNP. The reason of the observed quenching effect is the interaction between the molecules and nanoparticles, and is also the result of molecules aggregation on the gold particle surface. This result is consistent with the data from other studies dedicated to stabilization of AuNP with the various organic molecules. Due to the molecular aggregation and the proximity between molecules and the AuNP’s surface almost full quenching of luminescence is observed [3].

Using theoretical approach described above we modeled the extinction spectrum of the experimental gold nanoparticles and AuNP-CAP structures, taking into account their real size distribution and thickness of Pc shell (2.5 nm). As illustrated in figure 5 the experimental data is well approximated by the model curve.

![Figure 5. Model and Experimental extinction spectra of the AuNP.](image)

![Figure 6. Model and Experimental extinction spectra of the AuNP-CAP nanostructure.](image)

The changes observed in the extinction spectra of Core/Shell AuNP-CAP structures related to the plasmon - exciton interactions have a good agreement with the modeling results (figure 6). Figure 6 shows the experimental and model extinction spectra of the experimental obtained AuNP-CAP nanostructures. We obtained very similar results, the model spectrum includes all spectral features which were observed in the experimental dependence.

5. Conclusions

We proposed the model to describe active plasmonic spherical nanostructures, allowing modeling the linear optical properties. Using our model we calculated scattering and absorption cross sections, the near field distribution, changes in the radiative and nonradiative spontaneous decay rates, changes in the quantum yield of CAP luminescence, the total change in the luminescence. The analysis of the results let us to set mechanisms of changes in the linear optical properties which are explained throughout the plasmon-exciton interaction. The comparison experimental and theoretical results is one of the important parts of our research. We prepared the hybrid structures and determined their extinction and luminescence spectra. Good agreement between theory and experiment indicates that
The proposed model is able to explain linear optical properties of our AuNp-CAP structure and the same structures too.

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