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2015

Golmakaniyoon, S., Demir, H. V., & Sun, X. W. (2015). Nonradiative energy transfer in a layered metal-dielectric nanostructure mediated by surface plasmons. Proceedings of SPIE - Plasmonics: Metallic Nanostructures and Their Optical Properties XIII, 9547, 95470T-. doi:10.1117/12.2187970

<https://hdl.handle.net/10356/88892>

<https://doi.org/10.1117/12.2187970>

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Nonradiative Energy Transfer in a Layered Metal-Dielectric Nanostructure Mediated by Surface Plasmons

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ABSTRACT

Nonradiative energy transfer (NRET) has been applied in various applications of Nanosensors, Raman scattering, color tuning, light harvesting and organic light emitting structures. Due to the small range of donor-acceptor separation distance that NRET is effective, the improvement in energy transfer (ET) efficiency for thicker structures seems necessary. The plasmons resonance energy transfer (PRET) has been successfully employed to improve the NRET efficiency. The conventional plasmonic configuration consists of donor-metal nanostructure-acceptor shows remarkable improvement of PRET efficiency from the excited donor dipole to the acceptor molecule in longer separation distance. We report the first successful cascaded plasmons coupling in planar structure of donor/acceptor thin film that significantly gives rise to enhancement of ET efficiency. Moreover, the theoretical analysis shows an enhancement in induced electric field due to stratified metal-dielectric configuration compared to simple metal thin film. We observed ET efficiency increases more than 100% by applying dielectric layer between two metal films in plasmonic structure.

KEYWORDS: Surface plasmons, plasmonic energy transfer, silver film, organic dyes.

1. INTRODUCTION

Energy transfer from an excited donor dipole to the acceptor dipole may occur in radiative or nonradiative way that in both the emission spectrum of the donor should overlap with the absorption spectrum of the acceptor. Radiative transfer corresponds to emission and absorption of photons from a donor to an acceptor molecule respectively, in which the average distance of donor and acceptor should be larger than the wavelength. Moreover, the nonradiative energy transfer needs the distance much smaller than the wavelength, e.g. for dipole-dipole interaction in an order of 10nm and occurs without emission of real photons (virtual photons) [1-4]. Notably, it has been discussed by Andrews [5] that these two energy transfer mechanisms can be considered equivalently while, at the large separation distance of the donor and acceptor, the r^{-6} distance dependency of the nonradiative energy transfer modifies to r^{-2} . Recently localized surface plasmons (LSPs) mediated energy transfer through metal nanoparticles has received great attention in semiconductor nanoparticles. It has been studied in several works that LSPs enhance Förster resonance energy transfer (FRET) between donors and acceptors [6-9]. Particularly, in the quantum dots (QDs) based devices which suffer lower NRET efficiency because of large diameter of QDs, Lunz et al. reported 80 fold enhancement in FRET rate and an increase of 103% of the Förster radius for CdTe nanocrystal quantum dot monolayers [6]. In addition, metallic nano films and planar nanostructures show promising optical properties due to the surface plasmons coupling modes at the metal-dielectric interfaces. Here we demonstrate the layered structure consists of two silver thin films separated by the dielectric layer shows more than 100% percent enhancement in energy transferring compared to the single layer silver structure. This allows designing the structure with less photoluminous loss through the reduction in total metal thickness with the same amount of energy transfer efficiency.

2. NUMERICAL SIMULATION

The theoretical simulation is based on the structure of the donor dipole on one side of the finite silver film and the acceptor dipole at the other side [2, 10]. Following the Sommerfeld's theory [11], the electric field at any point can be calculated by definition of hertz vectors for each layer of interest and the boundary conditions at the interfaces.

$$\vec{E}_j = \frac{1}{\epsilon_d} (k_j^2 \vec{\Pi}_j + \nabla(\nabla \cdot \vec{\Pi}_j)) \quad (1)$$

Where j is the index for the region of the interest, $\vec{E}_j$ is the electric field at any point in region j , k_j is the propagation constant of region j , $\vec{\Pi}_j$ is the Hertz vector and ϵ_d is a dielectric constant of dielectric region. Here we define the problem separately for perpendicular and parallel dipoles. The geometry of the problem is depicted at figure 1, in which the single silver film in configuration I and two silver films and the separating dielectric layer in configuration II are called plasmonic structure.

Figure 1. Architectures of (I) single silver film structure and (II) stratified nanostructure consists of two silver films separated by dielectric films. The donor dipole is located at one side of the plasmonic layer and the acceptor dipole is at the opposite side.

First we consider the donor dipole is perpendicular to the interface, the Hertz vector at the acceptor dipole position for structures I ($\vec{E}_I$) and II ($\vec{E}_{II}$), can be determined (in cylindrical coordinates r, z, φ):

$$\vec{\Pi}_i^\perp = \hat{e}_z \frac{\mu_d k_d^3}{4\pi \epsilon_d} \int_0^\infty f_i^\perp \frac{u}{l_d} J_0(u\hat{r}) e^{l_d \hat{z}} du \quad (2)$$

Where μ_d is the donor dipole moment, k_d is the wavenumber at dielectric medium, $J_0(u\hat{r})$ is the zeroth-order Bessel function, $\epsilon_m(\omega)$ is a dielectric function of silver film, $\hat{z}$ is the acceptor dipole position normalized to k_d , $l_{d,m} = \sqrt{u^2 - \frac{\epsilon_{d,m}}{\epsilon_d}}$ and by applying the appropriate boundary conditions f_i are calculated as follows:

$$f_I^\perp = \frac{4\epsilon_d \epsilon_m l_d l_m e^{[(l_d - l_m)\hat{d}_m - l_d \hat{a}]}}{\alpha_d \alpha_m (1 + R_d R_m e^{-2l_m \hat{d}_m})} \quad (3)$$

$$f_{II}^\perp = \frac{\left(\frac{4\epsilon_d \epsilon_m l_d l_m}{\alpha_d \alpha_m}\right)^2 e^{[(l_d - l_m)(2\hat{d}_m') - l_d \hat{a}]}}{1 - R_d^2 e^{-2l_m \hat{d}_m'} + R_m e^{-2l_d \hat{d}_d'} (R_d + R_m e^{-2l_m \hat{d}_m'}) + R_d e^{-2l_d \hat{d}_d'} [R_m (1 - R_d^2 e^{-2l_m \hat{d}_m'}) + R_d e^{-2l_d \hat{d}_d'} (1 - e^{-2l_m \hat{d}_m'})]} \quad (4)$$

Where R_i and α_i are given by:

$$\alpha_d = \alpha_m = \varepsilon_d l_m + \varepsilon_m(\omega) l_d \quad (5)$$

$$R_d = -R_m = \frac{\varepsilon_d l_m - \varepsilon_m(\omega) l_d}{\varepsilon_d l_m + \varepsilon_m(\omega) l_d} \quad (6)$$

Next, the donor dipole is considered parallel with respect to the plasmonic interface and the Hertz vector at the acceptor dipole position can be expressed as

$$\vec{\Pi}_i^{\parallel} = \hat{e}_x \frac{\mu_d k_d}{4\pi\varepsilon_d} \int_0^{\infty} f_i^{\parallel} e^{l_d \hat{z}} J_0(u\hat{r}) \frac{u}{l_d} du + \hat{e}_z \frac{\mu_d k_d \hat{x}}{4\pi\varepsilon_d \hat{r}} \int_0^{\infty} g_i^{\parallel} e^{l_d \hat{z}} J_1(u\hat{r}) du \quad (7)$$

$$f_i^{\parallel} = \frac{4l_d l_m e^{l_d d_2} e^{-l_d d}}{(\alpha_d^{\perp} \alpha_m^{\perp})(e^{l_m d_2} + R_d^{\perp} R_m^{\perp} e^{-l_m d_2})} \quad (8)$$

$$g_i^{\parallel} = \left(\frac{1}{(\alpha_d^{\parallel} \alpha_m^{\parallel})(e^{l_m d_2} + R_d^{\parallel} R_m^{\parallel} e^{-l_m d_2})} - \frac{1}{(\alpha_d^{\perp} \alpha_m^{\perp})(e^{l_m d_2} + R_d^{\perp} R_m^{\perp} e^{-l_m d_2})} \right) 4l_d l_m e^{l_d d_2} e^{-l_d d} \quad (9)$$

Now we define the enhancement factor as the ratio of the electric field induced by donor dipole at the acceptor dipole, in presence $\vec{E}_{i,W}$ and absence of plasmonic layers $\vec{E}_{i,W/O}$:

$$\gamma_i(\omega) = \left(\frac{|\vec{E}_{i,W}|}{|\vec{E}_{i,W/O}|} \right)^2 \quad (10)$$

We employed this factor as a relative comparison between simple and layered structures. In this work the dielectric medium is considered organic material with refractive index of 1.7 and in stratified structure the thickness of 2 silver films and the separating organic layer is taken equally ($d'_m = d'_d = d_m/3$).

Figure 2. (Left) Enhancement factor of perpendicular (red), parallel (blue) and isotropic (black) dipole versus plasmonic layers thickness for simple (dashed line) and stratified (solid line) structures at emission wavelength 520 nm ($d_1 = d_2 = 5\text{nm}$, $d'_m = d'_d = 3d_m$). (Right) Normalized electric field map (enhancement factor) for perpendicular orientation donor dipole at wavelength 380 nm through all the layers.

Figure 2 represents the enhancement factor versus excitation wavelength for donor dipole oriented perpendicular, parallel and isotropic with respect to the surface of plasmonic layer in simple and stratified configurations. As expected through $\varepsilon_d l_m + \varepsilon_m(\omega) l_d$ term in electric field equation, the maximum enhancement for all cases occurs at 380 nm where the real part of silver dielectric function equals to organic dielectric constant in opposite sign. One can see that the enhancement factor of layered structure exceeds the simple with the maximum fold of 3. Note that different choice of plasmonic thickness and donor/ acceptor dipole distance to the nearest silver film will lead to the same conclusion that plasmonic

effect should be enhanced by layering the configuration. This effect can be explained through the full electric field map across the layers (figure 2). Notably, the near field coupling of the plasmonic modes at the metal/dielectric interface gives rise to electric field enhancement at the boundaries and eventually cause the higher donor dipole induced electric field at the acceptor dipole position.

3. EXPERIMENTAL RESULTS

It has been shown in section 2 that layered nano structure caused significant improvement in electric field enhancement at the acceptor position. In order to verify the simulation results by the experiment some practical points should be taken account. First, considering the fact that an evaporated metal film of thickness more than 20nm is formed in homogeneous film layer and less than that will be small islands [8,7], in preparation of the samples, all the silver films thicknesses are greater than 20nm, which leads to have the plasmonic layer thickness more than 60nm to be able to compare simple and scarified structures in a fair way as explained in previous section. Second, according to our experiments the thickness of donor and acceptor layers plays a leading role in energy transfer efficiency. It was observed that by excitation of the monolayer of donor, the acceptor would not be excited through 20 nm silver film structure (shown in figure 3). As it was discussed at section 2, moving from dipole-dipole interaction to layer-layer structure will modify the energy transfer rate; therefore, we expected to observe plasmon enhanced energy transfer for the configuration with thick layer of donor and acceptor.

Figure 3. The effect of donor and acceptor layer thickness on energy transfer efficiency for donor, acceptor thickness of 2nm (left) and 20 nm (right). The silver thickness is 20nm

Organic layers and silver films in all the structures presented here were deposited on quartz substrates, by thermal evaporation system under the pressure of 4×10^{-4} pa. TcTa, Tris (4-carbazoyl-9-ylphenyl) amine, was used as the spacing layer between donor/acceptor - silver and also as a dielectric layer sandwiched between two silver films in stratified structure. In all the samples Alq3, Tris (8-hydroxyquinolinato) aluminum, and R6G, Rhodamine 6G, were deposited as donor and acceptor respectively. The excitation is applied by the continues blue laser source (405 nm), which only excites the donor and has negligible effect on acceptor and organic spacer layer excitation. The samples were exposed to excitation pumping from the donor side and the photons were collected from the other side by CCD camera. Several methods are presented in literature to calculate nonradiative energy transfer efficiency such as donor/acceptor photo bleaching, donor quenching and acceptor sanitization in which the precision of measurement plays a leading role in accuracy of the results. According to our experiments, the ratio of donor intensity to acceptor intensity is independent of the measurement method, as a result η_{ET} can be determined from a single measurement through donor quenching and acceptor sensitization technique. The results are presented in table 1.

Table 1. Relative energy transfer efficiency for simple and stratified structures as a function of plasmonic thickness.

Configuration	Plasmonic Layer Thickness	Relative Energy Transfer Efficiency
Stratified	90 nm	0.28
	60 nm	0.22
Simple	90 nm	0.13
	60 nm	0.19

4. CONCLUSION

In this work, we present a theoretical model for the emitting dipole near a thin metal film and layered structure. The analytical expressions for dipole electric fields were obtained based on Hertz vectors method. Energy transfer efficiency and rate were then calculated for simple and stratified configuration and the improvement in NRET rate was observed in layered structure. Our findings show that multi-layer plasmonic structure enhanced the induced electric field of the emitting donor molecule due to surface plasmon created at the interfaces, which leads to more efficient energy transfer in layered structure. The experiments were then designed to verify the theoretical results therefore the improvement trend was obtained in experimental results. For instance for the structure with the plasmonic layer thickness of 90 nm, 100% enhancement was observed in stratified structure in comparison with single silver film configuration.

4. ACKNOWLEDGMENTS

The authors thank Yoga Divayana for his comments on numerical model and calculation. This project is financially supported by the National Research Foundation under its Competitive Research Programme No. NRF-CPR11-2012-01 and No. NRF-CPR-2010-2.

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