Effects of gain medium on the plasmonic enhancement of Forster resonance energy transfer in the vicinity of a metallic particle or cavity

Railing Chang,[1,*] P. T. Leung,[1,2,3] and D. P. Tsai[2,4,5]

[1]*Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, Taiwan*
[2]*Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan*
[3]*Department of Physics, Portland State University, P. O. Box 751, Oregon 97207-0751, USA*
[4]*Department of Physics, National Taiwan University, Taipei 10617, Taiwan*
[5]*dptsai@phys.ntu.edu.tw*
[*]*rlchang@mail.ntou.edu.tw*

Abstract: We perform theoretical studies on the plasmonic enhancement for the Forster resonance energy transfer (FRET) between a donor and an acceptor molecule in the vicinity of a metallic particle or cavity, with focus on the possible role of the addition of a clad layer of gain material can play in such a process. The results show that while the plasmonic resonances can be shifted with higher order plasmonic enhancements emerged in the presence of such a layer of gain material, optimal enhancement of the FRET rate can be achieved when gain just balances with the loss in the metal. This then leads to the existence of an optimal thickness for the gain material layer, for both particle and cavity enhancement. In addition, it is observed that the FRET efficiency can always be increased with the coating of the gain material even at the dipole plasmonic resonance when nonradiative transfer from the donor to the metal is high, provided that the gain level is not beyond a certain critical value.

References and links

1. T. Forster, "Intermolecular energy migration and fluorescence (in German)," Ann. Phys. **437**, 55–75 (1948).
2. T. Forster, "Transfer mechanisms of electronic excitation," Discuss. Faraday Soc. **27**, 7–17 (1959).
3. D. L. Dexter, "A theory of sensitized luminescence in solids," J. Chem. Phys. **21**(5), 836–850 (1953).
4. For a comprehensive review, see the recent text by: I. L. Medintz and N. Hildebrandt, *FRET - Förster Resonance Energy Transfer: From Theory to Applications* (John Wiley, 2013).
5. J. I. Gersten, "Fluorescence resonance energy transfer near thin films on surfaces," Plasmonics **2**(2), 65–77 (2007).
6. J. I. Gersten and A. Nitzan, "Accelerated energy transfer between molecules near a solid particle," Chem. Phys. Lett. **104**(1), 31–37 (1984).
7. X. M. Hua, J. I. Gersten, and A. Nitzan, "Theory of energy transfer between molecules near solid state particles," J. Chem. Phys. **83**(7), 3650–3659 (1985).
8. F. Reil, U. Hohenester, J. R. Krenn, and A. Leitner, "Förster-type resonant energy transfer influenced by metal nanoparticles," Nano Lett. **8**(12), 4128–4133 (2008).
9. H. Y. Chung, P. T. Leung, and D. P. Tsai, "Enhanced intermolecular energy transfer in the vicinity of a plasmonic nanorice," Plasmonics **5**(4), 363–368 (2010).
10. X. M. Hua and J. I. Gersten, "Enhanced energy transfer between donor and acceptor molecules near a long wire or fiber," J. Chem. Phys. **91**(2), 1279–1286 (1989).
11. Y. C. Yu, J. M. Liu, C. J. Jin, and X. H. Wang, "Plasmon-mediated resonance energy transfer by metallic nanorods," Nanoscale Res. Lett. **8**(1), 209 (2013).
12. H. Y. Xie, H. Y. Chung, P. T. Leung, and D. P. Tsai, "Plasmonic enhancement of Förster energy transfer between two molecules in the vicinity of a metallic nanoparticle: Nonlocal optical effects," Phys. Rev. B **80**(15), 155448 (2009).
13. M. Lessard-Viger, M. Rioux, L. Rainville, and D. Boudreau, "FRET enhancement in multilayer core-shell nanoparticles," Nano Lett. **9**(8), 3066–3071 (2009).

14. S. T. Kochuveedu, T. Son, Y. Lee, M. Lee, D. Kim, and D. H. Kim, "Revolutionizing the FRET-based light emission in core-shell nanostructures via comprehensive activity of surface plasmons," Sci. Rep. **4**, 4735 (2014).
15. J. A. Gonzaga-Galeana and J. R. Zurita-Sánchez, "A revisitation of the Förster energy transfer near a metallic spherical nanoparticle: (1) Efficiency enhancement or reduction? (2) The control of the Förster radius of the unbounded medium. (3) The impact of the local density of states," J. Chem. Phys. **139**(24), 244302 (2013).
16. G. A. Plotz, H. J. Simon, and J. M. Tucciarone, "Enhanced total reflection with surface plasmons," J. Opt. Soc. Am. **69**(3), 419–422 (1979).
17. M. Premaratne and G. P. Agrawal, *Light Propagation in Gain Media* (Cambridge, 2011).
18. M. P. Nezhad, K. Tetz, and Y. Fainman, "Gain assisted propagation of surface plasmon polaritons on planar metallic waveguides," Opt. Express **12**(17), 4072–4079 (2004).
19. M. A. Noginov, G. Zhu, M. Bahoura, J. Adegoke, C. E. Small, B. A. Ritzo, V. P. Drachev, and V. M. Shalaev, "Enhancement of surface plasmons in an Ag aggregate by optical gain in a dielectric medium," Opt. Lett. **31**(20), 3022–3024 (2006).
20. D. J. Bergman and M. I. Stockman, "Surface plasmon amplification by stimulated emission of radiation: quantum generation of coherent surface plasmons in nanosystems," Phys. Rev. Lett. **90**(2), 027402 (2003).
21. M. A. Noginov, G. Zhu, A. M. Belgrave, R. Bakker, V. M. Shalaev, E. E. Narimanov, S. Stout, E. Herz, T. Suteewong, and U. Wiesner, "Demonstration of a spaser-based nanolaser," Nature **460**(7259), 1110–1112 (2009).
22. R. F. Oulton, V. J. Sorger, T. Zentgraf, R.-M. Ma, C. Gladden, L. Dai, G. Bartal, and X. Zhang, "Plasmon lasers at deep subwavelength scale," Nature **461**(7264), 629–632 (2009).
23. J. H. Huang and R. Chang, "Theoretical investigation on the strong coupling between a molecule and a metallic nanosphere clad with a gain medium," J. Opt. **16**(1), 015005 (2014).
24. S. Biehs and G. S. Agarwal, "Large enhancement of Forster resonance energy transfer on graphene platforms," Appl. Phys. Lett. **103**(24), 243112 (2013).
25. V. Karanikolas, C. A. Marocico, and A. L. Bradley, "Spontaneous emission and energy transfer rates near a coated metallic cylinder," Phys. Rev. A **89**(6), 063817 (2014).
26. V. N. Pustovit and T. V. Shahbazyan, "Resonance energy transfer near metal nanostructures mediated by surface plasmons," Phys. Rev. B **83**(8), 085427 (2011).
27. See, e.g. Refs. [15] and [25] for models of such distributions.
28. F. Schleifenbaum, A. M. Kern, A. Konrad, and A. J. Meixner, "Dynamic control of Förster energy transfer in a photonic environment," Phys. Chem. Chem. Phys. **16**(25), 12812–12817 (2014).
29. M. Hopmeier, W. Guss, M. Deussen, E. O. Gobel, and R. F. Mahrt, "Enhanced dipole-dipole interaction in a polymer microcavity," Phys. Rev. Lett. **82**(20), 4118–4121 (1999).
30. W. L. Barnes and P. Andrew, "Energy transfer under control," Nature **400**(6744), 505–506 (1999).
31. P. Andrew and W. L. Barnes, "Förster energy transfer in an optical microcavity," Science **290**(5492), 785–788 (2000).
32. D. M. Basko, F. Bassani, G. C. La Rocca, and V. M. Agranovich, "Electronic energy transfer in a microcavity," Phys. Rev. B **62**(23), 15962–15977 (2000).
33. D. M. Basko, G. C. La Rocca, F. Bassani, and V. M. Agranovich, "Electronic energy transfer in a planar microcavity," Phys. Status Solidi (a) **190**(2), 379–382 (2002).
34. H. Fujiwara, K. Sasaki, and H. Masuhara, "Enhancement of Förster energy transfer within a microspherical cavity," ChemPhysChem **6**(11), 2410–2416 (2005).
35. A. Konrad, A. L. Trost, S. Skandary, M. Hussels, A. J. Meixner, N. V. Karapetyan, and M. Brecht, "Manipulating the excitation transfer in Photosystem I using a Fabry-Perot metal resonator with optical subwavelength dimensions," Phys. Chem. Chem. Phys. **16**(13), 6175–6181 (2014).
36. A. Veltri and A. Aradian, "Optical response of a metallic nanoparticle immersed in a medium with optical gain," Phys. Rev. B **85**(11), 115429 (2012).
37. Y. T. Wang, B. H. Cheng, Y. Z. Ho, Y. C. Lan, P. G. Luan, and D. P. Tsai, "Gain-assisted hybrid-superlens hyperlens for nano imaging," Opt. Express **20**(20), 22953–22960 (2012).

1. Introduction

Energy transfer between an excited molecule (a donor, D) and a neighboring molecule (an acceptor, A) is a process of fundamental importance in the understanding and control of many photophysical and photochemical processes in Nature and in the laboratory—ranging from photosynthesis to fluoresce probing in biotechnology. Successful theoretical models for such a process have been established in the literature depending on the separation (R) between the molecules D and A. For the most important range of application $R \sim$ 2 to 6 nm, the process known as Forster resonance energy transfer (FRET) can be well described by the electrostatic dipolar interaction between D and A with a rate falling off as R^{-6} [1,2]. For closer separations $(R < 2\,\text{nm})$, quantum mechanical treatment is necessary according to the Dexter theory [3], and for farther separations when $R \sim$ emission wavelength of the molecule, full electrodynamics is required to account for possible radiative transfer between D and A [4]. Moreover, in realistic applications, it is the FRET range of separation which is the most often

encountered in many important photo processes of significance, and hence is our focus in the present work.

Since FRET is a rather weak process and falls as R^{-6}, enhancement of such a process to achieve an increase in the Forster distance (R_0 defined as the D-A separation at which FRET is 50% efficient) has become an exciting area of research over the years. In particular, plasmonic enhancement employing both planar metallic structures [5] and metallic nanoparticles (MNP) has received great attention since the 1980's [6,7], soon after the dramatic surface enhancement of Raman scattering (SERS) was first understood to be accounted for via such a mechanism. In time, FRET enhancement from various MNP systems have been studied by many groups which include, for example, spherical and spheroidal MNP's [6, 7], nanodisc [8], nanorice [9], nanorods [10,11], and single [12] as well as multiple [13,14] spherical nanoshells. Depending on various factors of the geometry and material of the MNP system, as well as the relative locations and orientations of the donor and acceptor molecular dipoles, various enhancement outcome can be achieved on resonance conditions when the emission frequency of D is close to the absorption frequency of A and both are close to that of the plasmon resonance of the MNP. A very recent article has provided a detailed analysis of the various possible outcomes including the case when no enhancement (i.e. diminution) can take place under certain unfavorable conditions [15]. As is well-known, one adverse effect in employing plasmon excitation to achieve optical enhancement comes from the loss of the metals. The nonradiative transfer from the excited molecule to the metal will decrease the efficiency of the enhancement from the plasmon fields which will be significant when the molecules are in close proximity of the metallic structure. Hence any mechanism which may help to suppress this nonradiative loss in the MNP enhanced FRET process is worth to be explored.

It has been known over several decades [16] that certain medium (e.g. laser dyes) can act as a source in supplying energy to a dissipative medium (e.g. metal) to compensate for any undesired loss in various optical and spectroscopic processes. In time, these "gain media" [17] have been applied to achieve significant improvement in the performance of various device such as plasmonic waveguides [18] and spectroscopic probes such as in Raleigh and Raman scattering [19]. One of the more distinct applications proposed and demonstrated recently is the construction of the SPASER (i.e. a plasmonic nanolaser) in which the compensation of metal loss in a nanoparticle by a gain medium leads to a nano light source of coherent radiation [20–22]. One is thus tempted to further explore the possible applications of these gain-clad metallic nanoparticles (GMNP) to enhance other important optical processes, such as in the strong coupling between an emitting molecule and a MNP as has been recently studied [23]. It is the purpose of our following work to investigate the possible improvement of FRET between the two molecules excited in the vicinity of a GMNP. We shall also consider clad metallic cavity, and shall focus in particular on the manipulation of the various parameters of the molecule-MNP system to see how such plasmonic enhanced FRET process can be optimized using this approach.

2. Theoretical model

Let us consider two point dipoles interacting near a metallic nanoparticle (MNP) or within a metallic nano-cavity (MNC), with an additional shell-layer of gain materials clad in each case as shown in Fig. 1. The dipoles (D and A) can have arbitrary relative locations and orientations in each geometry. We assume all essential dimensions are small compared to the emission wavelength of D so that retardation effects can be ignored.
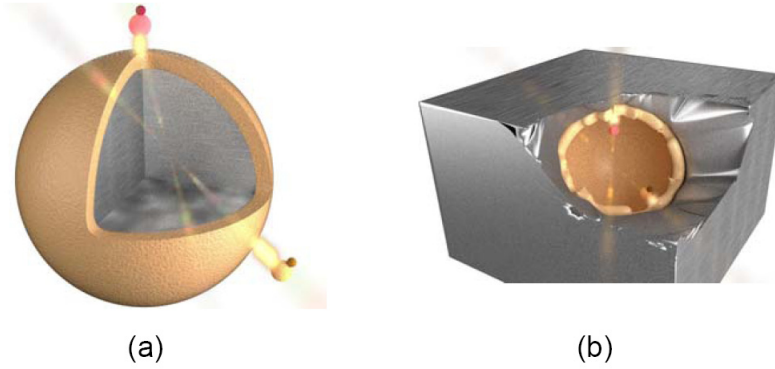
Fig. 1. Configurations of pair of donor and acceptor in the vicinity of a gain-clad (a) metallic nanosphere (b) metallic nanocavity.

To calculate the FRET rate between D and A in the presence of the nanostructure, there have been three different approaches in the literature. The conventional approach (adopted by most of the researchers [1,2, 5–12, 24, 25]) obtains such a rate simply from lowest order perturbation theory (Fermi's golden rule) to be expressed by the following spectral function:

$$K(\omega) = \frac{9c^4}{8\pi} \frac{\sigma_A(\omega)\Gamma_D(\omega)}{\omega^4} |U(\omega)|^2, \tag{1}$$

where $\sigma_A(\omega)$ is the absorption cross-section of the acceptor, $\Gamma_D(\omega)$ is the emission rate per unit frequency of the donor (with both treated as free molecules), and $U(\omega)$ is the interaction energy between D and A in the presence of the environment (MNP, MNC,…etc.). This approach has been criticized in the literature and free-molecule absorption and emission rates in (1) have been replaced by "dressed rates", together with the incorporation of the apparent quantum yield of the donor in the presence of the environment [26]. Nevertheless, we believe that such modifications using dressed rates are not necessary consistent with the spirit of perturbation theory in which zeroth-order (unperturbed) molecular states should be used together with first order correction in the interaction energy $U(\omega)$ in the calculation of the modified $K(\omega)$ to the lowest order [12]. Thus, in our following study, we shall focus on the effects of the structure only on $U(\omega)$ as was done in most of the previous works [1,2, 5–12, 24, 25]. Moreover, there is a third approach which introduces a concept known as "Forster efficiency" to account for the modified total decay rate of the donor in the presence of the MNP [8, 15, 25]. In this treatment, the Forster efficiency is calculated from Eq. (1) as a fraction of the sum of the total MNP-modified donor decay rate and the FRET rate in (1). Note that the FRET process in Eq. (1) has been optimized to be on resonance condition with the same transition frequency for each D and A, and we have simplified the analysis by ignoring possible distribution of the emission frequencies over a finite range of values [27]. Hence within such idealizations, we shall consider the following simplified FRET enhancement factor defined as [9, 12, 24, 25, 28]:

$$\xi = \left| \frac{U(\omega)}{U_0(\omega)} \right|^2, \tag{2}$$

where $U_0(\omega)$ is the dipole-dipole interaction energy when both D and A are in free space, and is given by the following expression:

$$U_0(\omega) = \frac{\bar{\mu}_A \bullet \bar{\mu}_D}{\left|\vec{r}_A - \vec{r}_D\right|^3} - \frac{3\bar{\mu}_A \bullet (\vec{r}_A - \vec{r}_D)\,\bar{\mu}_D \bullet (\vec{r}_A - \vec{r}_D)}{\left|\vec{r}_A - \vec{r}_D\right|^5}, \tag{3}$$

where the $\bar{\mu}$'s are the dipole moments and the $\vec{r}$'s are the position vectors of the donor and the acceptor, respectively. Hence in the long wavelength approximation, our calculation of ξ will involve the electrostatic solution of the boundary value problem with two interacting dipoles in the vicinity of a coated sphere (Fig. 1(a)) or coated cavity (Fig. 1(b)).

(i) <u>Dipoles outside a coated sphere</u>

The electrostatic potential in each of the three regions in this case can be expanded as follows:

For $b < r$:

$$\Phi = \sum_{\ell m}\left[G^o_{\ell m} r^{-\ell-1} + \psi^o_{\ell m D}(r) + \psi^o_{\ell m A}(r)\right] Y_{\ell m}(\theta, \varphi), \tag{4}$$

For $a < r < b$:

$$\Phi = \sum_{\ell m}\left[F^s_{\ell m} r^\ell + G^s_{\ell m} r^{-\ell-1}\right] Y_{\ell m}(\theta, \varphi), \tag{5}$$

For $a < r$:

$$\Phi = \sum_{\ell m} F^i_{\ell m} r^\ell Y_{\ell m}(\theta, \varphi), \tag{6}$$

where the superscripts "o", "s", "i" denote the cases outside, within, and inside the shell of the coating, respectively, whereas the terms $\psi^o_{\ell m D,A}$ denote the radial part of the free dipole potential expanded in terms of the spherical harmonics for the donor and acceptor, respectively [12]. Matching the standard boundary conditions for the potentials and the fields at the boundaries $r = a$ and $r = b$, our interest is to solve for the coefficient $G^o_{\ell m}$, which, after some algebra, can be obtained in terms of the potentials $\psi^o_{\ell m D,A}$ at the outer boundary as follows:

$$G^o_{\ell m} = \ell b^{\ell+1} S_1 \times$$
$$\frac{(\varepsilon^o - \varepsilon^s)\left[(\ell+1)\varepsilon^s + \ell\varepsilon^i\right] + (\varepsilon^s - \varepsilon^i)\left[(\ell+1)\varepsilon^s + \ell\varepsilon^o\right](a/b)^{2\ell+1}}{\left[\ell\varepsilon^s + (\ell+1)\varepsilon^o\right]\left[(\ell+1)\varepsilon^s + \ell\varepsilon^i\right] + \ell(\ell+1)(\varepsilon^o - \varepsilon^s)(\varepsilon^s - \varepsilon^i)(a/b)^{2\ell+1}}, \tag{7}$$

where $S_1 \equiv \psi^o_{\ell m D}(b) + \psi^o_{\ell m A}(b)$. Using this result, we can then calculate the modified interaction energy U in Eq. (2) for the acceptor which can be obtained as:

$$U = \bar{\mu}_A \bullet \vec{\nabla}\Phi'\Big|_{\vec{r}=\vec{r}_A}, \tag{8}$$

where

$$\Phi' = \sum_{\ell m}\left[G^o_{\ell m} r^{-\ell-1} + \psi^o_{\ell m D}(r)\right] Y_{\ell m}(\theta, \varphi), \tag{9}$$

(ii) <u>Dipoles inside a coated cavity</u>

With the exciting developments in the field of cavity quantum electrodynamics, the important process of FRET has also been studied actively for possible enhancement with the donor and acceptor confined in an optical cavity [29–35]. We consider the

possible role of gain medium in such cavity-enhanced FRET process. With reference to the geometry in Fig. 1(b), we have

For $b < r$:

$$\Phi = \sum_{\ell m} G_{\ell m}^o r^{-\ell-1} Y_{\ell m}(\theta, \varphi), \qquad (10)$$

For $a < r < b$:

$$\Phi = \sum_{\ell m} \left[F_{\ell m}^s r^\ell + G_{\ell m}^s r^{-\ell-1} \right] Y_{\ell m}(\theta, \varphi), \qquad (11)$$

For $r < a$:

$$\Phi = \sum_{\ell m} \left[F_{\ell m}^i r^\ell + \psi_{\ell m D}^i(r) + \psi_{\ell m A}^i(r) \right] Y_{\ell m}(\theta, \varphi), \qquad (12)$$

Again, we solve for $F_{\ell m}^i$ from matching the appropriate boundary conditions and obtain finally the following result:

$$F_{\ell m}^i = (\ell+1) a^{-\ell} S_1 \times$$

$$\frac{\left(\varepsilon^i - \varepsilon^s\right)\left[(\ell+1)\varepsilon^o + \ell\varepsilon^s\right] + \left(\varepsilon^s - \varepsilon^o\right)\left[(\ell+1)\varepsilon^i + \ell\varepsilon^s\right](a/b)^{2\ell+1}}{\left[\ell\varepsilon^s + (\ell+1)\varepsilon^o\right]\left[(\ell+1)\varepsilon^s + \ell\varepsilon^i\right] + \ell(\ell+1)\left(\varepsilon^o - \varepsilon^s\right)\left(\varepsilon^s - \varepsilon^i\right)(a/b)^{2\ell+1}}, \qquad (13)$$

The enhancement factor in (2) for this case can hence be computed by calculating U as defined in (8) with the potential Φ' given by the following expression:

$$\Phi' = \sum_{\ell m} \left[F_{\ell m}^i r^\ell + \psi_{\ell m D}^i(r) \right] Y_{\ell m}(\theta, \varphi), \qquad (14)$$

3. Numerical results

To illustrate what effects a gain medium can have on the plasmonic enhancement of FRET, we consider a silver sphere whose dielectric response can be described by the following Drude model [23]:

$$\varepsilon_m = \varepsilon_{IB} - \frac{\omega_P^2}{\omega(\omega + i\gamma)}, \qquad (15)$$

with an interband response given by $\varepsilon_{IB} = 4.0$, a bulk plasmon energy given by $\hbar\omega_p = 8.95\,\text{eV}$, and the damping constant for the nano-sphere given by $\gamma = \gamma_{bulk} + v_F / a$, where the boundary damping term is account for through the Fermi velocity $v_F = 1.39 \times 10^{15}\,nm/s$ of the metal with the bulk Drude damping constant for silver given by $2.56 \times 10^{13}/s$. On the other hand, the shell of gain material cladding the metal sphere will be described by the following response function [23, 36]:

$$\varepsilon_g = \varepsilon_B + \frac{g\Gamma}{\omega - \omega_r + i\Gamma}, \qquad (16)$$

where the background dielectric constant is taken to be that for water with $\varepsilon_B = 1.769$, the value of the gain level is restricted to be small so that no saturation will take place, the gain spectral width is chosen the same value as the Drude damping, i.e. $\Gamma = \gamma$, and the resonance frequency of the gain material (i.e. gain center) is chosen to be within the neighborhood of the particular value $0.3642\omega_p$, which is the dipole surface plasmon resonance (SPR) of the silver core in the ideal case when damping is absent. We shall also assumed the surrounding medium to be water for simplicity.

With all the dielectric functions specified as in the above, we can now use the formulation in the previous section to calculate the FRET enhancement ratio defined in Eq. (2), and study how this enhancement varies with the various parameters of the gain-clad metallic nanoparticle and how such gain material can be used to optimize the plasmonic enhancement of FRET.
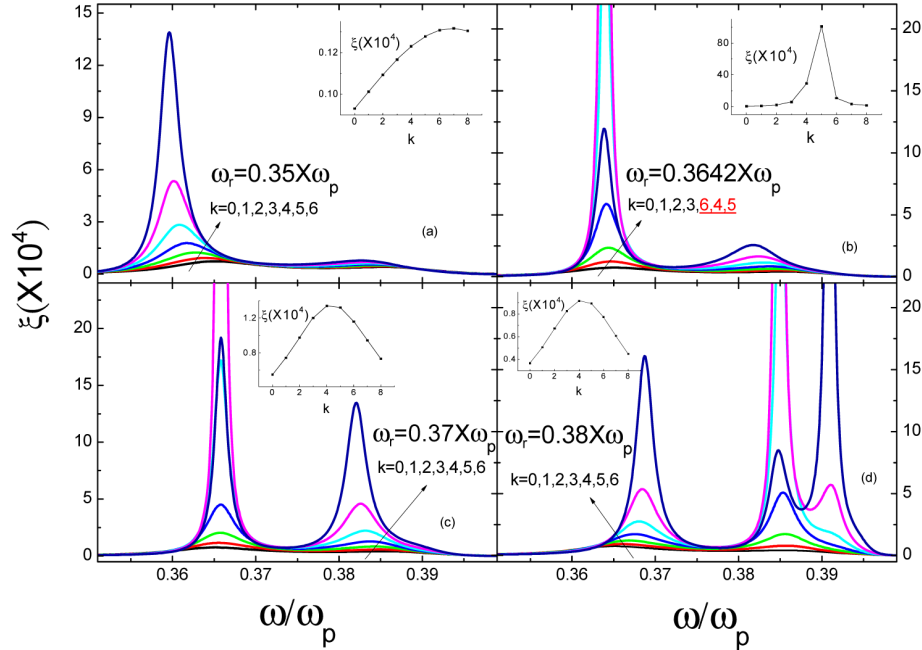

Fig. 2. Enhancement factor (ξ) of FRET as a function of frequency ω for different gain level g and gain center frequency ω_r. The inset in each subfigure is the enhancement factor versus k at frequency $\omega = \omega_r$. Other parameter values are given in the text.

We first study the frequency dependence of the enhancement factor in Eq. (2) at fixed locations of D and A. Figure 2 shows the results of ξ as a function of the emission (absorption) frequency of D (A) with the two dipoles oriented along the z-axis and located at the north and south poles, respectively. The MNP radius and the gain layer thicknness are set at 9.0 nm and 3.0 nm, respectively. The gain center is varied from $0.35\omega_p$ to $0.38\omega_p$ [from Figs. 2(a) to 2(d)] and the gain level is varied according to $g = 0.05k$ with integer k in the range of $[0,6]$. From these results, one first observes the two peaks from the dipole ($0.3642\omega_p$) and quadrupole ($\sim 0.38\omega_p$) SPR enhancement due to the silver core with the dipole enhancement achieving an order $\sim 10^4$ (k = 0, 1 in the gain level variation). The "turn on" of the gain cladding (k > 0) leads to red shifts of the SPR when the gain center is below the dipole SP resonance, as well as significant further enhancement of the FRET enhancement factor in (2): up to a further enhancement of 10^2 when the gain center is close to the dipole SPR frequency. It is interesting to note that, when the gain center is set very close to the dipole SPR frequency of the metal, a *reversed* trend in the magnitude of the enhancement is observed when the gain level is increased beyond a certain value [Fig. 2(b)]. This implies that overcompensation of the metal loss will lead to even less FRET enhancement. As the gain center is tuned to higher frequencies, it is observed that higher order SPR is now much enhanced to an extent that the quadrupole and even the octapole resonance can now lead to FRET enhancements dominating over that from the dipole SPR [Figs. 2(c) and 2(d)].

We next study the distance dependence of the induced FRET process by varying the distance of both the D and A at a fixed emission/absorption frequency in resonance with that of the dipole SP resonance, starting from the positions of the molecules as in Fig. 2. Figure 3 shows such a variation of ξ in Eq. (2) as both the D and A are moved farther from the gain-clad silver particle for different values of gain level at different fixed gain center frequencies. While it is expected to see a monotonic decrease in FRET enhancement as the molecules are moved farther from the clad silver particle, one observes that once again, up to 10^2 further enhancement is achievable when the gain center is close to the dipole SPR of the metal at higher gain level values [Fig. 3(b)], together with a more rapid decrease of such FRET enhancement with distance when these high gain values are set. In addition, a reverse behavior in ξ can again occur at higher gain levels when the gain center frequency is much above that of the dipole SPR in this case [Fig. 3(d)].
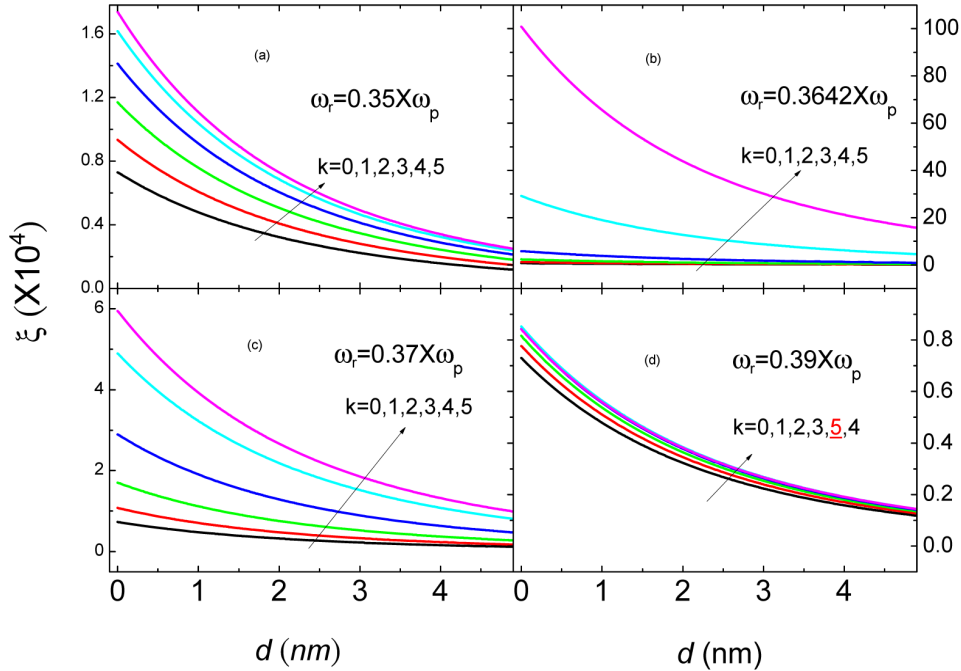

Fig. 3. Enhancement factor (ξ) of FRET as a function of distance d for different gain level

g and gain center frequency ω_r. The radial position of D (A) is at 12.5nm + d (15.0nm + d). Other parameter values are the same as those for Fig. 2.

We shall now investigate the effect of the amount of gain medium added on the FRET enhancement with D and A fixed at the same positions as in Fig. 2. For a fixed gain material with all the parameters in Eq. (16) specified in the same way as in Fig. 2 except that the range of k is [0,5], we shall see that there exists an optimal value for the cladding thickness which will yield the largest enhancement. Figure 4 shows the enhancement as a function of the outer radius b ($a = 0.9nm$) at different values of gain center ω_r, with the cladding goes from the MNP surface to almost touching one of the molecules outside the MNP. Note that different gain levels are considered from which an optimal thickness is seen to emerge at the highest gain level considered in each case, and is particularly obvious when the gain center is at the dipole SP resonance frequency [Fig. 4(b)]. This is due to the fact that D and A here are set to resonate with the MNP dipole SP, whose frequency will be shifted with the addition of the cladding layer. Hence the competition between the compensation of the metal loss and the resonance off-set due to the addition of the cladding leads to the emergence of such an optimal thickness for the gain medium added between the MNP and the molecules.
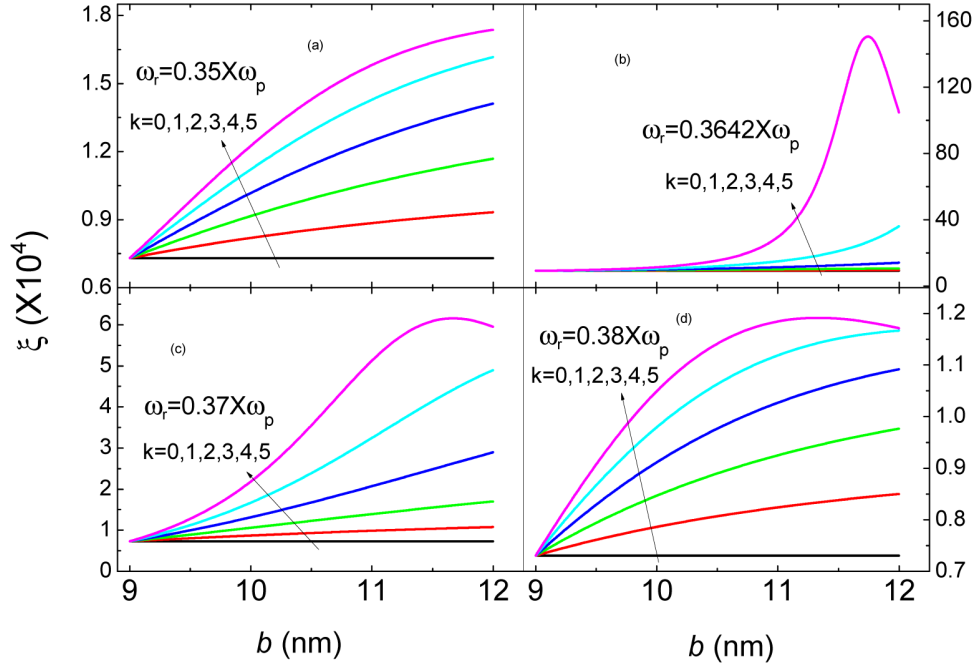
Fig. 4. Enhancement factor (ξ) of FRET as a function of the outer radius b with inner radius fixed at $a = 9.0nm$. Other parameters are given in the text.

Since the presence of the gain-clad metal particle does not only enhance the dipole-dipole interaction between the D and A, but also affects the (spontaneous) emission rate of the donor, it is more informative to study the overall effect on FRET by calculating the "Forster efficiency" which is defined as [8, 15, 25]

$$\eta = K / (K_D + K), \qquad (17)$$

where K and K_D are respectively the FRET rate as defined in Eq. (1), and the donor decay rate in the presence of the particle which can be obtained as [7]:

$$K_D(\omega) = \Gamma_D(\omega)[1 + \text{Im}(E_d) / (2\omega^3 \sqrt{\varepsilon_B} / 3c^3)], \qquad (18)$$

where

$$E_d = \sum_l \frac{l(l+1)^2}{r_d^{2l+2}} \alpha_l b^{2l+1}, \qquad (19)$$

with α_l the l-th pole polarizability of the gain-clad particle which appears as the fractional factor in Eq. (7). Figure 5 shows these results with 5 (c) showing the result of η as a function of gain level for various fixed values of emission (absorption) frequency, where we have assumed a simple case with delta-function spectral distribution [15] for the donor at the D-A resonance frequency. We have also assumed the same value for the polarizability of the acceptor as in [15] with $\text{Im}(\alpha) = 9.7 \times 10^{-30} C^2 \cdot nm \cdot N^{-1}$ for all cases. It is observed that for gain level above a certain critical value ($g_{cr} \sim 0.2$) the imaginary part of the effective dielectric function for the clad particle becomes negative leading to negative values for η (due to the fact that the donor decay rate has become negative in this case). What is more meaningful is the case for $g < g_{cr}$ where we observe a monotonic increase of η with g, with a relative slower rate of increase when the emission frequency is close to the dipole SP resonance of the silver particle. The small values of η are due to the relative large values of the donor decay rates [Fig. 5(a)] since D is located close to the particle. It is significant to

conclude that for $g < g_{cr}$, one can be assured that the application of the gain-cladding will lead to greater FRET efficiency between D and A despite the possible large nonradiative rate induced by the particle on the donor.
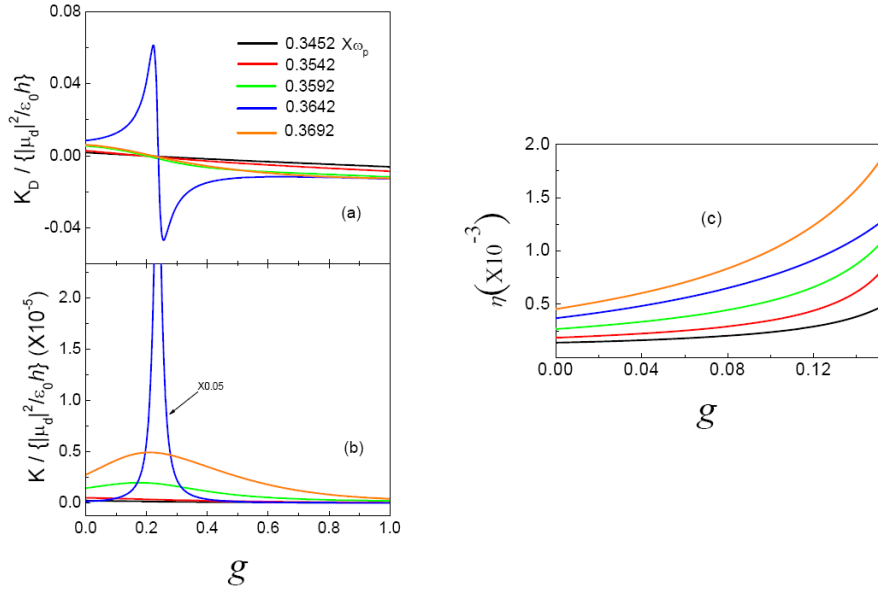

Fig. 5. (a) Decay rate of donor K_D, (b) FRET rate K, and (c) FRET efficiency η as a function of gain level g for various frequency ω for D and A.
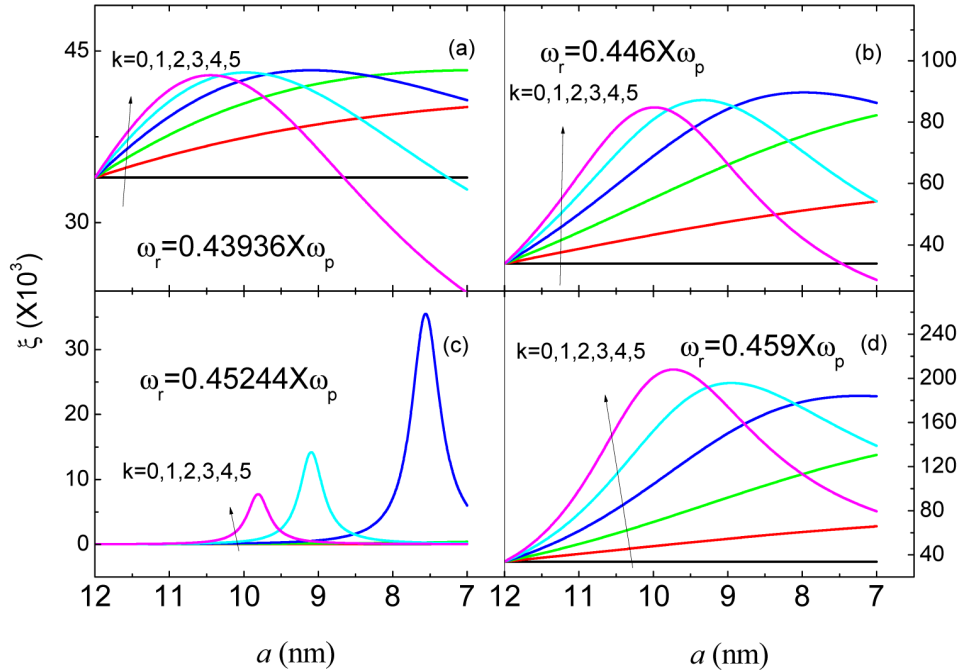

Fig. 6. Enhancement factor (ξ) of FRET for a gain-clad cavity as a function of inner radius a with outer radius fixed at $b = 12.0 nm$. The radial position of D (A) is 6.0 (3.5) nm. The resonance frequency of D and A is at $0.45244\,\omega_p$.

To have a more complete numerical study, we have also investigated the clad layer effect on cavity FRET enhancement [Fig. 1(b)]. Without showing all the detailed results as was done above for the clad MNP case, we show in Fig. 6 only the existence of an optimal cladding thickness as a function of gain level and gain center values. It is seen that such optimal thickness emerges rather distinctively when the gain center is set at the cavity SPR frequency. We also note that this optimal thickness goes down as the gain level increases which is what one should expect.

4. Conclusion

The application of gain material for loss compensation in various optical processes with metals has been initiated since the 1970's. Recently, with the developments in various exciting areas of plasmonics and nano-optics, this material has been applied to achieve improvement of performance on various optical devices and spectroscopic probes [18–23], as well as on nano-imaging [37]. In this work, we have initiated a possibly new application of this material to facilitate one of the most fundamental processes in photophysics and phochemistry, namely, Forster resonance energy transfer between two molecules. Our results show that in the MNP-induced plasmonic enhancement of FRET, optimal enhancement can be achieved when gain just balances with the loss in the metal, in the sense that the imaginary part of the dielectric functions for the metal and the gain medium just cancel. This then leads to the emergence of an optimal layer thickness for the gain material, in both the case with particle and cavity enhancement. In addition, it is observed that the FRET efficiency can always be increased with the coating of the gain material even at the dipole plasmonic resonance when nonradiative transfer from the donor to the metal is high, provided that the gain level is not beyond a certain critical value. Note that our present model has not accounted for the nonlocal optical response of the metallic structures which may become significant when the molecules are at very close distance to these structures. Moreover, from previous studies of these nonlocal effects on FRET [12], we expect that most of our results obtained here will remain qualitatively valid except that the nonlocal effects will slightly blue-shift the resonances and suppress the magnitude of the FRET enhancements. Given this scenario, we anticipate experimentalists will be motivated to study such possible novel application of gain materials in this new direction of plasmonic-enhanced photochemistry.