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Investigating Molecular Spontaneous Emission Rate Enhancement Close to Elliptical Nanoparticles by Boundary Integral Method

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Abstract: Utilizing boundary integral method (BIM), we investigate molecular spontaneous emission rate enhancement in the vicinity of plasmonic nanoparticles of elliptical cross section. These types of nanoparticles can considerably enhance the molecule decay rate. The spontaneous emission rate can be modified by altering the aspect ratio of the elliptical nanoparticle, the background refractive index and nanoparticles material. It is shown that the decay rate can be enhanced by two or three orders of magnitude for dipole distances below 10 nanometers. The position of enhancement peaks can be adjusted in the investigated spectral range (400-1000 nm) by changing the aspect ratio of the nanoparticle or the refractive index of background medium and nanoparticles material. To validate our result, we use BIM method to calculate light scattering by a circular gold nanowire and compare it with analytical result. Then the effect of various parameters, including aspect ratio and material of nanoparticle and the background refractive index, on the decay rate is investigated.

Keywords: Spontaneous emission rate enhancement, Plasmonic nanoparticles, boundary integral method.

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1. Introduction

Spontaneous emission was known as an uncontrollable process until Purcell predicted that the spontaneous emission properties of an emitter can be changed by its environment [1]. Plasmonic nanoparticles of appropriate shapes and sizes are able to control spontaneous emissions rate of molecules due to the existence

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of a localized surface plasmon resonance (LSPR) [2]. LSPR is the resonant oscillation of the surface electrons excited by incident light [3]. Localized surface plasmon in metallic nanoparticles depends on the shape, size, and dielectric property of nanoparticle as well as the surrounding material. When these parameters are appropriately chosen, we can remarkably increase the spontaneous emission rate of a molecular in the vicinity of the metal nanoparticle [4, 5].

The spontaneous emission rate of molecules close to nanoparticles of arbitrary shape can be calculated using classical electrodynamics [6]. However, due to the complexity of the problem, there is no analytical solution for this case. Therefore, one needs to exploit computational techniques, such as Multiple Multipole Program (MMP) [7], Finite-Difference Time-Domain (FDTD) method [8, 9], and Finite Element Method (FEM) [10], to solve full vectorial Maxwell's equations.

In this work, we employ the boundary integral method (BIM) [11] to calculate the decay rate enhancement of an emitter coupled to plasmonic nanoparticle of various shapes and sizes. BIM is considered as a semi-analytical boundary approach and is rather fast and accurate, as compared to the domain methods. We investigate the effect of nanoparticle's aspect ratio and its material together with the distance between nanoparticle and the emitter on the decay rates. We show that by this configuration, the decay rate is considerably enhanced. Moreover, one can easily tune the LSPR in the preferred spectral range by varying the aspect ratio.

2. BOUNDARY INTEGRAL METHOD (BIM)

boundary integral method is a semi-analytical frequency domain method which can be exploited to study the interaction of light with homogeneous, isotropic and linear materials. In this method, as shown in Figure 1, we first discretize the boundary of objects into small elements of length dσ.

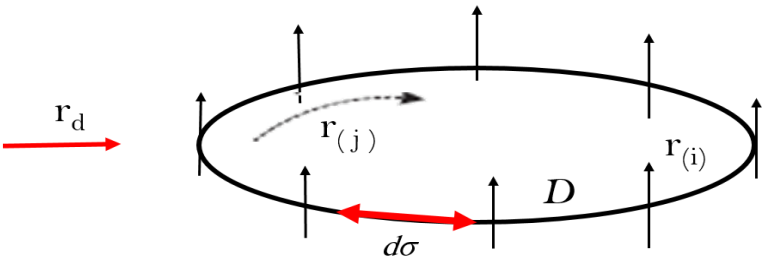

Fig. 1. Sketch of boundary integral method

On each element, $r_{(i)}$, a magnetic field (H) and the tangential component of the electric field (F) are positioned. Having the value of these quantities, one can

calculate magnetic fields in other points of the computational space. To obtain these values, we start with the wave equation which is obtained from the Maxwell's equation as follows:

$$\nabla\left(\frac{1}{\epsilon}\nabla H\right)+k_0^2 H=4\pi i k_0(e_z\times\nabla)\cdot\left(\frac{1}{\epsilon}\,\mathbf{p}\,\delta(|\mathbf{r}-\mathbf{r_d}|)\right) \quad (1)$$

where r is location of observation point; r_d is location of emitter and k_0 is the vacuum wave number.

To solve partial differential equation (1), this equation is changed into boundary integral equation by using Green's theorem as explained in [12]. When arbitrary point, r, is located in the material, magnetic field is given as follows:

$$H(\mathbf{r})=\frac{1}{2\pi}\int_{\partial D}\left[G_\epsilon(|\mathbf{r_i}-\mathbf{r}|)\epsilon\,F(\mathbf{r_i})-H(\mathbf{r_i})\frac{\partial G_\epsilon}{\partial n}(|\mathbf{r_i}-\mathbf{r}|)\right]d\sigma+F(\mathbf{r_i})S_\epsilon \quad (2)$$

where G_ϵ is Green's function that is given as $G_\epsilon = i\pi H_0^{(1)}(K_0\sqrt{\epsilon}\,r)$, and S_ε is obtained from [11]

$$S_\varepsilon=\frac{d\sigma}{2\pi}\varepsilon\left[-2\gamma+i\pi-2\left(log\frac{\sigma\,k_0\sqrt{\epsilon}}{4}-1\right)\right] \quad (3)$$

If arbitrary point, r, is chosen out of material, then magnetic field is obtained from:

$$H(\mathbf{r})=2H_{inc}-\frac{1}{2\pi}\int_{\partial D}\left[G_{\epsilon_0}(|\mathbf{r_i}-\mathbf{r}|)\epsilon_0\,F(\mathbf{r_i})-H(\mathbf{r_i})\frac{\partial G_{\epsilon_0}}{\partial n}(|\mathbf{r_i}-\mathbf{r}|)\right]d\sigma-F(\mathbf{r_i})S_{\epsilon_0} \quad (4)$$

where H_{inc} is radiation field that is caused by the emitter located out of the material.

In order to solve (2) and (4), we use Riemann approximation as shown in the following equation:

$$\int_{\partial D}[G_\epsilon(|\mathbf{r_i}-\mathbf{r}|)\epsilon\,F(\mathbf{r_i})]d\sigma(\mathbf{r_i})\rightarrow\sum_{j\neq i}d\sigma_i G_\epsilon\left(|\mathbf{r_i}-\mathbf{r_j}|\right)\epsilon\,F(\mathbf{r_i}) \quad (5)$$

In order to rewrite (2) and (4) based on the expansion of Riemann, we can get magnetic field and the tangential component of the electric field on the boundary. By using the values of magnetic field on the boundary, we can obtain magnetic field in all points of the computation space as follows:

$$H(\mathbf{r})^{in} = \frac{1}{4\pi} \int_{\partial D} \left[G_{\epsilon}(\mathbf{r_i}\text{-}\mathbf{r}) \epsilon F(\mathbf{r_i}) - H(\mathbf{r_i}) \frac{\partial G_{\epsilon}}{\partial n}(\mathbf{r_i}\text{-}\mathbf{r}) \right] d\sigma \quad (6)$$

$$H(\mathbf{r})^{out} = -\frac{1}{4\pi} \int_{\partial D} \left[G_{\epsilon_0}(\mathbf{r_i}\text{-}\mathbf{r}) \epsilon_0 F(\mathbf{r_i}) - H(\mathbf{r_i}) \frac{\partial G_{\epsilon_0}}{\partial n}(\mathbf{r_i}\text{-}\mathbf{r}) \right] d\sigma \quad (7)$$

To validate the approach, we compare light scattering by a nanoparticle with circular cross section of radius R=30nm located in vacuum and illuminated by a planewave with TM polarization. Comparison of the BIM result with the analytical result [13] is depicted in Figure 2. As observed the agreement between two methods is very promising.

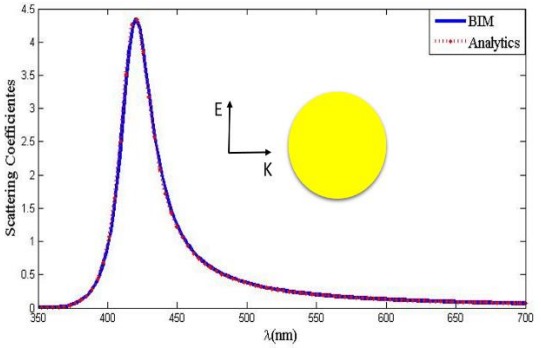

Fig. 2. The comparison of the BIM result with analytical result.

3. RESULT

In this section, we investigate the effect of various parameters, including the aspect ratio, emitter distance from nanoparticle, the material of nanoparticle and background refractive index on the spontaneous emission rate. To do so, we model the molecule as a classical dipole and calculate the radiated power when the dipole is in the vicinity of the nanoparticle and divide it by the radiated power in empty space to obtain the normalized radiative decay rate.

In order to study the impact of dipole distance from the nanoparticle on the rate of spontaneous emission, we fix the nanoparticle size (a = 20 nm and b= 80 nm), located in an environment with refractive index of 1.5 and change the emitter distance. The result is shown in Figure 3. As observed, by reducing the distance the decay rate is increased. For small distances it is increased by two orders of magnitudes. However, it should be noted that for such small distances, the probability of non-radiative decay, resulting in energy loss in the nanoparticles, is increased. Therefore, to achieve the highest radiative decay rate one needs to

optimize the distance.

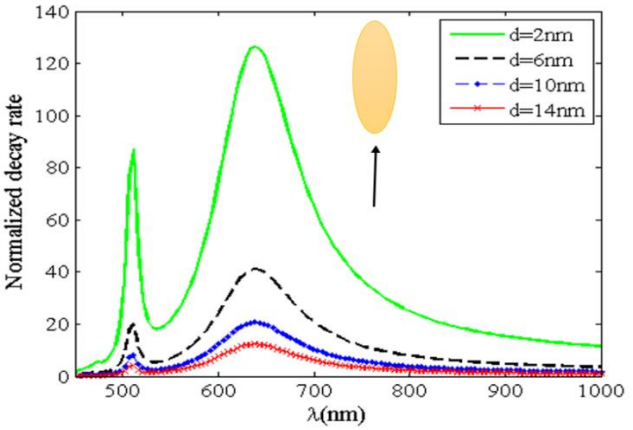

Fig. 3. Normalized decay rate versus wavelength for different distances between the emitter and nanoparticle.

It is also observed that changing the distance has no effect on the wavelength of the maximum decay rate. In order to adjust the maximums, we can change the aspect ratio which provides the ability to move the peaks in a wide range of wavelengths. In Figure 4(a) the semi-minor axis is constant, b=20 nm, and the semi-major one spans from 40 to 80 nm. When the aspect ratio gets smaller the LSPR shifts towards shorter wavelengths. In Figure 4(b) we keep the semi-major axis constant, a=70 nm, and vary the other axis. In this case, reducing the aspect ratio increases the volume such that radiative broadening increases and the LSPRs appear wider.

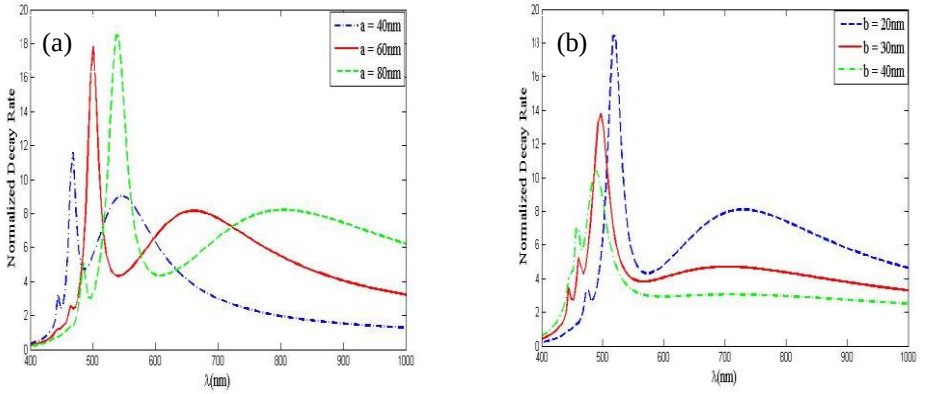

Fig. 4. Normalized decay rate versus wavelength for different aspect ratios, a and b are semi-major axis and semi-minor axis, respectively.

Another parameter which can move the maximum positions is the refractive index of the surrounding environment. In order to investigate its effect on the decay rate, we change the background refractive index and fix other parameters; a= 20 nm, b=80 nm, and d=5 nm. As shown in Figure 5, increasing the refractive index of background shifts the peaks toward longer wavelengths. Even a small change in the refractive index shifts the LSPR by more than hundred nanometers. Also, the resonance gets wider with increasing the refractive index.

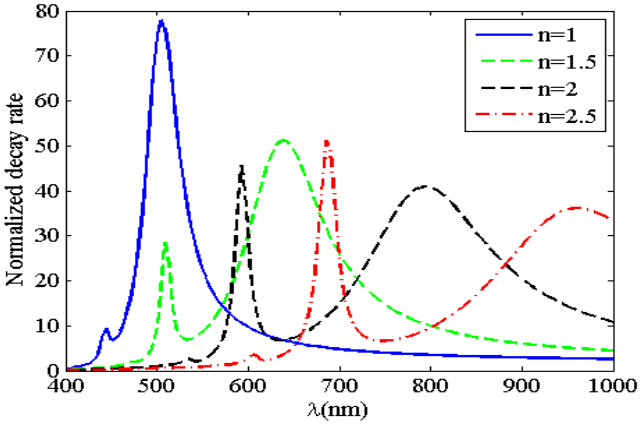

Fig. 5. Normalized decay rate for different refractive indexes

The last parameter which is studied is the nanoparticle's material and its effect on the decay rate. We compare decay rate enhancement induced by gold and silver nanoparticles. The emitter is located in the distance of 5 nm, the axes are fixed as a=20 nm and b = 80 nm, and the background refractive index is 1.5. Figure 6 illustrates the comparison. The obvious difference is that in the case of gold nanoparticle the maximums occur at longer wavelength as compared to silver nanoparticle.

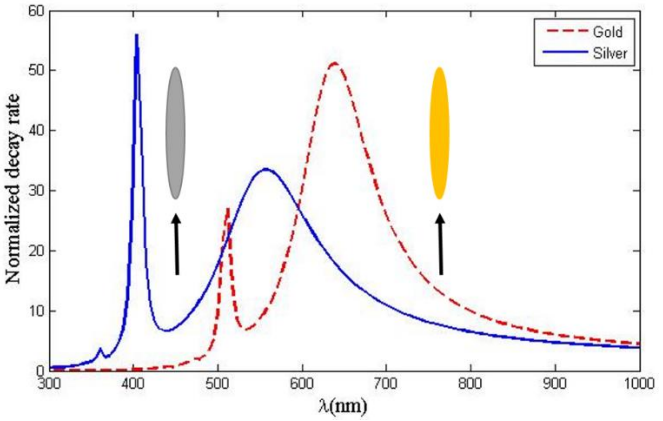

Fig. 6. Decay rate per different materials.

4. Conclusion

In this paper, we have employed the boundary Integral Method to investigate enhancement of spontaneous emission rate by metal nanoparticles. To validate its result, analytical solution based on Mie theory for 2-dimensional case has been employed. We have considered nanoparticles with elliptical cross section and found that there are various parameters by which one can adjust the spectral performance of proposed configuration. These parameters include nanoparticle's material, shape and size as well as the refractive index of surrounding environment, which provides the ability to move the peaks in a wide range of wavelengths. It has been shown that the distance between molecule and the increases the decay rate, but doesn't have any effect on the location of LSPR. The aspect ratio, has considerable effect on LSPR positions. Moreover, it has been shown that choosing different material for the nanoparticle and environment may provide extra ability to tune the characteristic of spontaneous emission rates.

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