PLASMON-EXCITON COUPLING IN A HYBRID FILMS OF METALLIC NANOPARTICLES AND J-AGGREGATES OF CYANINE DYES

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Abstract

The effect of the resonance overlapping of pseudoisocyanine J aggregates exciton and plasmon of the inhomogeneous ensemble of metallic nanoparticles was studied for thin films. The absorption of a hybrid structure was not the sum of the absorption of the cyanine dye layer and nanoparticle extinction. Regardless the increase of the molecular absorption due to near field of metal nanoparticles, the spectral dip at the absorption maximum of the J aggregates was observed for hybrid films. The magnitude of the increase in absorption and the shape of the dip were different for silver and gold nanoparticles, and depend on the equivalent thickness of the metal island films. The dip was explained by the strong coupling of the exciton transition in J aggregate with the plasmon resonance of nanoparticles.

Keywords: Plasmon, exciton, film, nanoparticle, J-aggregate

1. INTRODUCTION

Interaction of localized surface plasmons in metallic nanostructures and excitons in quantum-sized objects such as organic chromophores or quantum dots has been a subject of intense research on both the theoretical [1,2] and experimental [3,4] level recently. The strong interaction of J-aggregate excitons and plasmons of metallic nanostructures leads to the formation of a hybrid state, which called plexiton. The study of such plasmon−exciton systems improves the understanding of the interaction of light with matter and the development of novel sensors [5], harvesting solar cells [6] and other photonic devices [7]. There are many studies of plasmon-exciton structures in colloidal solutions [8,9], which are simple and good models for basic research. However, the dry solid samples, such as thin films, with thermal and photostability at room conditions are needed for practical application.

The optical properties of thin films obtained by coating of dye layer on an island metal film formed by the heterogeneous assembly of plasmonic nanoparticles were studied. Pseudoisocyanine (PIC) was used as dye to form self-organized J-aggregate with the maximum of exciton absorption of 583 nm. To adjust the overlap of the exciton and plasmon resonances, the properties of the island film such as deposited metal or the equivalent thickness. In the first case, it is possible to provide a shift of 100 nm by switching from silver to gold. The second is responsible for the characteristic sizes of nanoparticles in the ensemble.

2. SAMPLES AND METHODS

The sapphire substrates, transparent in the visible range, was used to obtain the dry thin-film samples. Metal island films were obtained by thermal deposition of metal (Ag or Au) with deposit rate of 0.01 nm/s on sapphire substrates heated to 200 ° C in a vacuum chamber Kurt Lesker PVD 75. The pressure of residual gases in the chamber at deposition was maintained at a level of ~ 3 • 10^{-7} Torr. The equivalent thickness of films (3.5 or 5 nm) was controlled by quartz microbalances [10]. Growth island film on sapphire substrates occurs according to the mechanism of Volmer-Weber [11]. The absorption spectrum of the island film is inhomogeneously broadened due to a size variation of the obtained nanoparticles (**Figure 1**).

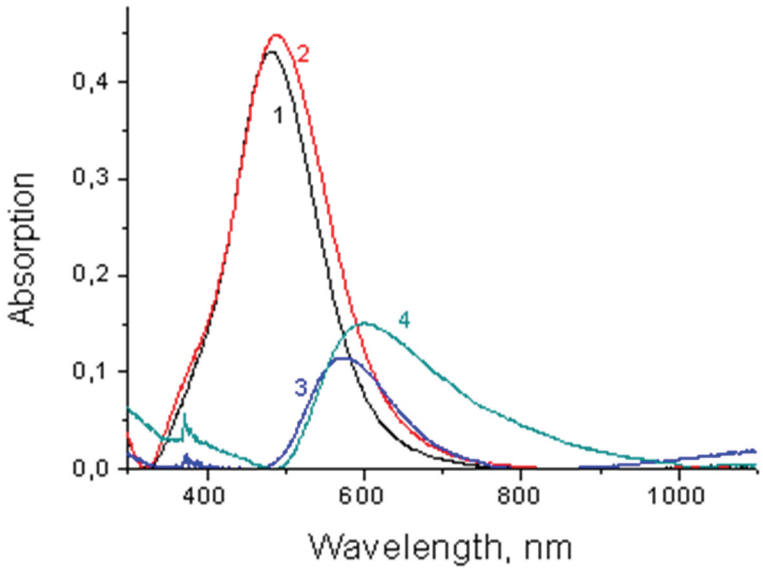

Figure 1 Absorption spectra of: Ag films with thickness of 3.5 nm (1) and 5 nm (2), Au films with thickness of 3.5 nm (3) and 5 nm (4)

1,1'-diethyl-2,2'-cyanine iodide (**Figure 2**), pseudoisocyanine dye (PIC), was used to form J-aggregates by self-organization. The standard method for obtaining J-aggregates is the dissolution of the dye in water with addition of salt to activate aggregation [12]. We have developed an original method of obtaining J-aggregates [13]. The saturated ethanol solution of PIC without the addition of salt was heated up to 60 °C to provide self-aggregation. After cooling for 10 minutes, 4 drops of the dye solution (total volume is 0.006 ml) was spin-coated upon substrate with island film. After rotation for 2 minutes with 1000 rpm the sample was dried under room conditions for 30 minutes. The thickness of the resulting dye layer varied from 30 to 50 nm.

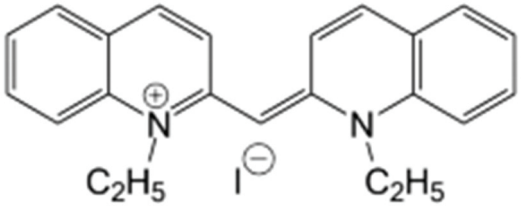

Figure 2 Chemical structure of PIC

The optical density spectra were measured in the range 200-1100 nm with a step of 1 nm by the spectrophotometer SF-56 (OKB "Spectrum" - LOMO).

3. EXPERIMENTAL RESULTS AND DISCUSSION

The absorption spectrum of the PIC ethanol solution, prepared by original method, is predominantly determined by the monomer, and the concentration of aggregates is insignificant [13]. The spectrum of the organic film, obtained from the solution, is broadened due to presence of different molecular forms (**Figure 3**), such as all-trans- (A) and cis-isomers (C), dimer (D), and J-aggregate (J) [14,15]. The most intense absorption band at 583 nm is demonstrated by the J-aggregate.

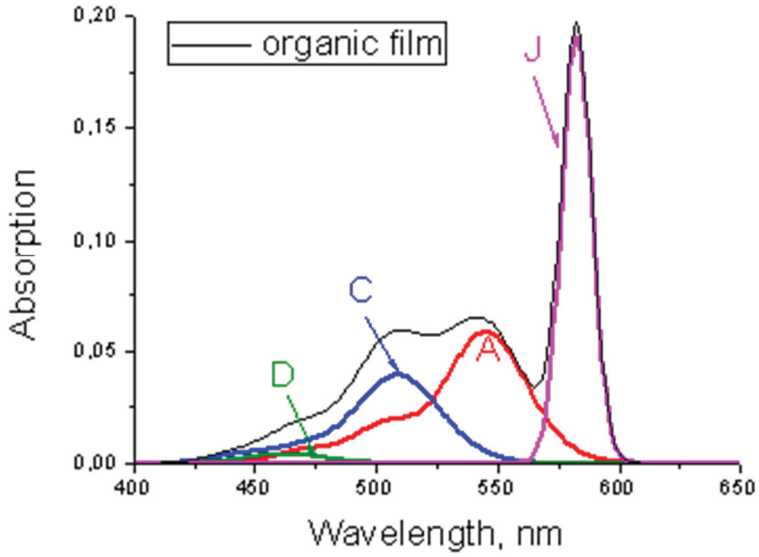

Figure 3 Absorption spectrum of PIC layer on sapphire substrate and its separation into the spectra of the molecular forms: all-trans- (A) and cis-isomers (C), dimer (D) and J-aggregates (J)

The absorption of a hybrid film was not the sum of the absorption of the cyanine dye layer and nanoparticle extinction. The increase of the absorption of all molecular forms is observed for hybrid film with silver nanoparticles in contrast to gold nanoparticles (**Figure 4**), assuming that the surface concentration of molecules is the same. Nevertheless, the spectral dip at a wavelength of 583 nm is noticed for the hybrid films with nanoparticles of both metals. The increase of the absorption of all molecular forms is observed for hybrid film with silver nanoparticles in contrast to gold nanoparticles (**Figure 4**), assuming that the surface concentration of molecules is the same. Nevertheless, the spectral dip at a wavelength of 583 nm is noticed for the hybrid films with nanoparticles of both metals. This is the wavelength of the exciton absorption maximum of the J-aggregate [12], which can overlap with the plasmon frequency of some nanoparticles of inhomogeneous ensemble of island film. This can lead to the strong interaction of the plasmon and the exciton, as well as, the formation of energy level splitting, which shows itself as a spectral dip [1,2,8].

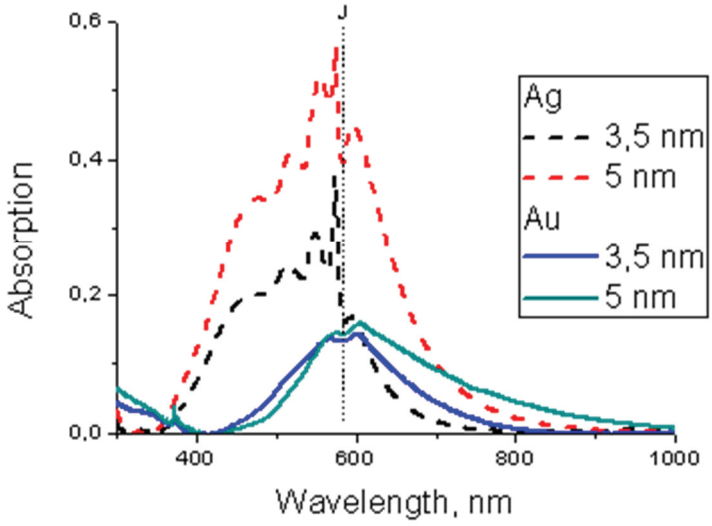

Figure 4 Absorption spectra of the organometallic films depending on the thickness of the island film

The ratio of the peaks near the spectral dip in the absorption maximum of J-aggregates changes depending on equivalent thickness (3.5 or 5 nm) of the island film (**Table 1**). This reflects the change in the formation and concentration of nanoparticles with plasmon resonance at the wavelength of the J-aggregates.

Table 1 Dependence of the ratio of the absorption intensities of the right and left peaks on the equivalent thickness of the island film for different metals

Equivalent thickness, nm	Ratio of the peaks, I_{right}/I_{left}	
	Ag film	Au film
3.5	0.45	1.05
5	0.80	1.09

4. CONCLUSION

The optical properties of thin films performed the resonance overlapping of pseudoisocyanine J aggregates exciton and plasmon of the inhomogeneous ensemble of metallic nanoparticles was studied. The absorption of a hybrid film was not the sum of the absorption of the cyanine dye layer and nanoparticle extinction. The increase of the absorption of all molecular forms is observed for hybrid film with silver nanoparticles in contrast to gold nanoparticles. The spectral dip in the absorption spectrum of the hybrid film at the maximum of the J-aggregate band at 583 nm was observed. The dip can be explained by the strong coupling of the exciton transition in J aggregate with the plasmon resonance of nanoparticles.

REFERENCES

[1] FOFANG, N.T., GRADY, N.K., FAN, Z., GOVOROV, A.O. and HALAS, N.J. Plexciton dynamics: exciton-plasmon coupling in a J-aggregate-Au nanoshell complex provides a mechanism for nonlinearity. *Nano Letters*. 2011. vol. 11, no. 4, pp. 1556-1560.

[2] CAOA, E., LINA, W., SUN, M., LIANG, W. and SONG, Y. Exciton-plasmon coupling interactions: from principle to applications. *Nanophotonics*. 2018. vol. 7, no. 1, pp. 145-167.

[3] BAUDRION, A.L., PERRON, A., VELTRI, A., BOUHELIER, A., ADAM, P.M. and BACHELOT, R. Reversible strong coupling in silver nanoparticle arrays using photochromic molecules. *Nano Letters*. 2013. vol. 13, no. 1, pp. 282-286.

[4] SCHLATHER A, E., LARGE, N., URBAN, A.S., NORDLANDER, P. and HALAS, N.J. Near-field mediated plexcitonic coupling and giant Rabi splitting in individual metallic dimmers. *Nano Letters*. 2013. vol. 13, no. 7, pp. 3281-3286.

[5] TANG, Y., YU, X., PAN, H., Chen, J., AUDIT, B., ARGOUL, F., ZHANG S. and XU J. Numerical study of novel ratiometric sensors based on plasmon-exciton coupling. *Applied Spectroscopy*. 2017. vol. 71, no. 10, pp. 2377-2384.

[6] NAN, F., DING, S., MA, L., CHENG, Z., ZHONG Y., ZHANG, Y., QIU, Y., LI, X., ZHOU L. and WANG Q. Plasmon resonance energy transfer and plexcitonic solar cell. *Nanoscale*. 2016. vol. 8, no. 32, pp. 15071-15078.

[7] FEDELE, S., HAKAMI, M., MURPHY, A., POLLARD, R. ans RICE, J. Strong coupling in molecular exciton plasmon Au nanorod array systems. *Applied Physics Letters*. 2016. vol. 108. pp. 053102:1-4.

[8] DELACY, B.G., MILLER, O.D., HSU, C.W., ZANDER, Z., LACEY, S., YAGLOSKI, R., FOUNTAIN, A.W., VALDES, E., ANQUILLARE, E., SOLJAČIĆ, M., JOHNSON, S.G. and JOANNOPOULOS, J.D. Coherent plasmon-exciton coupling in silver platelet-J-aggregate nanocomposites. *Nano Letters*. 2015, vol. 15, pp. 2588-2593.

[9] SIMON, T., MELNIKAU, D., SÁNCHEZ-IGLESIAS, A., GRZELCZAK, M., LIZ-MARZAN, L.M., RAKOVICH, Y.P., FELDMANN, J. and URBAN, A.S. Exploring the optical nonlinearities of plasmon-exciton hybrid resonances in coupled colloidal nanostructures. *The Journal of Physical Chemistry C*. 2016. vol. 120, no. 22, pp. 12226-12233.

[10] LEONOV, N.B., GLADSKIKH, I.A., POLISHCHUK, V.A. and VARTANYAN, T.A. Evolution of the optical properties and morphology of thin metal films during growth and annealing. *Optics and spectroscopy.* 2015, vol. 119, no. 3, pp. 450-455.

[11] OURA, K., LIFSHITS, V.G., SARANIN, A.A., ZOTOV, A.V. AND KATAYAMA M. *Surface Science: An Introduction*. Berlin: Springer, 2003, p.490. ISBN 3-540-00545-5.

[12] BRICKS, J.L., SLOMINSKII, Y.L., PANAS, I.D. and DEMCHENKO, A.P. Fluorescent J-aggregates of cyanine dyes: basic research and applications review. *Methods and Applications in Fluorescence*. 2017, vol. 6, no. 1, pp. 54:1-43.

[13] STAROVOYTOV, A.A., NABIULLINA, R.D., GLADSKIH, I.A., POLISCHUK, V.A., PARFENOV, P.S. and KAMALIEVA, A.N. Plasmon-exciton interaction in the thin film of inhomogeneous ensemble of silver nanoparticles and cyanine J aggregates. *Proceedings of SPIE*. 2018, vol. 10672, pp. 106723O.

[14] KALITEEVSKAYA, E. N., KRUTYAKOVA, V. P., RAZUMOVA, T. K. and STAROVOYTOV, A. A. The Influence of the Molecular Structure of Cyanine Dye on the Component Composition of Molecular Layers. *Optics and Spectroscopy.* 2016, vol. 120, no. 3, pp. 482-491.

[15] KALITEEVSKAYA, E. N., KRUTYAKOVA, V. P., RAZUMOVA, T. K. and STAROVOYTOV, A. A. Optical properties and component composition of layers of cyanine dyes on dielectric supports: influence of asymmetry of the molecular electron density distribution. Optical and Quantum Electronics. 2017, vol. 49, no. 1, pp. 32.