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Modification of the Optical Spectra of Organic Semiconductor Thin Films Doped by Plasmonic Nanoparticles

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Ag/CuPc nanocomposites and their components have been fabricated by means of a thermal evaporation in vacuum and their optical spectra have been investigated. The dependence of the matrix absorption enhancement on the Ag nanoparticle sizes and the CuPc film thicknesses has been established. For plasmonic nanoparticles placed into absorbing organic matrix the near-field pattern and the near field scattering factors have been simulated in the frame of the Mie theory and analyzed.

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Introduction

Organic semiconductors attract an attention of a wide range of researchers. The numbers of unique devices and instruments for optical and electronic applications based on organic semiconductors have been already created, that show a promise of such materials. An increased interest to organic semiconductors is due to their low cost and simpler process conditions as compared to conventional crystalline materials.

The possibility of applications of plasmonic nanostructures in functional optical elements and hybrid materials containing both inorganic and organic components has been studied in recent years. Significant prospects are connected with a fast and adjustable optical response of plasmonic metallic nanoparticles, as well as with a significant enhancement of electromagnetic fields near their surfaces. These effects are particularly pronounced in the visible spectral region near the surface plasmon resonance (SPR) absorption peak, which is highly sensitive to both the parameters of metallic nanoparticles, as well as to the characteristics of the matrix [1].

High inhomogeneity of the near field in metal nanostructures finds a practical use in enhancing the Raman scattering and luminescence of molecules placed near the surface of metal nanoparticles, as well as in enhancing the absorption of the solar cell active layers [2]. However the nature of plasmonic and near-field effects is not still clear and the problem of nanoparticle size and concentration optimization is now also under discussion.

As it was shown in [3], an assessment of the near field effects on an absorption spectrum modification of

the semiconductor matrix through the introduction of the plasmonic nanoparticles may be carried out by comparing the spectral absorption coefficient of matrix m_i and the product $m_i Q_{NF}$, where Q_{NF} is the scattering efficiency factor in the near field, which describes the effect of field enhancement near the metal nanoparticle. The quantity Q_{NF} characterizes the field intensity increase on the surface of a sphere of radius R when nanoparticle is introduced into the sphere center.

In this work we study experimentally obtained optical absorption spectra of nanocomposites Ag/CuPc and their components. With the use of numerical calculations for the plasmon nanoparticle placed in an absorbing matrix of copper phthalocyanine and other organic semiconductor materials we also analyze the near-field pattern and scattering factors in the near field.

I. Experimental methods

Experimental samples were prepared in a vacuum setting VU-1A by a thermal successive evaporation of CuPc and Ag on glass and quartz substrates at a room temperature. The pressure of residual gases was $(2 - 6) \times 10^{-5}$ Pa. The control of evaporated layer thicknesses was made with the use of a quartz sensor. Optical spectra were recorded at the spectrophotometer "Cary 500". Plasmon nanoparticle doping was produced by means of the Ag island film displacement into the CuPc thin-film matrix.

II. Method of numerical simulation

In order to define internal fields into metal

nanoparticles and electromagnetic fields near their surfaces we used the Mie theory. The method is based on the expansion of the incident, scattering and internal fields on vector spherical harmonics with a subsequent determination of the expansion coefficients from a numerical solution of a system of algebraic equations [4 - 6].

At the calculations of Q_{NF} we used the expression given in [7] and special computer codes developed for particles embedded in an absorbing medium. The integral on a sonar spectra effectiveness of a matrix absorbency due to the doping with plasmonic nanoparticles may be characterized in the following way:

$$A^R = \frac{\int G(I)m_i(I)Q_{NF}^R(I)dI}{\int G(I)m_i(I)dI}, \quad (1)$$

Here $m_i(I)$ is an absorption factor of matrix, or an imaginary part of a complex refractive index of matrix, $G(I)$ – spectral density of a solar radiation, R – nanoparticle size. At our numerical simulation the values of real and imaginary parts of a complex refractive index of organic semiconductor were taken from [8]. Optical constants of silver were taken from [9]. Besides, we corrected silver nanoparticles optical constants as it was described in [7] in order to take into account the so-called internal size effects leading to additional electron energy losses due to their scattering at nanoparticle surface.

III. Results and discussion

3.1. Modification of absorption spectra of copper phthalocyanine due to the doping by silver nanoparticles.

In practical applications of organic semiconductors as an active layer of photovoltaic elements one can remark copper phthalocyanine (CuPc). Since a process of light transformation into electric energy into organic semiconductors includes a step of an exciton formation then the high absorbency of the layers and their small thicknesses are important in order to exclude recombination effects.

We fabricated CuPc-bearing nanostructures with various constructive parameters and analyzed their optical spectra. For example, in Fig. 1 (curve 1) one can see an optical density spectrum of the CuPc film with a thickness ~ 5 nm, formed on a quartz substrate. It is seen that in the spectral range under consideration a copper phthalocyanine has two quite strong absorbency bands with maxima at wavelengths 350 nm and 630 nm, and third low intensive band with a maxima at a wavelength about 700 nm. One can see also that a CuPc film is the most transparent in the spectral range from 400 up to 540 nm.

Curve 2 in Fig. 1 corresponds to the Ag – CuPc double-layer system, which is consisted from a silver island film with a metal surface density (MSD) of $1,9 \times 10^{-6}$ g/cm² placed at a glass substrate and covered by a copper phthalocyanine layer of a thickness about 5 nm. Optical density spectra of a silver island film without an

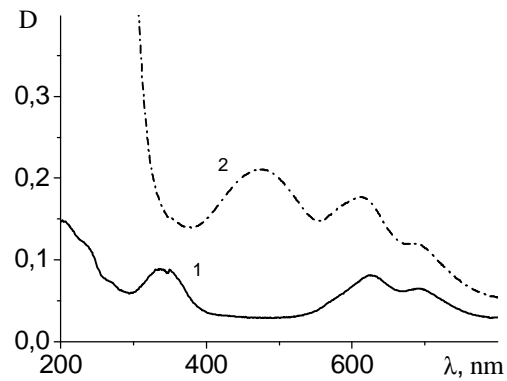


Fig. 1. Spectral dependence of the optical density of the phthalocyanine film with a thickness of 5 nm (1) and double-layer system Ag-CuPc (2) with the same thickness of the phthalocyanine film and a silver surface density of $1,9 \times 10^{-6}$ gcm⁻².

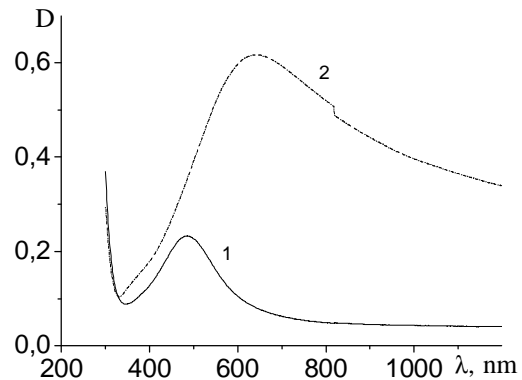


Fig. 2. Spectral dependence of the optical density of the island silver films with a metal surface density of $1,9 \times 10^{-6}$ gcm⁻² (1) and $8,7 \times 10^{-6}$ gcm⁻² (2) on the glass substrates.

organic coating are demonstrated in Fig. 2, curve 1. For the structures under consideration the SPR band is situated in the spectral range $\sim 400 - 600$ nm with the maxima at the wavelength 480 nm. At the same wavelength 480 nm that corresponds to the range of a CuPc matrix transparency one can see an optical density maxima of the double-layer Ag-CuPc system (Fig. 1, curve 2). There are also two maximum of the Ag- CuPc system optical density at wavelengths about 630 nm and 700 nm that associated with the absorption bands of CuPc.

As one can see from Fig. 2, the enlarge of a metal surface density at island films leads to the longwavelength shift of the SPR as well as to the increase of its half-width and intensity. These changes are connected with a lateral electrodynamic coupling enhance at the increase of an overlap factor η (overlap factor η characterizes a ratio of a sum of all particle cross-sections to a substrate square [1, 10]). This fact is illustrated by the data presented in Fig. 3. Fig. 3 demonstrates the optical density spectra of the phthalocyanine film with a thickness of 20 nm (curve 1)

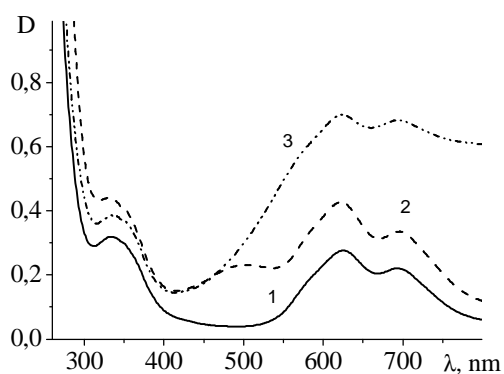


Fig. 3. Spectral dependence of the optical density of the phthalocyanine film with a thickness of 20 nm (1) and double-layer system Ag-CuPc (2) with the same thickness of the phthalocyanine film and a silver surface density of $1,9 \times 10^{-6} \text{ gcm}^{-2}$ (2), $8,7 \times 10^{-6} \text{ gcm}^{-2}$ (3).

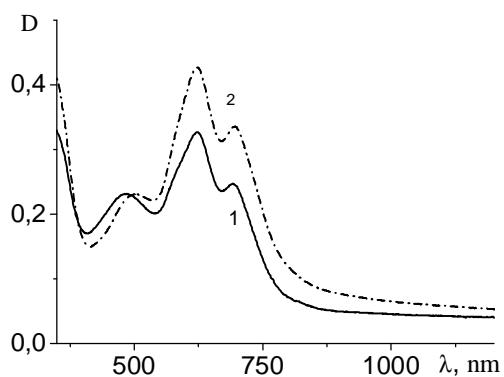


Fig. 4. Spectral dependence of the sum of the optical densities of the phthalocyanine film with a thickness of 20 nm and the island silver film with a metal surface density of $1,9 \times 10^{-6} \text{ gcm}^{-2}$ (1, $D(\text{Ag}) + D(\text{CuPc})$) and the optical density spectra of the double-layer system Ag-CuPc (2, $D(\text{Ag} + \text{CuPc})$) with the same parameters.

and two Ag-CuPc systems (curve 2, 3) each of them are a silver granular film with a definite metal density covered by a CuPc thin film and displayed on a glass substrate.

In order to regard the near-field effect in hybrid nanostructures we made a comparison of optical density spectrum of double-layer Ag-CuPc systems with spectrum of corresponding uncovered silver granular films and thin undoped CuPc films which were characterized by the same mass thicknesses as the components of double-layer systems involved. Fig. 4 shows a sum of the optical densities of the copper phthalocyanine film with a thickness of 20 nm ($D(\text{CuPc})$) and the island silver film with a metal surface density of $1,9 \times 10^{-6} \text{ gcm}^{-2}$ ($D(\text{Ag})$). Besides in Fig. 4 one can see the optical density spectra of the double-layer system Ag-CuPc ($D(\text{Ag} + \text{CuPc})$) with the same parameters. As it is seen, in the short-wavelength spectral range ($\lambda < 500 \text{ nm}$) an optical density of the double-layer system $D(\text{Ag} + \text{CuPc})$ is less than a sum of the optical

densities of the involved single layers $D(\text{Ag}) + D(\text{CuPc})$. At the same time for a wide spectral range $\lambda = 500 - 1000 \text{ nm}$ an optical density of double-layer system exceeds a sum of the optical densities of the independent constituents.

The highest increase of the double-layer system optical density in comparison with a sum of the optical densities of the included components amounts 65 % and is observed at the wavelength about 800 nm for island films with silver nanoparticle sizes about 5 nm imbedded into CuPc films with thickness of 20 nm.

It is worthwhile to note that in all cases considered both Ag and CuPc films were nanostructured. It is shown for example in Fig. 5 where the AFM-image of a CuPc film is presented. As one can see, lateral sizes of CuPc nanoparticles are about 20 – 80 nm in this case. The mean sizes of silver nanoparticles were found to be about 5 nm and 15 nm for island silver films with metal surface density of $1,9 \times 10^{-6} \text{ gcm}^{-2}$ and $8,7 \times 10^{-6} \text{ gcm}^{-2}$ correspondingly. Nanodimensions of Ag and CuPc films may give rise to strong near-field electrodynamic effects. In our opinion these effects is a general cause of experimentally observed modifications of the optical spectra of organic semiconductor thin films at their doping by plasmonic nanoparticles.

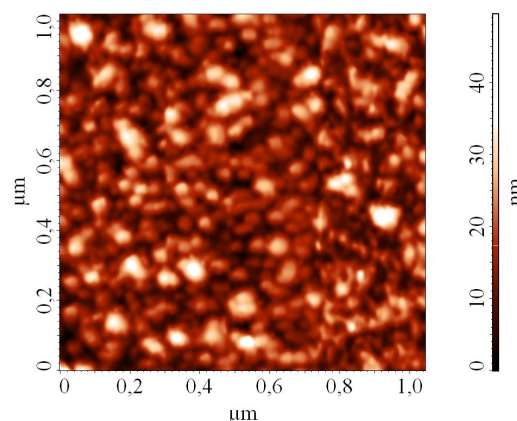


Fig. 5. AFM - image of the phthalocyanine film with a thickness of 20 nm.

3.2. Enhancement of fields near silver nanoparticles in absorbing matrices.

As it was already mentioned, one of the most important properties of plasmonic nanoparticles is their unique ability to enhance significantly the local field near their surfaces. Detailed study of the near-field distribution topology for silver nanoparticles of different sizes has been made in [3]. There also has been shown that for the definite wavelength the maximum values of the local field enhancement coefficients depend on the nanoparticle sizes and the refractive index of the surrounding matrix. Herewith the transparent matrices were considered, in which the absorption of radiation is entirely absent. For such systems, the scattering efficiency factor in the near field can be more than 10 times than the value of scattering efficiency factor in the far field. The value Q_{NF} for absorbing matrix, in particular copper phthalocyanine (CuPc), was analyzed in [7].

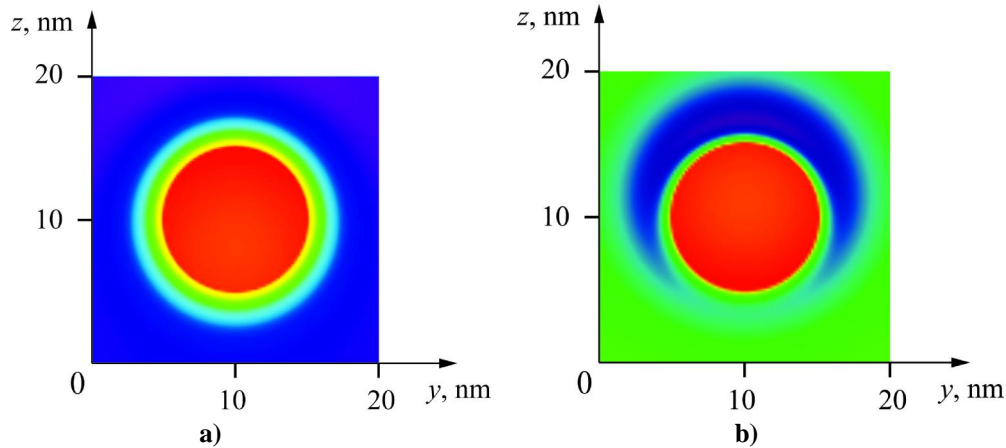


Fig. 6. Local field distribution at the central section of a silver nanosphere of the radius 5 nm imbedded into phthalocyanine. Wavelength is 450 nm (a) and 650 nm (b).

In cases when the host medium is absorbing, local field pattern near the SPR for small sizes of the nanoparticle ($R = 5 - 10$ nm) is faintly different from the case of transparent matrix. For all planes of section the local field is symmetrical both inside and outside the particle. In this case "hot spots" are also concentrated primarily on the particle surface, near its opposite poles along the polarization vector of the incident radiation. Field is rapidly waning with an increase of a distance from a particle surface. Presence of matrix absorption leads to the reduction of Q_{NF} and to the more rapid field weakening with a moving away from the nanoparticle surface.

It should be noted that the near field pattern changes when we consider particles cross sections at different wavelengths with respect to the plasmon resonance band. In this case, the local field distribution symmetry outside the particle in an absorbing matrix can be broken even for small particles with a radius of 5 - 10 nm. This is evident from the Figure 6, which shows the central section for silver sphere of radius $R = 5$ nm in copper phthalocyanine at the 450 nm and 650 nm. Absorption coefficients of copper phthalocyanine at these wavelengths are respectively ~ 0.05 and ~ 0.7 and so differ by more than an order of magnitude. One can see that while the local field is symmetric for all planes of section for $\lambda = 450$ nm, then at the wavelength $\lambda = 650$ nm the symmetry is broken for cross sections along to the direction of the incident radiation. This effect is due to the presence of absorption in the matrix.

The performed calculations of near-field characteristics show that the amplification effect can be significant. But as it was shown in [7] the enhancement manifests most strong in the blue region of the visible spectrum. In experiment the maximum enhancement occurs in the red part of visible range. This difference may be partly due to the fact that the calculations were performed for a single Ag particle, i.e., for a system with a localized plasmon resonance. In the case of a close-packed monolayer of nanoparticles, the scale of the plasmon localization changes and a collective plasmon resonance forms in a long-wavelength range relatively to the localized surface resonance. In this case, the effects of the near-field enhancement should occur at longer

wavelengths, as it was observed in the experiment.

Fig. 7 shows the size dependences of the value A which characterizes the total near-field enhancement effect being the result of the integration over the solar spectrum. Simulations were made with the use of the AM 1,5 standard for silver plasmonic nanoparticles embedded into different matrices. Calculations of quantity A were held for spherical region adjacent to the nanoparticles surface, taking into account the size dependence of optical constants. For example, the value of enhancement for the CuPc matrix depends on a size of introduced silver nanoparticles nonmonotonically and reaches a maximum ($A = 26$) for a nanoparticles diameter of 2 - 30 nm.

In Fig. 7 one can also see the similar features for a number of other organic materials such as 3, 4, 9, 10 - perylenetetracarboxylic bis-benzimidazole (PTCBI) and poly(3, 4 - ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT: PSS). This analysis has shown that CuPc is not the most effective matrix. For example, significantly greater effect can be achieved by using PEDOT: PSS. High values of the absorption enhancement effect integrated over the spectrum for the PEDOT: PSS organic matrix are due to the fact that this material is characterized by the widest region of a relative transparency in comparison with other materials

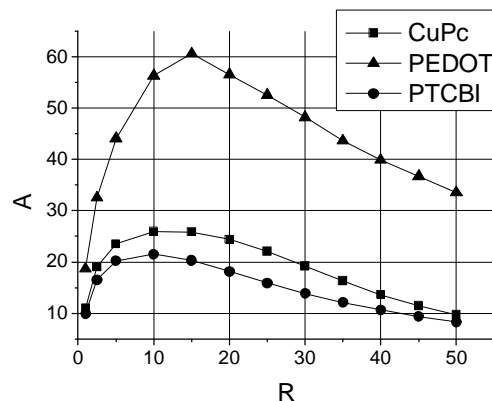


Fig. 7. Dependence of the integral enhancement coefficient A^R on the radius of silver nanoparticles, imbedded into various matrices.

of interest. Thus, there are good prospects for improving the efficiency of solar cells based on organic semiconductor materials through the doping by plasmonic nanoparticles.

Conclusion

Comparison of theoretical and experimental data show also that in order to describe the spectra of the Ag / CuPc nanocomposites one needs to take into account the near-field effects which results in strong absorbency increase of the CuPc matrix.

We found a strong modification of the Ag/CuPc

nanocomposite spectra in comparison with the spectra of the Ag island layer and the CuPc thin film. The degree of a spectra change was found to be dependent on silver nanoparticle sizes and their surface concentration, as well as on a CuPc film thickness. The most common feature is that the SPR of silver nanoparticles is pronounced weaker into the absorbing matrix. Besides, a matrix filling by plasmonic nanoparticle leads to matrix absorption enhancement especially in the long-wavelength (relative to the SPR) spectral range. This enhancement may reach 65 % at a special choice of silver nanoparticle sizes and a CuPc film thickness. .

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