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Resonant plasmon-stimulated nonlinear absorption in three-level systems.

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Abstract. Mechanisms of resonant nonlinear absorption in the hybrid exciton-plasmon systems based on gold nanoparticles and macroheterocyclical compounds are presented. We used novel substituted subphthalocyanines (SubPc) with \(14\pi\)-electronic system as powerful excitonic 3 – level systems, and 50 nm gold nanoparticles (AuNp) as plasmonic structures. We succeeded to define mechanisms of resonant nonlinearities and to show that local field factor (LFF) and Purcell factor (PF) lead to dramatic enhancement in SubPc nonlinearity. We suggest a theoretical model which describes exciton-plasmon interaction of porphyrin/phthalocyanine related compounds with gold nanoparticles in the resonant high power laser field.

Unique optical properties of hybrid structures based on metal nanostructures and chromaphore molecules are very promising in nonlinear optics. Nowadays different hybrid plasmonic nanosystems are used as a basic part of optical modulators and switches [1,2], nanolasers [3,4], high-sensitive sensors [5,6], harmonic generation materials [7], optical limiters etc. Tight “mixing” of plasmonic properties of metal structures with excitonic properties of chromophore is a key feature of resonant nonlinearity, it leads to dramatic changings in optical nonlinear properties in the whole exciton-plasmon system. There are two major reasons for it. The local field factor i.e. enhancement of the near field intensity would result to increase of the nonlinear responses, on the other hand enhancement of the decay rate of excited states would lead to acceleration of the rate in a radiative relaxation process. In spite of very different time scales of the processes in a uncoupled regime, when chromophore and plasmon structures don’t interact, in the tightly “mixing” exciton-plasmon regime both processes can have similar time scales. Therefore relaxation and excitation rates can turn from independent values into strong correlated ones. In addition to modification of the rates of electronic transitions in plasmon-coupled excitonic systems, the impact of strong near-field on chromophores can lead to appearance of parametric nonlinearities, such as multiphoton absorption and others. Therefore it is very difficult to predict a character of nonlinear properties in general, without full description of the exciton-plasmon system’s dynamics. Among promising nonlinear optical (NLO) organic materials, macroheterocyclical compounds hold a special place [8] due to their large conjugated electronic system. This is the origin of considerable nonlinear response in such compounds. High structural flexibility of the molecule allows one to construct new materials with prescribed NLO properties. According to this, researchers paid great attention to develop novel NLO devices based on different macroheterocyclical chromophores [9,10]. In particular, subphthalocyanine (SubPc) compounds are good candidates to be used in harmonic generation [11,12] and optical modulating/switching devices [13]. We believe that unique optical properties of plasmonic structures together with noticeable NLO properties of macroheterocyclical compounds are very encouraging to enhance the efficiency of...
existing NLO devices, as well as to reduce correspondent thresholds, and allow to discover completely new applications. The first step is a study of light absorption properties. Thus, the subject of our research is an experimental and theoretical study of resonant plasmon-stimulated nonlinear absorption in three-level chromophore systems, investigation of the involved mechanisms.

2. SYNTHESIS of nano-hybrids

An aqueous solution of gold nanoparticles (AuNp) capped with citric ion was prepared by reduction of HAuCl₄ with sodium citrate as described previously elsewhere [14]. The mean diameter evaluated from transmission electron microscopy (TEM) images was equal to 50±5 nm. Hexa-phenoxy substituted subphthalocyanines, bearing a halogen atom (chlorine) in axial position, were synthesized from corresponding phthalonitrides using the method described in literature [15]. Solution of PhO⁻SubPcBCl (0.6 mL, 3·10⁻⁵ M) in DMSO was mixed with aqueous solution of AuNP (0.6 mL, 50 nm gold particles), then 0.3 mL of DMSO:H₂O (1:1, V:V) was added. This mixture was stirred for 24 h for the stacking to take place. The completeness of reaction was monitored by quenching of free subphthalocyanine luminescence.

Figure 1.Scheme of possible AuNp - PhO⁻SubPcBCl conjugate formation.

There are two approaches to formation of interaction between the target subphthalocyanines and the surface of nanoparticles. First, the formation of new B-O bond between -OH fragments of citrate and central halogen atom of subphthalocyanine (Fig.1A). It resulted from high lability of extra ligand in subphthalocyanine complexes. Second, due to the appearance of π-π interactions between subphthalocyanine macrocycle and surface of nanoparticles (Fig.1B). We suppose, that these two directions of AuNp - PhO⁻SubPcBCl conjugate formation are equally possible.

3. LINEAR properties

In order to achieve a strong exciton-plasmon interaction in hybrid structures, it’s necessary to provide both excellent spectral overlap between absorption band of chromophores with plasmonic band of AuNp, and their extremely close spatial arrangement [16]. Figure 2A presents linear extinction spectra of synthesized PhO⁻SubPcBCl, AuNp and hybrid nanostructures. From Figure 2A it follows that energy of chromophores’ transitions from the ground state to the first excited state is tuned into plasmonic resonance. Linear spectrum of “hybrids” isn’t a direct superposition of correspondent spectra of structures’ components. Difference extinction spectrum (Fig.2B), formed by the difference between hybrid’s spectrum and the sum of the PhO⁻SubPcBCl and AuNp spectra, demonstrates a “dip”. We suppose that it is Fano “dip” with the energy splitting about 50 meV. Presence of Fano “dip” in extinction spectra is a widespread proof of strong exciton-plasmon coupling in such hybrid structures. Moreover, Yoshida et al. showed that strong couplings are possible between molecules which have only been directly attached to metal surface [17], therefore absence of the “dip” in the total extinction spectrum of “hybrids” (Fig.2A) is caused by little fraction of molecules which are directly attached onto the metal surface.
While photoluminescence (PL) study of “free” SubPc molecules showed that PL quantum yield (QY) is equal to 0.15, PL signal of nano-hybrid structures is strongly suppressed. More detailed investigations of PL have been done using time-correlated single photon counting (TCSPC) method. PL quenching rates of both structures are similar ($\tau_{PL} = 2.6$ ns). According to this, we can conclude that PL quenching is a result of coupling between radiative excitonic modes of chromophores and high-order plasmonic modes (nonradiative) of AuNp.

4. NONLINEAR resonant absorption

Experimental studying of resonant nonlinear absorption was carried out using open-aperture single beam Z-scan technique [18]. We utilized the second harmonic generation light of mode-locked Nd$^{3+}$:YAG laser operated in TEM$_{00}$ mode with the pulse duration of 350 ps and a low repetition rate of 5 Hz (to prevent heating processes). The beam was tightly focused by a lens, the radius of the beam waist was equal to 25-30 μm with the pulse energy equal to 40 μJ. The peak intensity in the focus was equal to $4.8 \times 10^{9}$ W/cm$^2$. All measurements were done using 5 mm quartz cuvette.

According to results of our experimental and theoretical research of nonlinear absorption in “free” SubPc molecules we established that the molecules are equivalent to 3-level quantum systems, in case of short-pulse resonant excitation. Figure 3A represents fitting results of the experimental data by the 3-level model. Absorption cross-section of $S_1$ – $S_2$ transition ($\sigma_{12}$) and relaxation rate of $S_2$–$S_1$transition ($\tau_{21}$) were determined during the fitting procedure. Nowadays, nonlinear absorption mechanisms and properties of metal nanoparticles are well-known [19], there are many papers showing that the nonlinear response of silver and gold nanoparticles in our set up conditions are well described by third order susceptibility $\chi^{(3)}$ [20,21].

An obvious feature of the nonlinear transmission of "hybrids" (Fig.3B) compared with "free" chromophores (Fig.3A) is a presence of considerable maximum near the beam focus. Since the experimental results contain both information about plasmon-stimulated absorption of 3-level systems and information about absorption in metal cores of the structures, it’s impossible to determine the impact of exciton-plasmon interaction on the resonant absorption of 3-level systems and the mechanism of observed changings in Z-scan without building the physical model and separating responses of each component. In the frame of Optical Bloch formalism the theoretical model of resonant nonlinear absorption of plasmon-coupled 3-level systems was proposed. In high intensity irradiation plasmonic excitation can be considered in classical Maxwell approximation, while 3-level systems operated by Hamiltonian, can be considered in density matrix formalism.
Behavior of 3-level systems in the electromagnetic field was described using density matrix $\hat{\rho}$ with time evolution given by quantum Liouville equation [22] within phenomenological relaxation operator $\hat{\Gamma}$.

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} \left[ \hat{H}, \hat{\rho} \right] + \hat{\Gamma}$$

where total Hamiltonian of the system in the electromagnetic field is a sum of Hamiltonian of the system without external field (unperturbed part) $\hat{H}_0$ and interaction Hamiltonian (in the dipole approximation) $\hat{H}_I$. According to that, motion equations of the density matrix elements can be expressed as follows:

\[
\begin{align*}
\hat{\rho}_{00} &= \gamma_{11} \rho_{11} - \frac{i}{\hbar} \left( \rho_{10} \mu_{01} E_{\text{loc}}^* - \rho_{01} \mu_{10} E_{\text{loc}} \right) \\
\hat{\rho}_{11} &= -\gamma_{11} \rho_{11} + \gamma_{22} \rho_{22} + \frac{i}{\hbar} \left( \rho_{10} \mu_{01} E_{\text{loc}} - \rho_{01} \mu_{10} E_{\text{loc}}^* \right) - \frac{i}{\hbar} \left( \rho_{21} \mu_{12} E_{\text{loc}}^* - \rho_{12} \mu_{21} E_{\text{loc}} \right) \\
\hat{\rho}_{22} &= -\gamma_{22} \rho_{22} + \frac{i}{\hbar} \left( \rho_{21} \mu_{12} E_{\text{loc}} - \rho_{12} \mu_{21} E_{\text{loc}}^* \right) \\
\hat{\rho}_{01} &= \rho_{10}^* = -\left( -i \omega_a + \gamma_{01} \right) \rho_{01} - \frac{i}{\hbar} \left( \mu_{01} E_{\text{loc}}^* (\rho_{11} - \rho_{00}) - \mu_{10} E_{\text{loc}} \rho_{02} \right) \\
\hat{\rho}_{12} &= \rho_{21}^* = -\left( -i \omega_a + \gamma_{12} \right) \rho_{12} - \frac{i}{\hbar} \left( \mu_{12} E_{\text{loc}}^* (\rho_{22} - \rho_{11}) + \mu_{21} E_{\text{loc}} \rho_{02} \right) \\
\hat{\rho}_{02} &= \rho_{20}^* = -\left( -i2 \omega_a + \gamma_{02} \right) \rho_{02} + \frac{i}{\hbar} \left( \mu_{12} E_{\text{loc}}^* \rho_{01} - \mu_{01} E_{\text{loc}} \rho_{12} \right)
\end{align*}
\]

Taking into account the modification of spontaneous decay rate (radiative) from the 1st excited state to the ground state of 3-level systems placed in vicinity to the AuNp (i.e. Purcell effect), the above equations describe the dynamics of plasmon-coupled systems completely. But electromagnetic field ($E_{\text{loc}}$) which acts on the systems, depends on the polarization of that systems. Moreover, according to Maxwell equations and boundary conditions the field is changed in space and time during the propagation through the sample. To obtain self-consistent system of differential equations we have to complete above presented motion equations by adding classical equations which bind the electric field with the induced polarization. Solving such self-consistent system of differential equations in general is a very tough issue, instead of that we can introduce some reasonable simplifications. Since the chromophore’s shell thickness is about 5 nm (it’s about 10% of total “hybrid” size) in accordance with TEM measurements, we can ignore a dependence of the near field which acts on 3-level systems on their polarization. Taking into account decay rates and transitions linewidths of 3-level systems we can also ignore rate equations of non-diagonal density matrix elements - it’s another assumption. Thus,
the nonlinear response of the ‘hybrids’ is determined only by population dynamics of 3-level systems and by the local near-field which depends on internal AuNp Kerr nonlinearity.

Figure 4. Simulated Z-scan curves of plasmon-coupled systems (a), “free” systems (b), coupled systems considering only field factor (c), coupled systems considering only Purcell factor (d).

Taking into account the assumptions, we numerically solved the problem using FDTD method without any adjustable parameters. The model curve is displayed by solid line in Figure 3B, it coincides well with the experimental results. In order to conduct quantitative comparison of nonlinear response of plasmon-coupled 3-level systems with “free” systems we simulated curves for relevant systems with similar concentration (Figure 4a,b). We also simulated curves with just one local field factor (Figure 4c) and just one Purcell factor (Figure 4d) to determine mechanisms of changes observed. The modeling results showed that there are approximately equal contributions to the total nonlinear response - the first is caused by Purcell factor and the second by the strong near-field. Difference transmittance of plasmon-coupled chromophores is three times as much than “free” molecules (Figure 4a,b), when concentration of both is equal to 2⋅10^{-6} M. It explained by a superposition of influence of two factors (field factor and Purcell factor). At the same time the total nonlinear response of plasmon–coupled systems (Figure 4a) cannot be described by the direct sum of each factor’s response. Analyzing dependence of the normalized populations on the intensity of laser radiation allows us to establish a reason of such dramatic differences in nonlinear transmittance. Thus, in case of “free” molecules the master mechanism which leads to the observed “saturation” effect in absorption is a decrease of ground state population especially near the beam focus. At the same time there is no significant contribution of transition from the 1st excited state to the second one to the saturation “effect”. It slightly appears only in the beam focus. However, in case of plasmon-coupled systems both transitions play significant role in saturation process. Therefore both transitions S_0 \rightarrow S_1 and S_1 \rightarrow S_2, turn out to be saturated in the beam focus – it explains dramatic changings of the transmittance in plasmon-coupled systems.

5. Conclusions

This is the first time when the synthesis of hybrid nanostructures based on 3-level chromophores with high resonant interaction was implemented. We experimentally studied their linear optical properties, found out the presence of Fano “dip” in the difference absorption spectrum conforming to strong exciton-plasmon coupling between SubPc and AuNp. Relaxation rates of both free chromophores and hybrid nanostructures were measured. The experiment claims to be the first Z-scan study of resonant absorption properties of similar structures in a wide range intensity of incident radiation. Based on Optical Bloch formalism, we proposed a model that properly represents the experiment results. By applying the model we succeeded to define mechanisms of nonlinear resonant response. According to our research Purcell effect and near-field
factor equally contribute to the nonlinear response. The enhancement of absorption “saturation” effect caused by Purcell effect has turned up the surprising result and, as far as we are aware, is observed for the first time.

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