Surface plasmon mediated nonradiative energy transfer and enhanced radiative emission in stratified planar nanostructures

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**SURFACE PLASMON MEDIATED
NONRADIATIVE ENERGY TRANSFER AND
ENHANCED RADIATIVE EMISSION IN
STRATIFIED PLANAR NANOSTRUCTURES**

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**SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

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Abstract

Planar plasmonic nanostructures have gained considerable attention due to their crucial role in the theoretical comprehension of surface enhanced fluorescent along with their wide applications in nonradiative energy transfer (NRET), plasmonic wave guided mode, Raman scattering spectroscopy, color filters, light emitting and light harvesting devices. With the availability of large density of states at the metallic surface, the radiative and nonradiative decay channels of an electric dipole in a vicinity of metal would be dramatically modified. However, the radiative enhancement cannot be realized for any desired emissive dipole as the existing plasmonic resonance frequency is limited to the well-known plasmonic materials. Despite the fact that recent studies in metamaterial structures demonstrate a promising approach of tuning Purcell factor across the emission wavelength, the structures still suffer from an inefficient radiative emission. Moreover, in the case of nonradiative energy transfer, the conventionally sandwiched donor-metal film-acceptor configurations lack the desired efficiency and suffer poor photoemission due to the high energy loss.

In this dissertation, we propose and demonstrate the nonradiative energy transfer mechanism between the donor and the acceptor through multi-layered metallic nanostructures – stratified configuration, in which an efficient energy transfer can be realized. This novel approach in NRET uniquely provides us with the ability to overcome the drawback of high energy absorption losses in a thick metal film by

inserting a non-absorbing dielectric layer between two thin metal films. Moreover, a strong plasmon-plasmon near-field coupling through the dielectric spacer layer is proven to profoundly extend the effective energy transfer distance/efficiency. The proposed architecture has been demonstrated through theoretical modeling and experiment.

A full theoretical model of an oscillating dipole behavior in front of the planar plasmonic nanostructure is given to calculate the radiative and nonradiative decay rates, radiative emission enhancement, electric field enhancement factor and nonradiative energy transfer. We present the results for the two most applicable plasmonic materials, silver and gold, and develop the model from the conventional metallic nanostructure to the stratified metal-dielectric-metal configuration, in which a remarkably enhanced energy transfer efficiency is obtained as a result of stronger surface plasmon coupling at the metal-dielectric boundaries as evidenced by the enhanced electric field enhancement factor.

Moreover, we present the theoretical and experimental demonstration of engineering surface plasmon mode to tune the maximum radiative decay rate frequency of an emitting dipole in a vicinity of a stratified metal-dielectric-metal nanostructure. This effect arises from an efficient surface plasmon coupling at the metal-dielectric interfaces that leads to the highest electric field enhancement at the dipole position in an optimized cascaded nanostructure. The design principle allows modifying the structure to obtain a maximum transmission efficiency at any desired frequency. The current approach uniquely provides the ability to get the highest plasmonic mode outcoupling to the far field emission at the interfaces by adjusting variable parameter including dielectric layer thickness and refractive index. Thanks to the effective cascaded plasmonic modes

coupling across the metal-dielectric interfaces, the proposed design uniquely illustrate the ability to optimize the plasmonic nanostructure for noticeable radiative transmission and emission enhancement.

In summary, this dissertation studies nonradiative energy transfer and radiative emission in the stratified plasmonic metal-dielectric nanostructures both numerically and experimentally. Our findings show that multilayer plasmonic configurations enhance the nonradiative energy transfer because of the strong surface plasmon near-field coupling created at the interfaces. Furthermore, we demonstrate the leading role of the decay rate improvement over the negligible contribution of excitation enhancement in the proposed stratified nanostructures. Exploiting this effect in light emitting devices, biosensors, and surface-enhance Raman spectroscopy may lead to structures with high radiated intensity at any desired emission frequency.

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List of Acronyms

SPPs	Surface Plasmon Polaritons
SP	Surface Plasmon
ET	Energy Transfer
SPET	Surface Plasmon Energy Transfer
LSP	Localized Surface Plasmon
CPS	Chans, Prock, Silbey
Iso	Isotropic
NRET	Nonradiative Energy Transfer
SET	Surface Energy Transfer
TRF	Time Resolved Fluorescence
DOS	Density Of States
PL	Photo-Luminescence
REF	Radiative Enhancement Factor
AFM	Atomic Force Microscopy

Chapter 1

Introduction

1.1. Perspective

In recent years, plasmonics has been known as one of the most attractive fields of research in nanophotonics area [1-8]. Notably, surface plasmon results from the interactions of the oscillating electrons at the surface of the metallic film with the electromagnetic waves that leads to the propagating waves at the metal-dielectric interface. In fact, the electromagnetics wave is trapped at the metal surface as a result of its coupling to the free electrons of the metal surface. Therefore, the resonance coupling of metal surface electrons with the electromagnetic field of the light wave leads to the formation of surface plasmons and provides many unique properties at the metal-dielectric interface [9-13]. Exploiting the surface plasmon in desired structures, results in a wide range of applications including light concentration in subwavelength structures [7, 14], enhanced light transmission [3, 8, 15, 16], enhanced optical imaging below the

diffraction limit [7, 17, 18], enhanced energy transfer efficiency beyond the Förster radius limit [19-24], colour filters [8, 25], solar cells and light emitting devices [26-28].

More specifically, surface plasmon mediated energy transfer has obtained exceptional attention due to the effect of surface plasmon on enhancing the effective energy transfer range [22, 29]. Considerable effort has been devoted to applying this effect in different nanostructures to obtain desirable energy transfer efficiency. Noted that the excitation energy migration from an excited donor molecule to an acceptor molecule can be occurred either radiatively or nonradiatively. In radiative energy transfer mechanism, the distance between donor and acceptor should be larger than an emission wavelength to have the real photons emitted from an excited donor molecule and consequently absorbed by acceptor dipole. On the other hand, in nonradiative energy transfer, the separation distance should be smaller than 10 nm to have an effective columbic interaction between donor and acceptor molecules and therefore, the energy transfer process occurs with an emission of virtual photons [20, 30]. As a result, utilizing the energy transfer mechanism within the moderate separation distance between the donors and the acceptors (larger than 10 nm and shorter than 1000 nm) lacks the desired efficiency. Instead, surface plasmon mediated energy transfer has been demonstrated to increase the energy transfer efficiency beyond the Förster radius limit. Surface plasmon mediated energy transfer results from the strong evanescent coupling of dipole moment with the surface plasmon modes of the metallic-dielectric interface, which considerably modifies the energy transfer efficiency. Surface plasmon mediated energy transfer offers great potential in numerous applications such as biosensing, light harvesting, and light emitting devices.

Furthermore, it has been well understood that the excitation of the surface plasmon modes at the surface of the metal gives rise to an optical behavior modification of a molecule in the vicinity of the metal surface due to the large enhancement of local electromagnetic field [31-36]. This mechanism results in manipulating the radiative and nonradiative decay channels of an emitting molecule near metallic nanostructures due to the large plasmonic density of states that are available at the metal-dielectric interfaces. Metal-enhanced fluorescence radiative emission field of study has been widely applied not only to enhance the photoluminescence emission of an emitting molecule but also to be able to tune the peak emission enhancement at any desired wavelength.

1.2. Motivation

Despite the great effort that has been devoted to enhancing the efficiency of energy transfer mechanism in planar plasmonic nanostructures, the conventional plasmonic structure still lacks the desired efficiency along with the poor photoluminescence emission intensity. It has been experimentally demonstrated that the energy transfer from an excited donor molecule to the acceptor molecule that is placed on either of the thick metal films is achievable for the metal film with the thickness up to 150 nm. However, both the efficiency and the photoluminescence intensity has dramatically dropped with increasing the metal film thickness.

It is also worth mentioning that the systematic theoretical study of the energy transfer mechanism in planar nanostructures is essential to give a complete picture and unified understanding of the problem. A comprehensive theoretical model provides the

opportunity to design the energy transfer based structures with the optimum parameters to obtain the maximum energy migration efficiency.

Furthermore, the radiative decay rate engineering of an emitting molecule in front of the plasmonic metallic nanostructures is limited to the existing plasmonic materials such as silver and gold. Since the resonance frequency of these materials is restricted, then the radiative decay rate enhancement cannot be achieved for any desired emission wavelength.

From the discussion above, this thesis addresses the following problems:

- Developing the existing theoretical models to describe the optical behavior modifications of an emitting molecule in front of the plasmonic planar nanostructures.
- Presenting a comprehensive theoretical model to explain the energy transfer mechanism in planar plasmonic nanostructures.
- Providing the experimental and theoretical solutions to overcome the drawbacks of the conventional plasmonic nanostructures in a field of nonradiative energy transfer.
- Providing the experimental and theoretical solutions to engineering the radiative decay rate and photoluminescence emission of an oscillating molecule in front of the planar plasmonic nanostructures.

1.3. Organization of the thesis

In Chapter 2, an introduction to fluorescent dynamics near planar metallic nanostructure will be given. The physics underlying this research, including the surface

plasmon theory, surface plasmon mediated energy transfer and surface plasmon enhance radiative emission along with the literature review on these fields will be explained in this chapter. Noted that more detailed description of mathematical expressions and equations will be demonstrated and set up for later chapters.

In Chapter 3, we present the theoretical study and analytical expressions to describe the behavior of an oscillating dipole near planar metallic nanostructures. A detailed discussion on lifetime modification of an emitting dipole in a vicinity of a finite metal film is given in this chapter. The theoretical study is also developed for the layered metal-dielectric-metal structure, and the decay rates modification is calculated for both the single and stratified configurations. Parallel, perpendicular and isotropic orientations of an emitting dipole has been taken into account, and the electric field map simulation is done to evaluate the effect of layered structure on electric field enhancement.

In Chapter 4, we present the theoretical model to illustrate the surface plasmon mediated nonradiative energy transfer mechanism in planar metallic nanostructures. Two different approaches, single-step and two-step models, are presented in this chapter to describe the overall energy transfer process. Moreover, we provide appropriate equations to describe the electric field enhancement factor, donor/acceptor emission intensity, energy transfer rate and energy transfer efficiency.

In Chapter 5, the experimental evidence of surface plasmon mediated energy transfer is provided, and we demonstrate that the energy transfer efficiency in the stratified metal-dielectric-metal structure is significantly enhanced compared to the conventional single metal film structure. Our claim has been demonstrated through both theoretical and experimental results that are in good agreements.

In Chapter 6, we theoretically and experimentally demonstrate the effect of stratified metal-dielectric-metal nanostructure on the engineering of the radiative decay rates of an emitting molecule near stratified plasmonic structure. The design principle allows for modifying the structure to obtain a maximum transmission efficiency at any desired frequency. The presented approach uniquely provides us with the ability to reach the highest plasmonic modes outcoupling to the far field emission at the interfaces by adjusting the variable parameters.

In Chapter 7 the overall conclusions on theoretical and experimental results are given. Moreover, future works on the development of both experimental structure, and the theoretical model is suggested.

Chapter 2

Emitter dynamics near metallic nanostructures

2.1. Introduction

Before a detailed discussion of the theoretical models and experimental observations of nonradiative energy transfer and enhanced radiative emission in planar plasmonic nanostructures, fundamental and comprehensive understanding of the emitters' dynamics near metallic structures is needed to be able to justify the near field and radiative emission properties of the emitters. In this chapter, we provide a brief introduction to the surface plasmon theory and its application in surface plasmon mediated energy transfer and surface plasmon enhanced radiative emission. Furthermore, a literature review on the most recent and significant studies that have been done on this field will be given to providing a complete picture and unified understanding on surface plasmon mediated energy transfer and enhanced radiative emission.

2.2. Surface plasmon

For the very first time, in 1956, the term “plasmons” was used by Pines and Bohm to explain the reason for the energy losses in the case of fast traveling of electrons through the metallic film [37]. Pines and Bohm came up with the bulk plasma oscillation theory, in which the excitation of the bulk plasma led to the energy absorption in a metal film. Collective oscillations of free electrons in the metallic structure were called plasmons which are known today as a “bulk plasmons.” Noted that this bulk plasmon is quite different from the “surface plasmon” which is our topic of interest. Surface plasmon was firstly introduced by Ritchie in 1957 [38]. According to his theoretical study, the existence of plasmon modes in a vicinity of the metal surface was demonstrated by considering electron oscillations at the surface of the metallic thin film. Surface plasmons are propagating electromagnetic waves along the surface of a metal film, which is trapped at the surface due to the interaction with the free electrons of the metals. This resonant interaction constitutes surface plasmon and its unique properties. It should also be noted that the term “surface plasmon polaritons” (SPPs) which are being frequently used in the literature has the advantage of reflecting the hybrid nature of SPPs (the interaction between the electromagnetic waves and the electrons of the conductors). Ten years later, the theoretical explanation of surface plasmon behavior on the metal grating was given by Ritchie’s research team. Despite the fact that several outstanding studies verified the surface plasmon theory on the metal surface, the optical excitation of surface plasmon was a challenging issue since 1968. At this year, significant progress in the field of surface plasmon was made by Andreas Otto, Erich Kretschmann and Heinz Raether [39, 40]. These researchers introduced the practical

methods of excitation of surface plasmons on a metal surface that are known as surface plasmon resonance Kretschmann- Raether (K-R) configuration and surface plasmon resonance Otto configuration.

2.3. Surface plasmon mediated energy transfer

Nonradiative energy transfer or in other words Förster resonance energy transfer (FRET) from an excited donor molecule to the acceptor dipole needs several conditions to meet including spectral overlap between donor emission and acceptor absorption and the short separation distance between donor and acceptor dipoles (less than 10 nm). The first condition can be easily full filled by selecting an appropriate pair of donor-acceptor molecules that provided by many studies [20, 24, 30]. However, the later condition needs to be understood more carefully to realize the limitations of short-distance FRET. More specifically, in the Förster theory of energy transfer, the excited donor molecule has been modeled as a group of electromagnetics oscillators that leads to the creation of the electromagnetic field around the donor. It has been discussed by Andrews et al. [9] that radiative and nonradiative energy transfer mechanisms can be considered equivalently as at the large separation of donor and acceptor the r^{-6} distance dependency of nonradiative transfer is modified to r^{-2} (r is the distance between donor and acceptor). He used quantum electrodynamic methods to show that a single excitation transfer function is adequate to describe both radiative and nonradiative energy transfer. This theory suggests that the virtual photon that is used in a description of the nonradiative process will be varied to a real photon at larger distances to modify the radiative energy

transfer. However, both of these mechanisms lacks the desired efficiency at the moderate donor-acceptor separation (10 to 1000 nm).

The area around the donor can be categorized into four regions: contact, near field, intermediate and far-field zones. The contact zone refers to the region wherein the Dexter energy transfer is effective by exchanging the charge between donor and acceptor molecules. As a result, the separation distance must be short enough (typically less than 1 nm) to be able to efficiently transfer the charge. In the near field zone (between 1 to 10 nm) Förster resonance energy transfer can be applied wherein the energy transfer mechanism occurs by emission of virtual photons by donor dipole. However, in the intermediate zone (between 10 to 1000 nm) the Förster theory cannot be applied, since the separation distance is too far to have an efficient electromagnetics coupling between donor and acceptor dipoles. Finally, within the radiation zone (greater than 1000 nm) the acceptor molecule absorbs the radiation field that is emitted from the donor, and the energy transfer process takes place by emission and absorption of real photons. As a result within the intermediate separation distance between donor and acceptor molecules, neither of the mentioned energy transfer mechanisms can be applied. Surface plasmon mediated nonradiative energy transfer has been demonstrated to enlarge the effective donor-acceptor pair separation distance up to 200 nm [30]. Due to the availability of large optical density of states at the metallic structures surface and because of plasmon enhanced electric field oscillations at the donor/acceptor dipole, metallic nanostructures provide the novel ability of an effective energy transfer mechanism at a longer separation distance. Notably, this effect strongly depends on the metallic nanostructure, material, shape, size and also the surrounding media. Planar

metallic nanostructures has been known as one of the most promising plasmonic configurations in many applicable areas including light emitting diodes, solar cells [16, 26, 27, 41-43], color filter devices [8, 25], optical communication systems, nanolithography [43] and Raman spectroscopy [5, 6, 10, 44]. Due to the availability of surface plasmon modes at the metal surface, unique and remarkable optical phenomenon can be observed by exploiting these structures in various applications. In this section, we review the most recent and significant studies on the effect of surface plasmon on energy transfer in planar nanostructures. Both the theoretical models and experimental observation that were done and developed by different groups would be discussed here.

It was recently reported that surface plasmon mediated energy transfer (SPET) can be applied in nanostructures to significantly increase the effective separation distance between donor and acceptor dipoles [45-47]. In fact, SPET provides us with the ability to obtain the desired NRET efficiency from nanostructures in which, the donor and the acceptor are placed at a distance much longer than conventional Förster energy transfer efficient range. It is worth mentioning that, surface plasmon mediated energy transfer should be considered differently from the traditional nonradiative energy transfer. In SPET mechanism, the direct interaction of donor and acceptor is not efficient (unlike the Förster energy transfer) and the near electric fields coupling of donor and acceptor molecules to the surface plasmon modes of metal, plays a major role in energy migration. In the case of plasmonic nanostructure that consists of a donor dipole that is placed on one side of the metal film and the acceptor dipole which is placed on the other side of the metal film, an oscillating donor dipole evanescent electric field, would excite the surface plasmon modes on either side of the metal film. The donor dipole energy

transfers to the SP modes of metal film and consequently makes them oscillate and couple with each other. This coupling with surface modes on either side of the metal film provides a path for transferring donor dipole energy to the acceptor.

Recently localized surface plasmons (LSPs) mediated energy transfer through metal nanoparticles has received significant attention in semiconductor nanoparticles [32, 48-51]. It has been studied in several works that LSPs enhance Förster resonance energy transfer between donors and acceptors. In recent years, the effect of metallic planar nanostructures on excited fluorescence is well studied by different authors. Notably, both the radiative and nonradiative relaxation processes would be modified due to the effect of metal surface modes on an oscillating molecule. However, the dominant relaxation process at the small distances is nonradiative transfer from an excited fluorescence to the metal film which is known as a quenching effect. Noted that, this quenching effect leads to the dramatic decrease of the emitting molecule quantum yield. The nature of this phenomenon can be explained by Sommerfeld theory of an antenna near the earth in which the surface plasmon modes of the metal-dielectric interface at both sides of the metal film are coupled to the evanescent electromagnetic field of emitting fluorescence [52]. The absorption and reflection of the emitted electromagnetic field through the absorbing (metal) and nonabsorbing (dielectric) media effect the lifetime of an excited dipole. Also, it was found that the lifetime of an excited oscillating dipole in front of a metallic structure is strongly dependent on the distance of the dipole to the metal surface; at a large distances from the surface of the metal, the lifetime of the fluorescent oscillated over the intrinsic value (due to the mirror effect of the metal), while at the close vicinity of the metal film, it damped to zero. The latter occurred

because of the high possibility of nonradiative decay channels close to the metal interface.

One of the very first deep analytical models for the energy transfer between the donor molecule and acceptor molecule near solid state particles is done by A. Nitzan et al. [12, 24]. They developed a formula in which the enhancement of radiative and nonradiative energy transfer in the specific conditions is explained. They built up their model by using spheroidal shape and frequency dependent dielectric function for the particles and Hertzian assumption for both donor and acceptor dipoles to study the effect of the particles on damping rate of the dipoles. Considering two cases, in absence and presence of the particles, provided the chance to understand the mechanism of enhancement due to the modification of the electric field. As a result, they found that the enhancement factor is independent of the acceptor angle orientation and they suggested by modification of solid-state particles; it is possible to adjust the structure to get the optimum energy transfer.

R. R. Chance et al. provides a full study of the fluorescent emission near the interfaces [11, 29, 53]. They used the classical theory of an oscillating dipole close to the mirror based on Sommerfeld's theory of antenna near the earth. The comparison between Kuhn's model and energy flux method in the theory of a single mirror is well studied, and the separation of radiative and nonradiative decay rates of the dipole is given using the energy flux method. The experimental data are obtained from different systems of Eu3 / Au, Eu3 / Ag, Eu3 / Al and Eu3 / cu, that the monolayer of Eu3 is deposited on the mirror, and the energy transfer rate is calculated from the proposed model and the experimental samples, in which the experimental results were in good agreement with

the theoretical study. They demonstrated that the thickness of the mirror plays a leading role in energy transfer rate, that the nonradiative decay rate is enhanced in thin metal films. Moreover, the study of energy transfer as a function of dipole distance to the metal film and the effect of a dielectric refractive index on surface plasmon resonance peak, have been well covered in R. R. Chance and his colleagues' work. Interestingly, that have proved that nonradiative energy transfer formula can also be obtained from simple electromagnetic calculations. Therefore, a systematic study on energy transfer mechanism from an excited molecule to the metal film was presented in their work.

The First experimental report on coupled surface plasmon polaritons mediated energy transfer from donor molecules to acceptor molecules through a thick metal film, gives the observation of energy transfer in a metallic film up to 120 nm. P. Andrew et al. [45] designed the structure consists of donor and acceptor doped dielectric material separated by thick silver layer. The silver thickness varied from 30 to 120 nm and the donor and acceptor are spun cast 60 nm. In planar configuration, 95% of the dipole emission can be coupled to the SPPs modes. Therefore these modes can be considered as the efficient mediator for NRET. In their structure, the excitation source only excites the donor and has the negligible effect on the acceptor. As a result, the acceptor emission at the output spectrum is the evidence of energy transferring from donor layer to the acceptor. According to their time-resolved results, the lifetime of the donor in the presence of the metal and the acceptor doesn't change compared with the donor with a metal only sample so they concluded that the indirect energy transfer from donor to acceptor occurred and the transfer should be radiative rather than Förster.

E. Collini et al. [46] tried to extend Andrew's research by proposing two multilayer structures, donor/metal/acceptor and donor/metal cathode/acceptor/anode to study the role of electric field on surface plasmon mediated energy transfer. They used DPA (9, 10-diphenylanthracene) as a donor, conjugated polymer MEH-PPV as the acceptor, and vary the thickness of silver in the range of 30 to 150 nm. It was observed that the acceptor emission is enhanced in the presence of the applied electric field compared to the case that only optical excitation was involved. Moreover, longer lifetime of the acceptor was concluded as the evidence of more efficient energy transfer from donor to the acceptor site.

2.4. Surface plasmon enhanced radiative emission

The very first study of the environmental effect on the spontaneous emission modification of the emitting molecule was performed by E. M. Purcell in 1946, in which he showed that the enhancement of the spontaneous emission is possible when the molecule emission and the environmental cavity are in resonance with each other [54]. It has been observed and proved that energy loss in the surrounding medium of an emitting molecule corresponds to the nonradiative decay rate modification, while the alternation of the radiative decay rate can be observed through the fluorescence photon emission. As been discussed before, both the radiative and nonradiative decay channels are influenced by the metallic structure and the separation distance between an emitting molecule and the surface of metallic nanostructure, plays a leading role on rates modification.

It has been well studied and proved by J. R. Lakowicz research group that the shape and the density of the metallic nanostructures have a significant effect on the decay rates modifications [33, 34, 55]. Moreover, the quantum yield of the emitting molecule has been demonstrated to be an important parameter to enhance the total radiative rate emission; the highest radiative emission enhancement can be achieved for the molecule with the low intrinsic quantum yield. They also demonstrated that plasmon-enhanced radiative emission occurs due to the spectral overlap between an excited fluorescence emission spectra and surface plasmon emission of the metallic structure. In an experimental piece of work, Lakowicz et al. studied the effect of an emitting molecule emission wavelength, the metal film thickness and the separation distance dependency of radiative emission enhancement factor. They have obtained a maximum radiative enhancement at the separation distance of 10 nm and for the metal film thickness of 20 nm in the system wherein the emission layer is Rabbit immunoglobulin G (IgG) [33, 34, 55].

P. Anger and his colleagues [56, 57] provided an appropriate theoretical equations and experimental demonstration to study the fluorescence emission rate dependency on its distance to the metal nanoparticle. They showed that by changing the separation distance between an emitting molecule and metallic nanoparticle, both the quenching and the enhancement of fluorescence emission can be obtained. In fact for the very first time they provided an experimental evidence that the transition from quenching area to the enhancing domain is a continuous behavior. These results that can be extended for the emitting molecule in front of the planar metallic nanostructure, provide us with the opportunity of deep understanding and control of the fluorescence emission in

nanometer scale. Moreover, based on the Fermi golden rule and by applying the Green's function approach, convenient equations are given by L. Novotny's group to derive the emitting molecule radiative and nonradiative rates modifications due to the presence of gold nanoparticles.

The role of the photonic mode density of states on behavior of the emitting fluorescence near interfaces is well studied by W. L. Barnes [10]. He suggested that the decay rates and the apparent quantum yield are highly affected by the metal-dielectric interfaces; if the reflection of the electromagnetic fields from the interfaces is in phase with the dipole emission, photonic mode densities will be improved and results in an emission enhancement. Otherwise it will attenuate the fluorescent emission. They described the decay mechanism into 3 ways: emission coupled to the SPPs modes, emission coupled to the waveguides mode and radiative decay. More recently, Y. C. Jun et al. [58] have been theoretically demonstrated the effect of metal-dielectric-metal cavity on the decay rates of the emitting molecule that is placed between two metal films, in the dielectric region. They have showed that waveguide mode of the metal-dielectric-metal cavity structure provides the surface plasmon modes that can be efficiently coupled to the emitter molecule and accordingly enhance the radiative rate emission.

Chapter 3

Theory of an oscillating dipole near planar metallic nanostructures

3.1. Introduction

The modification of an excited molecule lifetime in a vicinity of the metallic nanostructures can be explained through different theoretical models. In these models, the reflection and absorption of the excited molecule electromagnetic field at the metallic interface would lead to the dipole lifetime alteration. Notably, the appropriate analytical model provides the chance to develop the physical insight into this problem. In this chapter, we describe a model based on the energy flux method to adequately simulate the lifetime of the fluorescent near a metallic nanostructure and the electric field map. This model has the unique advantage of a separate calculation of the radiative and nonradiative components of an emitting dipole decay rates. The equations will be given for the parallel and perpendicular dipole orientations with respect to the single metal film surface and will be expanded for the stratified metal-dielectric-metal

nanostructures. The electric field map simulation is also performed to study the effect of layered structure on the electric field enhancement at the region of interest.

3.2. Model principles

The geometry of the problem for the single layer and stratified structures is depicted in Figure 3.1. The single layer structure is referred to the configuration in which an emitting dipole is placed in front of a single finite metal film, while in the stratified configuration, the dipole is placed in a vicinity of a layered metal-dielectric-metal nanostructure. In this simulation, we assumed that all the dielectric regions are the organic materials with the similar refractive index constant. The dielectric function of the metallic films in the single layer and the stratified structures are taken from Johnson and Christy 1972 [59] dielectric function, and we present the results for the two most applicable metal films in the plasmonic structures, silver, and gold. There are some assumptions considered in the theoretical model as follow:

- The size of an excited dipole is approximated to be much smaller than the emission wavelength, and the Hertzian point-like dipole model is used in this simulation.
- An excited dipole emission frequency shift that has occurred due to the effect of the metallic surface is negligible.
- All the surrounding and spacing dielectric mediums are assumed to be non-absorbing materials.

- The metallic film is not perfect, and the partially absorbing-partially reflecting model is used for the metallic layers.
- The isotropic dielectric constants are applied to all the regions.

Noted that despite all these assumptions, the model is valid for broad applications. As a matter of fact, the first assumption is valid for most of the organic fluorescent materials that the molecule size is small enough to be approximated as the Hertzian dipole (point-like dipole approximation). The second assumption was studied in reference [29] and demonstrated that the frequency shift due to the effect of metallic structure, is too small to affect the lifetime results considerably.

Figure 3.1 | Single layer and stratified nanostructures. Architectures of the single silver film structure (a) and stratified structure (b) consists of two silver films separated by dielectric films. The excited Hertzian dipole is placed at one side of the metallic structure. The dielectric mediums are isotropic and non-absorbing.

In order to evaluate the performance of the structures, we employed the theoretical model based on R.R Chance, A. Prock and R. Silbey (CPS) theory of an excited dipole

molecule near a metal surface [11]. Briefly, the electric ($\vec{E}_i$) and magnetic ($\vec{H}_i$) fields of an excited dipole is expressed by defining the Hertz vectors at the region of interest as

$$\vec{E}_i = k_i^2 \vec{\Pi}_i + \nabla(\nabla \cdot \vec{\Pi}_i) \quad (3.1)$$

$$\vec{H}_i = -i\omega \nabla \times \vec{\Pi}_i \quad (3.2)$$

where $\vec{\Pi}_i$ is the Hertz vector and k_i is the propagation constant at the region i . The boundary conditions at each interface would be applied later to simulate the near field surface modes between the metal and the dielectric layers. The Poynting vectors (S^*) can be formulated using the electric and magnetic fields

$$S^* = \left(\frac{c}{8\pi}\right) \vec{E} \times \vec{H}^* \quad (3.3)$$

which allows defining the total energy flux (F) through all the layers by

$$F = Re \int S^* \cdot n \, dA \quad (3.4)$$

where c is a speed of light in vacuum, $S^* \cdot n$ is the normal component of Poynting vector and dA is the surface element of the constant height z in cylindrical coordinates ($dA = r dr d\varphi$). The decay constant is obtained as the ratio of the total energy flux to the total energy of the dipole ($\frac{1}{2\omega^2 m |\mu|^2 e^2}$). The distinct and notable advantage of this approach is that explicitly shows the radiative and nonradiative decay rates of an emitting dipole, based on the separation of the trivial and evanescent energy transfer terms in the decay rates expressions. The approach is unique for each dipole, parallel ($\parallel$) or perpendicular ($\perp$) to the interfaces and can be extended to an isotropic (*iso*) one by applying

$$\gamma^{iso} = 1/3 \gamma^{\perp} + 2/3 \gamma^{\parallel} \quad (3.5)$$

where γ is the decay rate for different dipole orientations. Following the CPS model, we initially define the Hertz vectors in cylindrical coordinates (r, z, φ) for parallel and perpendicular dipoles that will be explained in the next sections.

3.3. Single metal film structure

In this section, the Hertz vectors definition for the parallel and perpendicular orientations of an emitting dipole near a single finite metal film will be given based on applying appropriate boundary conditions at the metal-dielectric and dielectric-metal interfaces.

3.3.1. Dipole perpendicular to the interface

Here we consider that the dipole is aligned perpendicular to the metal interface. The dipole is placed at the region 1 where the surrounding medium has the dielectric constant of ε_1 and the separation distance of dipole to the metal surface is d_1 . The second region is a finite metal film with the thickness of d_2 , and the dielectric function of $\varepsilon_2(\omega)$ and region 3 is a non-absorbing dielectric medium with the dielectric constant of ε_3 . As mentioned before, in this simulation all the dielectric media are considered similar, therefore $\varepsilon_1 = \varepsilon_3$. The Hertz vectors for the single metal film structure at each of the regions can be obtained as follows

$$\vec{\Pi}_1^\perp = \hat{e}_z \frac{\mu_1 k_1}{4\pi\epsilon_1} \int_0^\infty (e^{l_1(\hat{z}-\hat{d}_1)} + f_1^\perp e^{-l_1\hat{z}}) J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.6)$$

$$\vec{\Pi}_2^\perp = \hat{e}_z \frac{\mu_1 k_1}{4\pi\epsilon_1} \int_0^\infty (f_2^\perp e^{l_2\hat{z}} + f_3^\perp e^{-l_2\hat{z}}) J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.7)$$

$$\vec{\Pi}_3^\perp = \hat{e}_z \frac{\mu_1 k_1}{4\pi\epsilon_1} \int_0^\infty f_4^\perp e^{l_3\hat{z}} J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.8)$$

where μ_1 is the donor dipole moment, $J_0(u\hat{r})$ is the zeroth-order Bessel function, k_1 is the propagation constant at the region I , $\hat{z}$ is the normalized distance from the metal surface ($z = 0$), $\hat{d}_1$ is the dipole normalized distance to the nearest metal interface, u is the integral variable and l_i is defined as $l_i = \sqrt{u^2 - \frac{\epsilon_i}{\epsilon_1}}$. The terms $f_{1-4}^\perp$ are calculated by fitting appropriate boundary conditions at the interface $= 0$:

$$\epsilon_1 \vec{\Pi}_1^\perp = \epsilon_2(\omega) \vec{\Pi}_2^\perp \quad (3.9)$$

$$\frac{\partial \vec{\Pi}_1^\perp}{\partial z} = \frac{\partial \vec{\Pi}_2^\perp}{\partial z} \quad (3.10)$$

and the boundary conditions at the interface $z = -d_2$ are:

$$\epsilon_2(\omega) \vec{\Pi}_2^\perp = \epsilon_3 \vec{\Pi}_3^\perp \quad (3.11)$$

$$\frac{\partial \vec{\Pi}_2^\perp}{\partial z} = \frac{\partial \vec{\Pi}_3^\perp}{\partial z} \quad (3.12)$$

By applying these boundary conditions in equations 3.6 to 3.8, we have

$$f_1^\perp = -\frac{(R_1^\parallel + R_2^\parallel e^{-2l_2\hat{d}_2})}{(1 + R_1^\parallel R_2^\parallel e^{-2l_2\hat{d}_2})} e^{-l_1\hat{d}_1} \quad (3.13)$$

$$f_2^\perp = \frac{2\varepsilon_1 l_1}{\alpha_1} \frac{1}{(1 + R_1^\parallel R_2^\parallel e^{-2l_2\hat{d}_2})} e^{-l_1\hat{d}_1} \quad (3.14)$$

$$f_3^\perp = -\frac{2\varepsilon_1 l_1}{\alpha_1} \frac{R_2^\parallel}{(1 + R_1^\parallel R_2^\parallel e^{-2l_2\hat{d}_2})} e^{-2l_2\hat{d}_2} e^{-l_1\hat{d}_1} \quad (3.15)$$

$$f_4^\perp = \frac{4\varepsilon_1 \varepsilon_2(\omega) l_1 l_2}{\alpha_1 \alpha_2} \frac{1}{(1 + R_1^\parallel R_2^\parallel e^{-2l_2\hat{d}_2})} e^{(l_3-l_2)\hat{d}_2} e^{-l_1\hat{d}_1} \quad (3.16)$$

where α_i and $R_i^\parallel$ (reflection coefficient) are defined as follow:

$$\alpha_i = \varepsilon_i l_{i+1} + \varepsilon_{i+1} l_i \quad (3.17)$$

$$R_i^\parallel = \frac{\varepsilon_i l_{i+1} - \varepsilon_{i+1} l_i}{\varepsilon_i l_{i+1} + \varepsilon_{i+1} l_i} \quad (3.18)$$

3.3.2. Dipole parallel to the interface

Here the problem will be solved for the dipole parallel to the interface and following the same trends in the previous part we determine the Hertz vectors as follows

$$\begin{aligned} \vec{\Pi}_1^\parallel = & \hat{e}_x \frac{\mu_1 k_1}{4\pi\varepsilon_1} \int_0^\infty (e^{l_1(\hat{z}-\hat{d}_1)} + f_1^\parallel e^{-l_1\hat{z}}) J_0(u\hat{r}) \frac{u}{l_1} du \\ & + \hat{e}_z \frac{\mu_1 k_1}{4\pi\varepsilon_1} \frac{\hat{x}}{\hat{r}} \int_0^\infty g_1^\parallel e^{-l_1\hat{z}} J_1(u\hat{r}) du \end{aligned} \quad (3.19)$$

$$\begin{aligned}\vec{\Pi}_2^{\parallel} = & \hat{e}_x \frac{\mu_1 k_1}{4\pi\epsilon_1} \int_0^\infty (f_2^{\parallel} e^{l_2 \hat{z}} + f_3^{\parallel} e^{-l_2 \hat{z}}) J_0(u\hat{r}) \frac{u}{l_1} \\ & + \hat{e}_z \frac{\mu_1 k_1}{4\pi\epsilon_1} \frac{\hat{x}}{\hat{r}} \int_0^\infty (g_2^{\parallel} e^{l_2 \hat{z}} + g_3^{\parallel} e^{-l_2 \hat{z}}) J_1(u\hat{r}) du\end{aligned}\quad (3.20)$$

$$\begin{aligned}\vec{\Pi}_3^{\parallel} = & \hat{e}_x \frac{\mu_1 k_1}{4\pi\epsilon_1} \int_0^\infty f_4^{\parallel} e^{l_3 \hat{z}} J_0(u\hat{r}) \frac{u}{l_1} du \\ & + \hat{e}_z \frac{\mu_1 k_1}{4\pi\epsilon_1} \frac{\hat{x}}{\hat{r}} \int_0^\infty g_4^{\parallel} e^{l_3 \hat{z}} J_1(u\hat{r}) du\end{aligned}\quad (3.21)$$

The boundary conditions at $z = 0$ are:

$$\frac{\partial \vec{\Pi}_{1z}^{\parallel}}{\partial z} - \frac{\partial \vec{\Pi}_{2z}^{\parallel}}{\partial z} = \frac{\partial \vec{\Pi}_{2x}^{\parallel}}{\partial x} - \frac{\partial \vec{\Pi}_{1x}^{\parallel}}{\partial x} \quad (3.22)$$

$$\epsilon_1 \frac{\partial \vec{\Pi}_{1x}^{\parallel}}{\partial z} = \epsilon_2(\omega) \frac{\partial \vec{\Pi}_{2x}^{\parallel}}{\partial x} \quad (3.23)$$

$$\epsilon_1 \vec{\Pi}_{1x}^{\parallel} = \epsilon_2(\omega) \vec{\Pi}_{2x}^{\parallel} \quad (3.24)$$

$$\epsilon_1 \vec{\Pi}_{1z}^{\parallel} = \epsilon_2(\omega) \vec{\Pi}_{2z}^{\parallel} \quad (3.25)$$

and the boundary conditions at $z = -d_2$ are:

$$\frac{\partial \vec{\Pi}_{2z}^{\parallel}}{\partial z} - \frac{\partial \vec{\Pi}_{3z}^{\parallel}}{\partial z} = \frac{\partial \vec{\Pi}_{3x}^{\parallel}}{\partial x} - \frac{\partial \vec{\Pi}_{2x}^{\parallel}}{\partial x} \quad (3.26)$$

$$\epsilon_2(\omega) \frac{\partial \vec{\Pi}_{2x}^{\parallel}}{\partial z} = \epsilon_3 \frac{\partial \vec{\Pi}_{3x}^{\parallel}}{\partial x} \quad (3.27)$$

$$\varepsilon_2(\omega)\vec{\Pi}_{2x}^{\parallel} = \varepsilon_3\vec{\Pi}_{3x}^{\parallel} \quad (3.28)$$

$$\varepsilon_2(\omega)\vec{\Pi}_{2z}^{\parallel} = \varepsilon_3\vec{\Pi}_{3z}^{\parallel} \quad (3.29)$$

Consequently by substituting boundary conditions into Hertz vector equations, the terms

$f_{1-4}^{\parallel}$ and $g_{1-4}^{\parallel}$ are obtained:

$$f_1^{\parallel} = \frac{R_1^{\perp}e^{l_2\hat{d}_2} + R_2^{\perp}e^{-l_2\hat{d}_2}}{e^{l_2\hat{d}_2} + R_1^{\perp}R_2^{\perp}e^{-l_2\hat{d}_2}}e^{-l_1\hat{d}_1} \quad (3.30)$$

$$f_2^{\parallel} = \frac{2\varepsilon_1l_1}{\varepsilon_2(\omega)}\frac{1}{\alpha_1^{\perp}(e^{l_2\hat{d}_2} + R_1^{\perp}R_2^{\perp}e^{-l_2\hat{d}_2})}e^{l_2\hat{d}_2}e^{-l_1\hat{d}_1} \quad (3.31)$$

$$f_3^{\parallel} = \frac{2\varepsilon_1l_1}{\varepsilon_2(\omega)}\frac{R_2^{\perp}}{\alpha_1^{\perp}(e^{l_2\hat{d}_2} + R_1^{\perp}R_2^{\perp}e^{-l_2\hat{d}_2})}e^{-l_2\hat{d}_2}e^{-l_1\hat{d}_1} \quad (3.32)$$

$$f_4^{\parallel} = \frac{4\varepsilon_1l_1l_2}{\varepsilon_3}\frac{1}{(\alpha_1^{\perp}\alpha_2^{\perp})(e^{l_2\hat{d}_2} + R_1^{\perp}R_2^{\perp}e^{-l_2\hat{d}_2})}e^{l_3\hat{d}_2}e^{-l_1\hat{d}_1} \quad (3.33)$$

$$g_1^{\parallel} = \left(\frac{R_1^{\parallel}e^{l_2\hat{d}_2} + R_2^{\parallel}e^{-l_2\hat{d}_2}}{e^{l_2\hat{d}_2} + R_1^{\parallel}R_2^{\parallel}e^{-l_2\hat{d}_2}} - \frac{R_1^{\perp}e^{l_2\hat{d}_2} + R_2^{\perp}e^{-l_2\hat{d}_2}}{e^{l_2\hat{d}_2} + R_1^{\perp}R_2^{\perp}e^{-l_2\hat{d}_2}} \right) e^{-l_1\hat{d}_1} \quad (3.34)$$

$$g_2^{\parallel} = \frac{2\varepsilon_1l_1}{\varepsilon_2(\omega)} \left(\frac{1}{\alpha_1^{\parallel}(e^{l_2\hat{d}_2} + R_1^{\parallel}R_2^{\parallel}e^{-l_2\hat{d}_2})} - \frac{1}{\alpha_1^{\parallel}(e^{l_2\hat{d}_2} + R_1^{\parallel}R_2^{\parallel}e^{-l_2\hat{d}_2})} \right) e^{l_2\hat{d}_2}e^{-l_1\hat{d}_1} \quad (3.35)$$

$$g_3^{\parallel} = \frac{2\varepsilon_1 l_1}{\varepsilon_2(\omega)} \left(\frac{R_2^{\parallel}}{\alpha_1^{\parallel}(e^{l_2 \hat{d}_2} + R_1^{\parallel} R_2^{\parallel} e^{-l_2 \hat{d}_2})} - \frac{R_2^{\perp}}{\alpha_1^{\parallel}(e^{l_2 \hat{d}_2} + R_1^{\parallel} R_2^{\parallel} e^{-l_2 \hat{d}_2})} \right) e^{-l_2 \hat{d}_2} e^{-l_1 \hat{d}_1} \quad (3.36)$$

$$g_4^{\parallel} = \frac{4\varepsilon_1 l_1 l_2}{\varepsilon_3} \left(\frac{1}{(\alpha_1^{\parallel} \alpha_2^{\parallel})(e^{l_2 \hat{d}_2} + R_1^{\parallel} R_2^{\parallel} e^{-l_2 \hat{d}_2})} - \frac{1}{(\alpha_1^{\perp} \alpha_2^{\perp})(e^{l_2 \hat{d}_2} + R_1^{\perp} R_2^{\perp} e^{-l_2 \hat{d}_2})} \right) e^{l_3 d_2} e^{-l_1 \hat{d}_1} \quad (3.37)$$

where $R_i^{\perp}$ and $\alpha_i^{\perp}$ are defined as follow:

$$\alpha_i^{\perp} = l_{i+1} + l_i \quad (3.38)$$

$$R_i^{\perp} = \frac{l_i - l_{i+1}}{l_{i+1} + l_i} \quad (3.39)$$

At this point, we are able to define the decay rates by employing the energy flux method and calculate the total energy flowing away from the emitting dipole. Noted that for the sake of simplicity, the decay rates were normalized to the free space dipole decay rate. Therefore, based on the far field and near field distance dependency, the normalized radiative and nonradiative terms can be assigned.

3.3.3. Radiative and nonradiative decay rates

The metallic layer has a leading effect on both radiative and nonradiative components of the dipole lifetime. The nonradiative components mostly affected due to the nonradiative energy transfer from the dipole to the metallic structure. Thanks to the

advantageous of the energy flux method, we are now able to separate radiative and nonradiative decay channels. The decay rate is then can be obtained by dividing the flux by the total energy of the dipole. In order to determine the total flux, we need to suppose two planes, one above the dipole ($F_{\uparrow}$) and the other one below it ($F_{\downarrow}$). The planes are considered infinite and the total energy flux through these planes is calculated by integrating the Poynting vector over the planes.

Then, we substitute $\vec{I}$ from equations 3.6 to 3.8 (for perpendicular dipole), 3.19 to 3.21 (for parallel dipoles) and calculate the integral over the surface element of the constant height z in cylindrical coordinates ($dS_z = r dr d\phi$). After dividing by total energy of the dipole ($\frac{1}{2\omega^2 m |\mu|^2 e^2}$) and normalizing to the decay rate in absence of the metallic structure, the normalized decay rates for perpendicular and parallel dipole through up and down planes are:

$$\begin{aligned} \hat{b}_{\uparrow}^{\perp} = & q - \frac{3}{4} q \operatorname{Im} \int_0^1 \left(1 - \left| \frac{(R_{\parallel 1}^{\parallel} + R_{\parallel 2}^{\parallel} e^{-2l_2 \hat{d}_2})}{(1 + R_{\parallel 1}^{\parallel} R_{\parallel 2}^{\parallel} e^{-2l_2 \hat{d}_2})} \right|^2 \right) \frac{u^3 du}{l_1} \\ & - \frac{3}{2} q \operatorname{Im} \int_0^1 \frac{(R_{\parallel 1}^{\parallel} + R_{\parallel 2}^{\parallel} e^{-2l_2 \hat{d}_2})}{(1 + R_{\parallel 1}^{\parallel} R_{\parallel 2}^{\parallel} e^{-2l_2 \hat{d}_2})} e^{-2l_1 \hat{d}_1} \frac{u^3 du}{l_1} \end{aligned} \quad (3.40)$$

$$\begin{aligned} \hat{b}_{\downarrow}^{\perp} = & \frac{3}{4} q \operatorname{Im} \int_0^1 \left(1 - \left| \frac{(R_{\parallel 1}^{\parallel} + R_{\parallel 2}^{\parallel} e^{-2l_2 \hat{d}_2})}{(1 + R_{\parallel 1}^{\parallel} R_{\parallel 2}^{\parallel} e^{-2l_2 \hat{d}_2})} \right|^2 \right) \frac{u^3 du}{l_1} \\ & - \frac{3}{2} q \operatorname{Im} \int_1^{\infty} \frac{(R_{\parallel 1}^{\parallel} + R_{\parallel 2}^{\parallel} e^{-2l_2 \hat{d}_2})}{(1 + R_{\parallel 1}^{\parallel} R_{\parallel 2}^{\parallel} e^{-2l_2 \hat{d}_2})} e^{-2l_1 \hat{d}_1} \frac{u^3 du}{l_1} \end{aligned} \quad (3.41)$$

$$\begin{aligned}
\hat{b}_{\uparrow}^{\parallel} = & q - \frac{3}{8}q \operatorname{Im} \int_0^1 \left[\left(1 - \left| \frac{R_1^{\perp} e^{l_2 \hat{d}_2} + R_2^{\perp} e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^{\perp} R_2^{\perp} e^{-l_2 \hat{d}_2}} \right|^2 \right) \right. \\
& + (1 - u^2) \left(- \left| \frac{R_1^{\parallel} e^{l_2 \hat{d}_2} + R_2^{\parallel} e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^{\parallel} R_2^{\parallel} e^{-l_2 \hat{d}_2}} \right|^2 \right) \left. \right] \frac{udu}{l_1} \\
& + \frac{3}{4}q \operatorname{Im} \int_0^1 \left(\frac{R_1^{\perp} e^{l_2 \hat{d}_2} + R_2^{\perp} e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^{\perp} R_2^{\perp} e^{-l_2 \hat{d}_2}} \right. \\
& \left. + (1 - u^2) \frac{R_1^{\parallel} e^{l_2 \hat{d}_2} + R_2^{\parallel} e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^{\parallel} R_2^{\parallel} e^{-l_2 \hat{d}_2}} \right) e^{-2l_1 \hat{d}_1} \frac{udu}{l_1}
\end{aligned} \tag{3.42}$$

$$\begin{aligned}
\hat{b}_{\downarrow}^{\parallel} = & \frac{3}{8}q \operatorname{Im} \int_0^1 \left[\left(1 - \left| \frac{R_1^{\perp} e^{l_2 \hat{d}_2} + R_2^{\perp} e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^{\perp} R_2^{\perp} e^{-l_2 \hat{d}_2}} \right|^2 \right) \right. \\
& + (1 - u^2) \left(- \left| \frac{R_1^{\parallel} e^{l_2 \hat{d}_2} + R_2^{\parallel} e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^{\parallel} R_2^{\parallel} e^{-l_2 \hat{d}_2}} \right|^2 \right) \left. \right] \frac{udu}{l_1} \\
& + \frac{3}{4}q \operatorname{Im} \int_1^{\infty} \left(\frac{R_1^{\perp} e^{l_2 \hat{d}_2} + R_2^{\perp} e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^{\perp} R_2^{\perp} e^{-l_2 \hat{d}_2}} \right. \\
& \left. + (1 - u^2) \frac{R_1^{\parallel} e^{l_2 \hat{d}_2} + R_2^{\parallel} e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^{\parallel} R_2^{\parallel} e^{-l_2 \hat{d}_2}} \right) e^{-2l_1 \hat{d}_1} \frac{udu}{l_1}
\end{aligned} \tag{3.43}$$

By considering the intrinsic nonradiative damping constant of the dipole $(1 - q)$, the total decay rate can be obtained as:

$$\hat{b} = \hat{b}_{\uparrow} + \hat{b}_{\downarrow} + (1 - q) \tag{3.44}$$

where q is an intrinsic quantum yield of the donor dipole. Noted that now we separate the far field and near field components of the equations 3.40 to 3.43 as the first term in all these equations are in dependent of the dipole distance to the surface and is the

dominant part in far distances for the $\hat{b}_\perp^{\parallel,\perp}$, as a result it covers a far field transfer. Equations 3.45 to 3.48 represent the radiative ($\hat{b}_r$) and nonradiative ($\hat{b}_{nr}$) components of the decay rate for perpendicular and parallel dipoles, respectively:

$$\hat{b}_r^\perp = q - \frac{3}{2}q \operatorname{Im} \left(\int_0^1 \frac{(R_1^\parallel + R_2^\parallel e^{-2l_2 \hat{d}_2})}{(1 + R_1^\parallel R_2^\parallel e^{-2l_2 \hat{d}_2})} e^{-2l_1 \hat{d}_1} \frac{u^3}{l_1} du \right) \quad (3.45)$$

$$\hat{b}_{nr}^\perp = 1 - q - \frac{3}{2}q \operatorname{Im} \left(\int_1^\infty \frac{(R_1^\parallel + R_2^\parallel e^{-2l_2 \hat{d}_2})}{(1 + R_1^\parallel R_2^\parallel e^{-2l_2 \hat{d}_2})} e^{-2l_1 \hat{d}_1} \frac{u^3}{l_1} du \right) \quad (3.46)$$

$$\begin{aligned} \hat{b}_r^\parallel = q - \frac{3}{4}q \operatorname{Im} \left(\int_0^1 \left[(1 - u^2) \frac{R_1^\parallel e^{l_2 \hat{d}_2} + R_2^\parallel e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^\parallel R_2^\parallel e^{-l_2 \hat{d}_2}} \right. \right. \\ \left. \left. + \frac{R_1^\perp e^{l_2 \hat{d}_2} + R_2^\perp e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^\perp R_2^\perp e^{-l_2 \hat{d}_2}} \right] e^{-2l_1 \hat{d}_1} \frac{u}{l_1} du \right) \end{aligned} \quad (3.47)$$

$$\begin{aligned} \hat{b}_{nr}^\parallel = 1 - q - \frac{3}{4}q \operatorname{Im} \left(\int_1^\infty \left[(1 - u^2) \frac{R_1^\parallel e^{l_2 \hat{d}_2} + R_2^\parallel e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^\parallel R_2^\parallel e^{-l_2 \hat{d}_2}} \right. \right. \\ \left. \left. + \frac{R_1^\perp e^{l_2 \hat{d}_2} + R_2^\perp e^{-l_2 \hat{d}_2}}{e^{l_2 \hat{d}_2} + R_1^\perp R_2^\perp e^{-l_2 \hat{d}_2}} \right] e^{-2l_1 \hat{d}_1} \frac{u}{l_1} du \right) \end{aligned} \quad (3.48)$$

Note that the first and the second terms (the integral expression), in these equations (3.45 to 3.48), refers to an intrinsic decay rates of the dipole in the absence of the metallic mirror and the normalized decay rates modification due to the presence of the metallic nanostructures, respectively. Consequently, the total normalized decay rate of an emitting donor dipole can be expressed as $\hat{b}_r + \hat{b}_{nr}$. We should stress that the key factor in separating the total decay rate constant to radiative and nonradiative components, is the variation of the integral limits. As one can see in equations 3.45 and

3.47, in which the normalized radiative decay rates of the dipole have been expressed, the integral limits varies from 0 to 1, while for the normalized nonradiative decay rate expression in equations 3.46 and 3.48, the integral limits varies from 1 to ∞ . This can be explained through the dipole behavior near the metal surface, which includes both, the far ($0 < u < 1$) and evanescent fields ($u > 1$), the corresponding region can be independently defined versus u to cover either the real ($0 < u < 1$) or complex ($u > 1$) angles of incidence.

3.4. Stratified metal-dielectric-metal nanostructure

In this section, we will expand the equations for the stratified metal-dielectric-metal structure (depicted in Figure 3.1 b). The equations were solved for the parallel and perpendicular dipoles, and in order to avoid the complexity of the text in this report, we present the results for perpendicular dipole only. However, for the depicted results in all the figures that will be discussed later (lifetime and electric field map results) both the dipole orientations are taken into account. As a result, the Hertz vectors ($\vec{\Pi}'_i{}^\perp$) in 5 regions of the stratified structure will be defined as follow:

$$\vec{\Pi}'_1{}^\perp = \hat{e}_z \frac{\mu_1 k_1}{4\pi\epsilon_1} \int_0^\infty (e^{l_1(\hat{z}-\hat{d}'_1)} + f_1'^\perp e^{-l_1\hat{z}}) J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.49)$$

$$\vec{\Pi}'_2{}^\perp = \hat{e}_z \frac{\mu_1 k_1}{4\pi\epsilon_1} \int_0^\infty (f_2'^\perp e^{l_2\hat{z}} + f_3'^\perp e^{-l_2\hat{z}}) J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.50)$$

$$\vec{\Pi}'_3{}^\perp = \hat{e}_z \frac{\mu_1 k_1}{4\pi \varepsilon_1} \int_0^\infty (f_4'^\perp e^{l_3 \hat{z}} + f_5'^\perp e^{-l_3 \hat{z}}) J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.51)$$

$$\vec{\Pi}'_4{}^\perp = \hat{e}_z \frac{\mu_1 k_1}{4\pi \varepsilon_1} \int_0^\infty (f_6'^\perp e^{l_4 \hat{z}} + f_7'^\perp e^{-l_4 \hat{z}}) J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.52)$$

$$\vec{\Pi}'_5{}^\perp = \hat{e}_z \frac{\mu_1 k_1}{4\pi \varepsilon_1} \int_0^\infty f_8'^\perp e^{l_5 \hat{z}} J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.53)$$

The boundary conditions in the stratified nanostructure at the interface $z = 0$ are defined as:

$$\varepsilon_1 \vec{\Pi}'_1{}^\perp = \varepsilon_2(\omega) \vec{\Pi}'_2{}^\perp \quad (3.54)$$

$$\frac{\partial \vec{\Pi}'_1{}^\perp}{\partial z} = \frac{\partial \vec{\Pi}'_2{}^\perp}{\partial z} \quad (3.55)$$

and the boundary conditions at the interface $z = -d'_2$ are:

$$\varepsilon_2(\omega) \vec{\Pi}'_2{}^\perp = \varepsilon_3 \vec{\Pi}'_3{}^\perp \quad (3.56)$$

$$\frac{\partial \vec{\Pi}'_2{}^\perp}{\partial z} = \frac{\partial \vec{\Pi}'_3{}^\perp}{\partial z} \quad (3.57)$$

and the boundary conditions at the interface $z = -d'_2 - d'_3$ are:

$$\varepsilon_3 \vec{\Pi}'_3{}^\perp = \varepsilon_4(\omega) \vec{\Pi}'_4{}^\perp \quad (3.58)$$

$$\frac{\partial \vec{\Pi}'_3{}^\perp}{\partial z} = \frac{\partial \vec{\Pi}'_4{}^\perp}{\partial z} \quad (3.59)$$

and finally the boundary conditions at the interface $z = -d'_2 - d'_3 - d'_4$ are:

$$\varepsilon_4(\omega)\vec{\Pi}'_4{}^\perp = \varepsilon_5\vec{\Pi}'_5{}^\perp \quad (3.60)$$

$$\frac{\partial \vec{\Pi}'_4{}^\perp}{\partial z} = \frac{\partial \vec{\Pi}'_5{}^\perp}{\partial z} \quad (3.61)$$

The terms $f'_{1-8}{}^\perp$ are calculated by fitting appropriate boundary conditions (equations 3.54 to 3.61) in the Hertz vector equations at each region (equations 3.49 to 3.53) as follows:

$$f_1'^\perp = - \left(\begin{array}{l} R^\parallel_1 e^{l_2 \hat{d}'_2} \left[\begin{array}{l} e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R^\parallel_3 R^\parallel_4 e^{-l_4 \hat{d}'_4}) \\ + R^\parallel_2 e^{-l_3 \hat{d}'_3} (R^\parallel_3 e^{l_4 \hat{d}'_4} + R^\parallel_4 e^{-l_4 \hat{d}'_4}) \end{array} \right] \\ + e^{-l_2 \hat{d}'_2} \left[\begin{array}{l} R^\parallel_2 e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R^\parallel_3 R^\parallel_4 e^{-l_4 \hat{d}'_4}) \\ + e^{-l_3 \hat{d}'_3} (R^\parallel_3 e^{l_4 \hat{d}'_4} + R^\parallel_4 e^{-l_4 \hat{d}'_4}) \end{array} \right] \end{array} \right) e^{-l_1 \hat{d}'_1} \quad (3.62)$$

$$f_2'^\perp = \frac{2 \varepsilon_1 l_1}{\alpha_1} \times$$

$$\left(\begin{array}{l} \left[\begin{array}{l} e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R^\parallel_3 R^\parallel_4 e^{-l_4 \hat{d}'_4}) \\ + R^\parallel_2 e^{-l_3 \hat{d}'_3} (R^\parallel_3 e^{l_4 \hat{d}'_4} + R^\parallel_4 e^{-l_4 \hat{d}'_4}) \end{array} \right] e^{-l_1 \hat{d}'_1} e^{l_2 \hat{d}'_2} \\ \frac{e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R^\parallel_3 R^\parallel_4 e^{-l_4 \hat{d}'_4})}{e^{l_2 \hat{d}'_2} \left[\begin{array}{l} + R^\parallel_2 e^{-l_3 \hat{d}'_3} (R^\parallel_3 e^{l_4 \hat{d}'_4} + R^\parallel_4 e^{-l_4 \hat{d}'_4}) \end{array} \right]} \\ + R^\parallel_1 e^{-l_2 \hat{d}'_2} \left[\begin{array}{l} R^\parallel_2 e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R^\parallel_3 R^\parallel_4 e^{-l_4 \hat{d}'_4}) \\ + e^{-l_3 \hat{d}'_3} (R^\parallel_3 e^{l_4 \hat{d}'_4} + R^\parallel_4 e^{-l_4 \hat{d}'_4}) \end{array} \right] \end{array} \right) \quad (3.63)$$

$$f_3'^{\perp} = -\frac{2 \varepsilon_1 l_1}{\alpha_1} \times \left(\frac{\left[R_{\parallel 2}^{\parallel} e^{l_3 \hat{d}_3'} (e^{l_4 \hat{d}_4'} + R_{\parallel 3}^{\parallel} R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'}) \right] \times [e^{-l_1 \hat{d}_1'} e^{-l_2 \hat{d}_2'}]}{e^{l_2 \hat{d}_2'} \left[\frac{e^{l_3 \hat{d}_3'} (e^{l_4 \hat{d}_4'} + R_{\parallel 3}^{\parallel} R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'})}{+ R_{\parallel 2}^{\parallel} e^{-l_3 \hat{d}_3'} (R_{\parallel 3}^{\parallel} e^{l_4 \hat{d}_4'} + R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'})} \right]} + R_{\parallel 1}^{\parallel} e^{-l_2 \hat{d}_2'} \left[\frac{R_{\parallel 2}^{\parallel} e^{l_3 \hat{d}_3'} (e^{l_4 \hat{d}_4'} + R_{\parallel 3}^{\parallel} R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'})}{+ e^{-l_3 \hat{d}_3'} (R_{\parallel 3}^{\parallel} e^{l_4 \hat{d}_4'} + R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'})} \right]} \right) \quad (3.64)$$

$$f_4'^{\perp} = \frac{4 \varepsilon_1 \varepsilon_2(\omega) l_1 l_2}{\alpha_1 \alpha_2} \times \left(\frac{\left[\frac{[e^{l_4 \hat{d}_4'} + R_{\parallel 3}^{\parallel} R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'}] \times [e^{-l_1 \hat{d}_1'} e^{l_3 \hat{d}_2'} e^{l_3 \hat{d}_3'}]}{e^{l_2 \hat{d}_2'} \left[\frac{e^{l_3 \hat{d}_3'} (e^{l_4 \hat{d}_4'} + R_{\parallel 3}^{\parallel} R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'})}{+ R_{\parallel 2}^{\parallel} e^{-l_3 \hat{d}_3'} (R_{\parallel 3}^{\parallel} e^{l_4 \hat{d}_4'} + R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'})} \right]} + R_{\parallel 1}^{\parallel} e^{-l_2 \hat{d}_2'} \left[\frac{R_{\parallel 2}^{\parallel} e^{l_3 \hat{d}_3'} (e^{l_4 \hat{d}_4'} + R_{\parallel 3}^{\parallel} R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'})}{+ e^{-l_3 \hat{d}_3'} (R_{\parallel 3}^{\parallel} e^{l_4 \hat{d}_4'} + R_{\parallel 4}^{\parallel} e^{-l_4 \hat{d}_4'})} \right]} \right]} \right) \quad (3.65)$$

$$f_5'^{\perp} = -\frac{4 \varepsilon_1 \varepsilon_2(\omega) l_1 l_2}{\alpha_1 \alpha_2} \times \quad (3.66)$$

$$\begin{aligned}
 & \left(\frac{[R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}] \times [e^{-l_1 \hat{d}'_1} e^{-l_3 \hat{d}'_2} e^{-l_3 \hat{d}'_3}]}{e^{l_2 \hat{d}'_2} \left[\begin{aligned} & e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R_{\parallel 3} R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \\ & + R_{\parallel 2} e^{-l_3 \hat{d}'_3} (R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \end{aligned} \right]} \right. \\
 & \left. + R_{\parallel 1} e^{-l_2 \hat{d}'_2} \left[\begin{aligned} & R_{\parallel 2} e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R_{\parallel 3} R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \\ & + e^{-l_3 \hat{d}'_3} (R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \end{aligned} \right] \right) \\
 & f_6'^{\perp} = \frac{8 \varepsilon_1 \varepsilon_2(\omega) \varepsilon_3 l_1 l_2 l_3}{\alpha_1 \alpha_2 \alpha_3} \times \\
 & \left(\frac{[e^{-l_1 \hat{d}'_1} e^{l_4 \hat{d}'_2} e^{l_4 \hat{d}'_3} e^{l_4 \hat{d}'_4}]}{e^{l_2 \hat{d}'_2} \left[\begin{aligned} & e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R_{\parallel 3} R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \\ & + R_{\parallel 2} e^{-l_3 \hat{d}'_3} (R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \end{aligned} \right]} \right. \\
 & \left. + R_{\parallel 1} e^{-l_2 \hat{d}'_2} \left[\begin{aligned} & R_{\parallel 2} e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R_{\parallel 3} R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \\ & + e^{-l_3 \hat{d}'_3} (R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \end{aligned} \right] \right) \\
 & f_7'^{\perp} = -\frac{8 \varepsilon_1 \varepsilon_2(\omega) \varepsilon_3 l_1 l_2 l_3}{\alpha_1 \alpha_2 \alpha_3} \times
 \end{aligned} \tag{3.67}$$

$$\left(\frac{R_{\parallel 4} [e^{-l_1 \hat{d}'_1} e^{-l_4 \hat{d}'_2} e^{-l_4 \hat{d}'_3} e^{-l_4 \hat{d}'_4}]}{e^{l_2 \hat{d}'_2} \left[\begin{aligned} & e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R_{\parallel 3} R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \\ & + R_{\parallel 2} e^{-l_3 \hat{d}'_3} (R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \end{aligned} \right]} \right. \\
 & \left. + R_{\parallel 1} e^{-l_2 \hat{d}'_2} \left[\begin{aligned} & R_{\parallel 2} e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R_{\parallel 3} R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \\ & + e^{-l_3 \hat{d}'_3} (R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \end{aligned} \right] \right)
 \end{aligned} \tag{3.68}$$

$$f_8'^{\perp} = -\frac{16 \varepsilon_1 \varepsilon_2(\omega) \varepsilon_3 \varepsilon_4(\omega) l_1 l_2 l_3 l_4}{\alpha_1 \alpha_2 \alpha_3 \alpha_4} \times$$

$$\left(\frac{[e^{-l_1 \hat{d}'_1} e^{l_5 \hat{d}'_2} e^{l_5 \hat{d}'_3} e^{l_5 \hat{d}'_4}]}{e^{l_2 \hat{d}'_2} \left[\begin{aligned} &e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R_{\parallel 3} R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \\ &+ R_{\parallel 2} e^{-l_3 \hat{d}'_3} (R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \end{aligned} \right]} \right. \\ \left. + R_{\parallel 1} e^{-l_2 \hat{d}'_2} \left[\begin{aligned} &R_{\parallel 2} e^{l_3 \hat{d}'_3} (e^{l_4 \hat{d}'_4} + R_{\parallel 3} R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \\ &+ e^{-l_3 \hat{d}'_3} (R_{\parallel 3} e^{l_4 \hat{d}'_4} + R_{\parallel 4} e^{-l_4 \hat{d}'_4}) \end{aligned} \right] \right) \quad (3.69)$$

Noted that the term α_i and $R_{\parallel i}$ can be calculated from equations 3.17 and 3.18, respectively. Following the procedure explained at section 3.3.3, we are now able to define the radiative and nonradiative decay rates of an emitting dipole which is located in front of the metal-dielectric-metal nanostructure. After minor simplification the rates are obtained as follow:

$$\hat{b}_r'^{\perp} = \left(q - \frac{3}{2} q \right) \times$$

$$Im \left(\int_0^1 \frac{\left(\begin{aligned} &R_{\parallel 1} e^{l_2 \hat{d}'_2} \left[\begin{aligned} &e^{l_3 \hat{d}'_3} (1 - R_{\parallel 1}^2 e^{-2l_4 \hat{d}'_4}) \\ &- R_{\parallel 1}^2 e^{-l_3 \hat{d}'_3} (1 - e^{-2l_4 \hat{d}'_4}) \end{aligned} \right] \\ &+ e^{-l_2 \hat{d}'_2} \left[\begin{aligned} &R_{\parallel 2} e^{l_3 \hat{d}'_3} (1 - R_{\parallel 1}^2 e^{-2l_4 \hat{d}'_4}) \\ &+ R_{\parallel 1} e^{-l_3 \hat{d}'_3} (1 - e^{-2l_4 \hat{d}'_4}) \end{aligned} \right] \end{aligned} \right)}{e^{l_2 \hat{d}'_2} \left[\begin{aligned} &e^{l_3 \hat{d}'_3} (1 - R_{\parallel 1}^2 e^{-2l_4 \hat{d}'_4}) \\ &- R_{\parallel 1}^2 e^{-l_3 \hat{d}'_3} (1 - e^{-2l_4 \hat{d}'_4}) \end{aligned} \right]} \right. \\ \left. + R_{\parallel 1} e^{-l_2 \hat{d}'_2} \left[\begin{aligned} &R_{\parallel 2} e^{l_3 \hat{d}'_3} (1 - R_{\parallel 1}^2 e^{-2l_4 \hat{d}'_4}) \\ &+ R_{\parallel 1} e^{-l_3 \hat{d}'_3} (1 - e^{-2l_4 \hat{d}'_4}) \end{aligned} \right] \right) e^{-2l_1 \hat{d}'_1} \frac{u^3}{l_1} du \quad (3.70)$$

$$\hat{b}_{nr}^{\prime \perp} = \left(1 - q - \frac{3}{2}q\right) \times$$

$$Im \left(\int_1^\infty \frac{\begin{pmatrix} R_{\parallel 1} e^{l_2 \hat{d}_2'} \left[\begin{matrix} e^{l_3 \hat{d}_3'} (1 - R_{\parallel 1}^2 e^{-2l_4 \hat{d}_4'}) \\ - R_{\parallel 1}^2 e^{-l_3 \hat{d}_3'} (1 - e^{-2l_4 \hat{d}_4'}) \end{matrix} \right] \\ + e^{-l_2 \hat{d}_2'} \left[\begin{matrix} R_{\parallel 2} e^{l_3 \hat{d}_3'} (1 - R_{\parallel 1}^2 e^{-2l_4 \hat{d}_4'}) \\ + R_{\parallel 1} e^{-l_3 \hat{d}_3'} (1 - e^{-2l_4 \hat{d}_4'}) \end{matrix} \right] \end{pmatrix}}{\begin{pmatrix} e^{l_2 \hat{d}_2'} \left[\begin{matrix} e^{l_3 \hat{d}_3'} (1 - R_{\parallel 1}^2 e^{-2l_4 \hat{d}_4'}) \\ - R_{\parallel 1}^2 e^{-l_3 \hat{d}_3'} (1 - e^{-2l_4 \hat{d}_4'}) \end{matrix} \right] \\ + R_{\parallel 1} e^{-l_2 \hat{d}_2'} \left[\begin{matrix} R_{\parallel 2} e^{l_3 \hat{d}_3'} (1 - R_{\parallel 1}^2 e^{-2l_4 \hat{d}_4'}) \\ + R_{\parallel 1} e^{-l_3 \hat{d}_3'} (1 - e^{-2l_4 \hat{d}_4'}) \end{matrix} \right] \end{pmatrix}} e^{-2l_1 \hat{d}_1} \frac{u^3}{l_1} du \right) \quad (3.71)$$

3.5. Electric field map

In order to study the effect of each layer (metal/dielectric) on the electric field distribution of an oscillating dipole, we calculate the electric field at any desired point to evaluate the field map within the single metal film and stratified metal-dielectric-metal structures. As mentioned before, the electric field can be expressed as a function of Hertz vector, $\vec{E}_i = k_i^2 \vec{\Pi}_i + \nabla(\nabla \cdot \vec{\Pi}_i)$ for both the parallel and perpendicular dipoles. Since the procedure of solving this equation will be similar for all the layers in both configurations (single layer and stratified structure), we present the results only for the outermost layer in the single layer structure (region 3 in Figure 3.1 a). Therefore, the second term in electric field equation ($\nabla(\nabla \cdot \vec{\Pi}_i)$) for the perpendicular and parallel dipoles are

$$\nabla \cdot \vec{\Pi}_3^\perp = \frac{\mu_1 k_1^2}{4\pi\epsilon_1} \int_0^\infty l_3 f_4 e^{l_3 \hat{z}} J_0(u\hat{r}) \frac{u}{l_1} du \quad (3.72)$$

$$\begin{aligned} \nabla \left(\nabla \cdot \vec{\Pi}_3^\perp \right) &= \hat{e}_z \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty l_3^2 f_4 e^{l_3 \hat{z}} J_0(u\hat{r}) \frac{u}{l_1} du \\ &\quad - \hat{e}_x \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty l_3 f_4 e^{l_3 \hat{z}} J_1(u\hat{r}) \frac{u^2}{l_1} \frac{\hat{x}}{\hat{r}} du \\ &\quad - \hat{e}_y \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty l_3 f_4 e^{l_3 \hat{z}} J_1(u\hat{r}) \frac{u^2}{l_1} \frac{\hat{y}}{\hat{r}} du \end{aligned}$$

$$\nabla \cdot \vec{\Pi}_3^\parallel = \frac{\mu_1 k_1^2}{4\pi\epsilon_1} \int_0^\infty \left(-f_4^\parallel \frac{u^2}{l_1} + g_4^\parallel l_3 \right) e^{l_3 \hat{z}} \left(\frac{x}{r} \right) J_1(u\hat{r}) du \quad (3.73)$$

$$\begin{aligned} \nabla \left(\nabla \cdot \vec{\Pi}_3^\parallel \right) &= \hat{e}_z \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty J_1(u\hat{r}) \left(\frac{x}{r} \right) \left(-f_4^\parallel \frac{u^2 l_3}{l_1} + g_4^\parallel l_3^2 \right) e^{l_3 \hat{z}} du \\ &\quad + \hat{e}_x \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty \left[\left(\frac{J_0(u\hat{r}) - J_2(u\hat{r})}{2} \right) \left(\frac{x}{r} \right)^2 + \left(\frac{J_1(u\hat{r})}{u\hat{r}} \right) \left(\frac{y}{r} \right)^2 \right] \left(-f_4^\parallel \frac{u^3}{l_1} \right. \\ &\quad \left. + g_4^\parallel u l_3 \right) e^{l_3 \hat{z}} du \\ &\quad + \hat{e}_y \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty \left(\frac{xy}{r^2} \right) \left[\left(\frac{J_0(u\hat{r}) - J_2(u\hat{r})}{2} \right) + \left(\frac{J_1(u\hat{r})}{u\hat{r}} \right) \right] \left(-f_4^\parallel \frac{u^3}{l_1} \right. \\ &\quad \left. + g_4^\parallel u l_3 \right) e^{l_3 \hat{z}} du \end{aligned}$$

Therefore by substituting these equations in equation 3.1 the electric field for each dipole orientation is

$$\begin{aligned}
 \vec{E}_3^\perp = & \hat{e}_z \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty f_4 e^{l_3 \hat{z}} J_0(u\hat{r}) \frac{u^3}{l_1} du \\
 & - \hat{e}_x \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty l_3 f_4 e^{l_3 \hat{z}} J_1(u\hat{r}) \frac{u^2}{l_1} \frac{\hat{x}}{\hat{r}} du \\
 & - \hat{e}_y \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty l_3 f_4 e^{l_3 \hat{z}} J_1(u\hat{r}) \frac{u^2}{l_1} \frac{\hat{y}}{\hat{r}} du
 \end{aligned} \tag{3.74}$$

$$\begin{aligned}
 \vec{E}_3^\parallel = & \hat{e}_z \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty J_1(u\hat{r}) \left(\frac{x}{r} \right) \left(-f_4^\parallel \frac{u^2 l_3}{l_1} + g_4^\parallel u^2 \right) e^{l_3 \hat{z}} du \\
 & + \hat{e}_x \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty \left[J_0(u\hat{r}) \frac{\epsilon_3}{\epsilon_1} \frac{u}{l_1} f_4^\parallel \right. \\
 & \quad + \left[\left(\frac{J_0(u\hat{r}) - J_2(u\hat{r})}{2} \right) \left(\frac{x}{r} \right)^2 \right. \\
 & \quad \left. \left. + \left(\frac{J_1(u\hat{r})}{u\hat{r}} \right) \left(\frac{y}{r} \right)^2 \right] \left(-f_4^\parallel \frac{u^3}{l_1} + g_4^\parallel u l_3 \right) e^{l_3 \hat{z}} \right] du \\
 & + \hat{e}_y \frac{\mu_1 k_1^3}{4\pi\epsilon_1} \int_0^\infty \left(\frac{xy}{r^2} \right) \left[\left(\frac{J_0(u\hat{r}) - J_2(u\hat{r})}{2} \right) + \left(\frac{J_1(u\hat{r})}{u\hat{r}} \right) \right] \left(-f_4^\parallel \frac{u^3}{l_1} \right. \\
 & \quad \left. + g_4^\parallel u l_3 \right) e^{l_3 \hat{z}} du
 \end{aligned} \tag{3.75}$$

3.6. Results

Figures 3.2 to 3.5 show the calculated normalized lifetime results versus the oscillating dipole distance to the nearest metal-dielectric interface for the dipoles that are aligned parallel, perpendicular and isotropic to the metal surface. In Figures 3.2 and 3.3, the plasmonic structure is a single metal film with the different thickness of 10, 30,

50 and 70 nm while in Figures 3.4 and 3.5 the dipole is placed in front of the stratified metal-dielectric-metal structures where the two metal films and the dielectric layer are equally distributed in each stratified structures: $d'_2 = d'_3 = d'_4 = 10, 30, 50, 70$ nm. The metal film material is chosen silver in Figures 3.2 and 3.4 and gold in Figures 3.3 and 3.5. Noted that in all these figures the dipole emission wavelength is selected 520 nm. All the dielectric media materials are taken to be the same with the refractive index of $n_1 = n_3 = n_5 = 1.7$. From Figure 3.2 that presented the results for the single silver layer structure, the very first point to notice is that the modifications of the lifetime curve versus dipole distance for the metal film thickness of 30, 50 and 70 are undetectable. As a matter of fact, it has been observed that for the metal film with the thickness of greater than 35 nm, the difference of the lifetime versus dipole distance is negligible. It is worth mentioning that these results are compatible with the measured transmission data that shows less than 10% field transmission for the metal film with the thickness of greater than 35 nm [29]. Noted that in Figure 3.3 that showed the lifetime curves for the single gold film, the above conclusion can be drawn for the metal film with the thickness of greater than 50 nm. Moreover, the lifetime oscillations at the dipole distance greater than 100 nm, accounts for the dominant effect of radiative channels oscillations as a result of in-phase/off-phase resonance between the dipole electric field and the reflected field from the metal surface. If the reflected electric field from the metal interface is in phase with the dipole electric field, the normalized lifetime would be greater than unity otherwise it may be less than one and accordingly results in the lifetime oscillations around unity. However, the results for the stratified structures are needed to be interpreted differently. Although, the lifetime oscillations can be observed in the lifetime

curves versus dipole distance to the metal film, it happens at the dipole distance much closer to the metal surface compared to the single layer structures, which may indicate the ability of the stratified structures in the engineering of the radiative decay rates. More detailed discussions on the effect of the stratified structures on the nonradiative and radiative decay rates of the emitting dipole will be discussed in Chapters 5 and 6, respectively.

The electric field map for the single layer and the stratified structures are depicted in Figure 3.6. At this simulation the emitting dipole is placed at the separation of 5 nm from the nearest metal surface. The thickness of metal film in single layer structure and stratified metal-dielectric-metal layer in the layered configuration is 30 nm (starts at the position of $z=0$). Noted that in stratified structure the thickness of each of the metal films and the separation dielectric layer is 10 nm. The simulation was carried out for silver metal film (Figure 3.6 a) and gold (Figure 3.6 b) metal films at their corresponding resonance frequency. One can see that, in the stratified structure each of the metal-dielectric interfaces leads to the electric field enhancement and consequently the dipole induced electric field at any desired position is highly increased in stratified structure compared to the single configuration. More detailed discussion on electric field map will be given in Chapter 5.

Figure 3.2 | Normalized lifetime, single silver film structure. The normalized lifetime versus dipole distance to the metal surface for parallel (dashed line), perpendicular (solid line) and isotropic (dot line) dipole; the silver film thickness is (a) 10 nm, (b) 30 nm, (c) 50 nm and (d) 70 nm. The dipole emission wavelength is 520 nm.

Figure 3.3 | Normalized lifetime, single gold film structure. The normalized lifetime versus dipole distance to the metal surface for parallel (dashed line), perpendicular (solid line) and isotropic (dot line) dipole; the silver film thickness is (a) 10 nm, (b) 30 nm, (c) 50 nm and (d) 70 nm. The dipole emission wavelength is 520 nm.

Figure 3.4 | Normalized lifetime, stratified dielectric-gold film structure. The normalized lifetime versus dipole distance to the metal surface for parallel (dashed line), perpendicular (solid line) and isotropic (dot line) dipole; each silver film and dielectric layer thickness are equal to (a) 10 nm, (b) 30 nm, (c) 50 nm and (d) 70 nm. The dipole emission wavelength is 520 nm.

Figure 3.5 | Normalized lifetime, stratified dielectric-gold film structure. The normalized lifetime versus dipole distance to the metal surface for parallel (dashed line), perpendicular (solid line) and isotropic (dot line) dipole; each silver film and dielectric layer thickness are equal to (a) 10 nm, (b) 30 nm, (c) 50 nm and (d) 70 nm. The dipole emission wavelength is 520 nm.

Figure 3.6 | Electric field map. The simulated normalized electric field squared versus the z position along the single (dashed line) and stratified (solid line) structures, for (a) the silver and (b) gold metal film.

3.7. Summary

The modification of an excited molecule lifetime in a vicinity of the metallic nanostructures can be explained through different theoretical models. In these models, the reflection and absorption of the excited molecule electromagnetic field at the metallic interface would lead to the dipole lifetime alteration. Notably, the appropriate analytical model provides the chance to develop the physical insight into this problem. In this chapter, we describe a model based on the energy flux method to fully simulate the lifetime of the fluorescent near a metallic nanostructure and the electric field map. This model has the unique advantage of a separate calculation of the radiative and nonradiative components of an emitting dipole decay rates. The equations will be given for the parallel and perpendicular dipole orientations with respect to the single metal film surface and will be expanded for the stratified metal-dielectric-metal nanostructures. The electric field map simulation is also performed to study the effect of stratified structure on electric field enhancement at the region of interest.

Chapter 4

Theory of surface plasmon mediated energy transfer in planar nanostructures

In this chapter, we propose comprehensive theoretical models to describe the nonradiative energy transfer mechanism between the donor and the acceptor dipoles through planar metallic nanostructures. The coupling between surface plasmon modes and the donor dipole evanescent electric field leads to the field enhancement at the acceptor dipole position and accordingly modifies the energy transfer efficiency between donor and acceptor dipoles. Based on the study that has been done in Chapter 3, we exploit the radiative and nonradiative decay rate equations to illustrate the effect of metallic structure on donor and acceptor dipoles decay channels. Moreover, the electric field enhancement factor is defined to address the effect of surface plasmon coupling on the energy transfer rate. The overall nonradiative energy transfer process would be modeled using two different approaches, two-step, and single-step models.

4.1. Introduction

It is well known that the decay rate of an emitting molecule in vicinity of a metallic surface has been extremely modified due to a) dipole electric field coupling with the surface plasmon mode at the interface of metal-dielectric at short distances and b) the mirror like behaviour of a metal surface at the large distances which leads to the dipole lifetime oscillations. While the radiative decay channel is mostly affected by the recent behavior, the nonradiative decay rate is a dominant channel at the short distances (energy transfer zone). As been mentioned in Chapter 3, a distinct separation of radiative and nonradiative decay rates is provided in CPS model of an oscillating dipole near a metallic layer, in which an optimum metal film thickness is obtained for the maximum energy transfer (ET) rate from dipole to the metal film [11, 29].

In this chapter, we theoretically illustrate the nonradiative energy transfer (NRET) mechanism between donor and acceptor molecules through a planar metallic nanostructure. The modification of NERT rate between donor-acceptor pair in the presence of the plasmonic structure is investigated to allocate the effect of a plasmonic layer on the energy transfer rate compared to the reference configuration in the absence of any plasmonic nanostructures. In this study, the donor and the acceptor dipoles are considered to be placed on either side of the finite metal film. It is demonstrated that NRET arises from the coupling of the dipole evanescent electric field to the surface plasmon modes of the metal-dielectric interface. To the best of our knowledge, this near field coupling on either side of the metallic nanostructure gives rise to an efficient path for transferring energy from donor dipole to the acceptor dipole. In fact, the cross

coupling of surface plasmon modes plays a mediating role between donor and acceptor and overcomes the limitation of short-range FRET.

Here we numerically modeled the overall NRET process in planar nanostructures using two different approaches; single-step and two-step models. The framework of our models is based on the energy flux method developed by CPS (explained and expanded in Chapter 3) to conveniently derive the radiative and nonradiative decay rates of an oscillating molecule in a vicinity of the metallic structure. While in the two-step model we adopted the plasmon-enhanced NRET theory to describe the energy transfer (ET) mechanism in 2 consecutive processes, in the single-step model we simplified the formalism with the aid of defining the effective donor/acceptor concepts. Our results show an excellent agreement between the two proposed approaches and suggest that the nonradiative energy transfer rate can be enhanced in presence of the planar metallic nanostructures.

4.2. Model principles

The geometry of the problem is depicted in Figure 4.1. The donor dipole is placed at the distance d_1 from the metal surface and the acceptor dipole is located at the other side of the metal film with the separation of d_2 from the nearest metal surface. The metal film material is considered silver and gold. The radiative and nonradiative decay rates equations for both the donor and acceptor dipoles in front of a metal film are modeled based on the theoretical study explained in Chapter 3. Both the donor and acceptor are modeled as the point-like Hertzian dipole, and the surrounding media of the dipoles are considered isotropic and non-absorbing. The external excitation source has been

considered to excite the donor dipole which does not overlap with the absorption spectrum of the acceptor dipole.

Figure 4.1 | Schematics of planar plasmonic system. The geometry of the problem in which the donor and acceptor dipoles are placed on either side of the metal film. The donor dipole is assumed to be externally excited.

From the Förster theory of energy transfer in a donor-acceptor pair system, it is well understood that the lifetime of the donor dipole would be extremely modified due to the presence of the acceptor dipole. In fact, the acceptor dipole introduces a new decay channel (nonradiative channel) for the donor dipole that leads to the transferring energy from donor to the acceptor. Consequently, the donor photoluminescence emission/lifetime would be quenched/reduced in the presence of the acceptor dipole. However, in a planar metallic structure that the acceptor and donor dipoles are placed on either side of the optically thick metal film, it has been observed by many studies that the presence of the acceptor dipole does not modify the donor dipole photoluminescence emission/lifetime [20, 46, 53]. As a result, to the best of our knowledge, the surface

plasmon modes of metal surface act as a preliminary acceptor site to the donor dipole that accepts the donor excitons energy. Then, through the surface modes couplings along the metal film, the energy would be transferred to the acceptor dipole. In other words, the overall system can be assumed as two different subsystems: first, the donor dipole and the SP modes of the metallic structure and second, the coupled SP modes and the acceptor dipole. As a result, in order to explain NRET in planar structures through theoretical modeling, we should define the electric field enhancement factor to allocate the effect of SP modes coupling in NRET efficiency.

4.3. Electric field enhancement factor

From the discussion above, the cross coupling of the surface plasmon modes on each side of the metal film is essential to generate an efficient path for energy migration of donor dipole to the acceptor dipole. Through the classical electrodynamics model, it has been shown that the strength of the electric field induced by the donor exciton at the acceptor dipole, indicates the capability of the plasmonic nanostructure in energy transfer mechanism [22].

Therefore, the surface plasmon mediated nonradiative energy transfer mechanism can be explained by the electric field enhancement factor which is defined as the ratio of the donor-induced electric field at the acceptor dipole position in the presence and absence of a plasmonic nanostructure:

$$A_{SPET} = \frac{\gamma_{SP-NRET}}{\gamma_{NRET}} = \frac{|E_{A,W}(\omega_D)|^2}{|E_{A,W/O}(\omega_D)|^2} \quad (4.1)$$

$$\gamma_{SP-NRET} = A_{SPET} \times \gamma_{NRET}$$

where A_{SPET} is the electric field enhancement factor; $E_{A,W}$ and $E_{A,W/O}$ are the induced electric field at the acceptor position with and without the plasmonic nanostructure, respectively; ω_D is a dipole peak emission frequency; $\gamma_{SP-NRET}$ is the nonradiative energy transfer rate to the acceptor in the presence of the plasmonic structure; and γ_{NRET} is the nonradiative ET rate from the donor to the acceptor in absence of any plasmonic structure. The term γ_{NRET} is defined as

$$\gamma_{NRET} = \tau_D^{-1} \left(\frac{R_0}{r} \right)^6 \quad (4.2)$$

where τ_D is the donor dipole intrinsic lifetime, r is a separation between donor and acceptor in absence of the metallic structure and R_0 is the Förster radius,

$$R_0 = 0.02108 \left(\kappa^2 Q_D n^{-4} J \right)^{\frac{1}{6}} nm \quad (4.3)$$

where κ^2 is a donor dipole orientation factor; Q_D is the donor dipole intrinsic quantum yield; n is a refractive index of the medium where the NRET occurs, and J is the overlapping integral of donor emission and acceptor absorption spectra. The simulated electric field enhancement factor results versus donor dipole emission wavelength and the metal film thickness, for the dipole aligned perpendicular and parallel to the metal interface wherein the metal film material is chosen silver or gold are depicted in Figures 4.2. In this simulation, the donor and acceptor dipole are placed on opposite sides of the

metal film with the separation of 5 nm to the nearest metal interface ($d_1 = d_2 = 5 \text{ nm}$). The metal film thickness varies from 0 to 100 nm, and the dipole peak emission wavelength ranges from 300 to 800 nm. The simulation results for the perpendicular dipole are shown in Figures 4.2a and c while Figures 4.2b and d are corresponded to the parallel orientation of the donor dipole. In Figure 4.2a and b the metal film material is silver while in Figure 4.2c and d the dielectric function of gold is chosen for the metal film.

From Figure 4.2, the very first point to note is the strong dependency of the electric field enhancement factor on the metal film material. For the silver film structure, the maximum enhancement factor is obtained at the donor peak emission wavelength of 380 nm while 520 nm is the donor dipole emission wavelength where the enhancement factor has the maximum value in the gold film structure. Taking into account the electric field equations in Chapter 3 (equations 3.72 to 3.75), it can be clearly seen that the term $\varepsilon_i l_{i+1} + \varepsilon_{i+1} l_i$ in the denominator of the reflection coefficient R_i , is playing a leading role in electric field definition in the region of the interest. For instance, the induced electric field of the donor dipole at the region 3 wherein the acceptor dipole is located, and the calculation of the enhancement factor is also done for this region, the reflection coefficient, and consequently $\vec{E}$ would be the function of $\varepsilon_d l_m + \varepsilon_m(\omega_D) l_d$, where ε_d and $\varepsilon_m(\omega)$ are the dielectric function of the dielectric medium and metal film, respectively (ω_D is the donor dipole peak emission wavelength). As a result, the maximum enhancement factor would take place at the donor emission wavelength where the ε_d is equal to $\varepsilon_m(\omega_D)$ in opposite sign.

Figure 4.2 | Electric field enhancement factor. Simulation results of the enhancement factor versus donor dipole peak emission wavelength and metal film thickness, for perpendicular (a, c) and parallel (b, d) donor dipole orientations. The metal film is silver (a, b) and gold (c, d). The distance of both the donor dipole and acceptor dipole to the nearest metal film is 5 nm. Noted that the color bar is not scaled.

The other significant point to notice from Figure 4.2 is that these results suggest that by choosing the optimum metal film thickness one can get the maximum enhancement factor. To the best of our knowledge, the physical origins of these optimum thicknesses can be explained by the fact that a very thick metal film suffers from weak overlaps of surface plasmon modes at the interfaces due to the long distance between them, while in a very thin metal film the surface modes are not strong enough to efficiently enhance the induced electric fields at the acceptor position. This claim can be verified through an electric field distribution calculation across the layers in which the highest electric field enhancement at the metal-dielectric interfaces is obtained in the structure with an optimized metal film thickness that leads to the maximum enhancement factor at the acceptor position (Chapter 3, Figure 3.6). The numerical calculation suggests that if the metal film is too thin, the electric field at the metal-dielectric interfaces cannot be sufficiently enhanced and in the structure with a very thick metal film the interfaces are too far from each other to be able to considerably increase the electric field at the acceptor position.

4.4. Two-step model

As discussed before, the very important assumption to be considered in our proposed model is that the presence of the acceptor dipole does not modify the donor dipole decay rates. We should stress that the nature of this energy transfer mechanism is needed to be interpreted differently from radiation field coupling to the surface plasmon polaritons modes of the surface. Since the near field of an emitting dipole contains all the k vectors

(wave number vectors), it can be coupled to the surface modes, makes them oscillate and accordingly accept/absorb the dipole energy.

In this section, we propose a numerical treatment to calculate nonradiative energy transfer rate in planar nanostructures. The geometry of the problem is depicted in Figure 4.1. The donor dipole which has the higher energy level (compared to the acceptor dipole) is placed at a distance of d_1 from a metal surface. The incident excitation emission would be absorbed by a donor molecule and a resultant exciton will nonradiatively transfer the energy to the metal surface via surface energy transfer (SET) mechanism. This process arises from large spontaneous emission enhancement of a donor dipole in front of metallic surface, in which the virtual photons are absorbed by surface plasmon modes of the metal surface. We believe that unlike the plasmon-enhanced FRET mechanism in semiconductor- metal nanoparticles system, the possibility of direct FRET from donor to the acceptor in planar nanostructure is thin enough to disregard it, however the accuracy of this claim has been observed in several works [20, 46, 47, 60]. For this reason, at the first step of ET from donor dipole to the plasmonic layer, the presence of FRET between donor-acceptor dipoles has been considered impracticable and all the donor dipole decay channels modifications take place due to the solo effect of metallic surface plasmon modes.

These excited modes on either side of the metallic layer, cross coupled and provide the excitation source for the acceptor dipole. The energy relaxation of an acceptor dipole which is placed at the distance of d_2 from its nearest metal surface, is also been altered in presence of SPs modes; both the radiative and nonradiative decay rates of an acceptor dipole are prone to enhanced or suppressed at the acceptor emission frequency. It is

worth mentioning that, since the ET mechanism is a unidirectional process, the excitation of the SPs mode of metal surfaces at an acceptor emission frequency, would not lead to ET from acceptor to the donor dipole. As a result, the total decay rates of an emitting donor dipole as a result of the first step (NRET from donor to the SP modes of metal film) can be expressed as

$$\gamma_D = \gamma_{D,nr}^0 + \gamma_{D,nr}^{ET} + \gamma_{D,r}^0 + \gamma_{D,r}^{metal} \quad (4.4)$$

where $\gamma_{D,nr}^{ET}$ is nonradiative energy transfer rate from donor dipole to the surface modes of the metallic nanostructure, $\gamma_{D,r}^{metal}$ is modified radiative decay rate of a donor in front of plasmonic configuration and $\gamma_{D,nr}^0$ and $\gamma_{D,r}^0$ are the intrinsic nonradiative and radiative decay rates of a donor dipole, respectively. We should stress that the term $\gamma_{D,nr}^{ET}$ in donor dipole total decay rates equation, refers to the modification of the nonradiative decay rate of the emitting molecule in front of the metallic nanostructures that is discussed in chapter 3. Consequently, following the Chapter 3 equations we would be able to define the donor dipole radiative and nonradiative decay rates modifications due to the presence of the metallic structure.

The next step of the energy transfer mechanism would be the cross coupling of surface plasmon modes along the metal film (expressed through the enhancement factor) and transferring the excitation energy to the acceptor dipole. Therefore, the excited acceptor dipole would be decayed in vicinity of the metal film and both the radiative and nonradiative decay channel have been effected through the presence of the metal film:

$$\gamma_A = \gamma_{A,nr}^0 + \gamma_{A,nr}^{metal} + \gamma_{A,r}^0 + \gamma_{A,r}^{metal} \quad (4.5)$$

where $\gamma_{A,r}^{metal}$ and $\gamma_{A,nr}^{metal}$ are the modified radiative and nonradiative decay rates of an acceptor molecule in front of plasmonic configuration, respectively and $\gamma_{A,nr}^0$ and $\gamma_{A,r}^0$ are the intrinsic nonradiative and radiative decay rates of an acceptor dipole, respectively. Now we can express the donor (I_D) and acceptor (I_A) peak photoluminescence intensities through the rates modifications and the energy transfer equation by

$$I_D = \frac{\gamma_{D,r}(\omega_D)}{\gamma_D(\omega_D)} I_{Di} \quad (4.6)$$

$$I_A = \frac{\gamma_{A,r}(\omega_A)}{\gamma_A(\omega_A)} \left(I_{Ai} + I_{Di} \frac{\gamma_{SP-NRET}(\omega_D)}{\gamma_{D,nr}^{metal}(\omega_D)} \right) \quad (4.7)$$

where ω_D and ω_A are the donor and acceptor peak emission wavelength, respectively; I_{Di} and I_{Ai} are the donor and acceptor photoluminescence intensities as re result of the external source excitation, respectively. As can be seen in equations 4.6 and 4.7, the donor emission intensity is only the result of the external excitation source while the acceptor emission has been effected by both the external and NERT excitation sources.

4.5. Single-step model

In the single-step approach, we propose a model to describe the energy transfer mechanism in only one step. The schematic of the proposed model is depicted in Figure

4.3, where the definition of effective donor/acceptor is used to simplify the ET equations.

Figure 4.3 | Single-step model schematics. Two different approaches that has been applied in the single-step modeling, (a) effective donor and (b) effective acceptor.

As can be seen in Figure 4.3, the donor dipole plus the metal film has been united and considered as a single unit called the effective donor which is located at the distance d_2 from the acceptor dipole. As a result, the energy transfer problem is now a nonradiative energy migration from the effective donor to the acceptor dipole that can be expressed through Förster equation. Similarly, for the case of the effective acceptor system, the problem is simplified to the energy transfer from the donor dipole to the effective acceptor wherein the separation distance is d_1 . In the following, we give the

appropriate equations to illustrate the NRET mechanism in effective donor and effective acceptor approaches.

4.5.1. Effective donor approach

To describe the energy transfer mechanism for the effective donor approach via Förster equation, we should stress that since the effective donor is completely different from the donor dipole, then the quantum yield, the Förster radius and the total decay rate must be redefined for the new system. In equations 4.2 and 4.3 that are used to explain the two-step model, the values are given for an intrinsic quantum yield and decay rates. Now, the effective donor has 3 different decay channels: radiative, nonradiative and Förster ET decay rates:

$$\gamma_{D'} = \gamma_{D',nr} + \gamma_{D',r} + \gamma'_{NRET} \quad (4.8)$$

where D' is the notation of the effective donor, $\gamma_{D',nr}$ and $\gamma_{D',r}$ are the nonradiative and radiative decay rates of the effective donor, respectively and γ'_{NRET} is the energy transfer rate from effective donor to the acceptor dipole that is given by

$$\gamma'_{NRET} = A_{SPET} \tau_{D'}^{-1} \left(\frac{R'}{r'} \right)^6 \quad (4.9)$$

where A_{SPET} is the electric field enhancement factor, $\tau_{D'}$ is the effective donor lifetime, r' is the separation distance between effective donor and the acceptor dipole and R' is the Förster radius of the effective donor-acceptor dipole pair defined as

$$R' = 0.02108 \left(\kappa^2 Q_{D'} n^{-4} J \right)^{\frac{1}{6}} nm \quad (4.10)$$

where the effective donor quantum yield equals to

$$Q_{D'} = \frac{\gamma_{D',r}}{\gamma_{D',nr} + \gamma_{D',r} + \gamma'_{NRET}} \quad (4.11)$$

Moreover, from Figure 4.3 it can be seen that the separation distance between effective donor and an acceptor dipole is equal to d_2 . However, through the numerical simulation we have realized that the separation distance needs a correction factor to allocate the effect of imperfect dipole-like effective donor. Since, in the new system the effective donor is no longer a point-like dipole, therefore the separation distance should be modified. Our simulation shows that r' is also a function of a donor dipole distance to the metal surface

$$r' = d_2 + 0.8 d_1 \quad (4.12)$$

Eventually, the effective donor and acceptor dipole photoluminescence intensity can be respectively expressed as

$$I_{D'} = \frac{\gamma_{D',r}(\omega_{D'})}{\gamma_{D'}(\omega_{D'})} I_{D'i} \quad (4.13)$$

$$I_A = \frac{\gamma_{A,r}(\omega_A)}{\gamma_A(\omega_A)} \left(I_{Ai} + I_{D'i} \frac{\gamma'_{NRET}(\omega_{D'})}{\gamma_{D'}(\omega_{D'})} \right) \quad (4.14)$$

4.5.2. Effective acceptor approach

In order to illustrate the energy transfer mechanism for the effective acceptor approach in the single-step model, the decay rates of the donor dipole and the effective acceptor should be modified. The donor dipole would have 3 different decay channels: intrinsic radiative, intrinsic nonradiative and Förster ET decay rates (γ_{NRET}''):

$$\gamma_D = \gamma_{D,nr}^0 + \gamma_{D,r}^0 + \gamma_{NRET}'' \quad (4.15)$$

Similar to the case of the effective donor approach, the effective acceptor decay rates would be altered compared to the acceptor dipole and can be expressed as

$$\gamma_{A'} = \gamma_{A',nr} + \gamma_{A',r} \quad (4.16)$$

where A' is the notation for the effective acceptor $\gamma_{A',nr}$ and $\gamma_{A',r}$ are the nonradiative and radiative decay rates of the effective acceptor, respectively. The energy transfer rate from donor to the effective acceptor (γ_{NRET}'') is given by

$$\gamma_{NRET}'' = A_{SPET} \tau_D^{-1} \left(\frac{R}{r''} \right)^6 \quad (4.17)$$

where r'' is the separation distance between the donor dipole and the effective acceptor

$$r'' = d_1 + 0.8d_2 \quad (4.18)$$

Consequently, the donor dipole and the effective acceptor dipole photoluminescence intensity can be respectively expressed as

$$I_D = \frac{\gamma_{D,r}^0}{\gamma_{D,nr}^0 + \gamma_{D,r}^0 + \gamma_{NRET}''} I_{Di} \quad (4.19)$$

$$I_{A'} = \frac{\gamma_{A',r}(\omega_A)}{\gamma_{A'}(\omega_A)} \left(I_{A'i} + I_{Di} \frac{\gamma_{NRET}''(\omega_D)}{1 + \gamma_{NRET}''(\omega_D)} \right) \quad (4.20)$$

4.6. Results and discussion

The simulation results for the single-step model by two different approaches, effective donor and effective acceptor, are presented in Figure 4.4. In this simulation the (effective) donor photoluminescence intensity, the (effective) acceptor PL intensity, energy transfer rate and the ratio of the (effective) acceptor photoluminescence intensity to the (effective) donor photoluminescence intensity are plotted versus the metal film thickness. As can be seen in this figure, the PL intensities and the energy transfer rate are distinguishably different for the effective donor and effective acceptor approaches. These results are predictable and reasonable since the donor and the acceptor sites are totally different within the two approaches; in the effective donor approaches the donor site is a combination of the donor dipole and the metal film while in the effective acceptor approach the donor site is a single dipole. Similarly, the acceptor site in the effective acceptor approach is considered a dipole plus the metal film and in the effective donor approach the acceptor site is a solo dipole. Consequently, the nature of the donor and acceptor sites are different in the approaches that results in dissimilar results. However, the total energy transfer efficiency must stay constant and is independent of the approaches. As shown in Figure 4.4 d, the ratio of the (effective) acceptor emission

intensity to the (effective) donor emission intensity that accounts for the energy transfer efficiency, is indistinguishable and demonstrating the fact that both the approaches has been designed and calculated correctly.

Figure 4.4 | Effective donor/acceptor. The simulation results of the single-step model by effective donor (solid line) and effective acceptor (dashed line) approaches. (a) The (effective) acceptor calculated photo emission, (b) (effective) donor photoluminescence, (c) simulated energy transfer rate from the effective donor to the accept (donor to the effective acceptor) and the ratio between the photoluminescence of the effective acceptor and the donor dipole (acceptor dipole and effective donor).

Now we discuss the simulated results obtained via single-step and two-step models. The calculated energy transfer results versus donor dipole emission wavelength are

presented in Figure 4.5. In this simulation the donor and acceptor dipoles are placed on opposite side of a 30 nm-metal film wherein the dipoles distance to the nearest metal film are chosen 2 nm. The metal layer is either silver or gold film. The energy transfer rate is calculated by the single step model (red) and two-step model (black) and also for the case that the donor and acceptor are placed in dielectric medium in absence of any metallic nanostructure (green line).

Noted that since in both the effective donor approach of single step model and the two-step model, the energy transfer rate has been calculated for the acceptor dipole, therefore the presented results arrowed to the single-step model in Figure 4.5 are obtained using effective donor approach. The first point to notice from this figure is that as been expected from Chapter 3, the maximum energy transfer rate for the silver and gold film is obtained at the different emission frequency. Moreover, for most of the donor emission frequencies, the energy transfer rate has been significantly increased in presence of the metal film compared the reference configuration (in absence of the metal film) and more importantly, the calculated results that are obtained from single-step model and two-step model are in a very good agreement. Furthermore, in order to study the effect of metal film on the consistency of the models, we have computed the energy transfer rate and efficiency for the structures wherein the metal film thickness varies from 2 nm to 100 nm (Figure 4.6). As can be seen in this figure the very good agreement between the two different models has been obtained for different metal film thickness.

Figure 4.5 | Simulated energy transfer rate. Calculated energy transfer rate versus donor dipole emission wavelength for the structure that the donor and acceptor dipoles are located on either side of a 30 nm-thick metal film with the distance of 2 nm to the nearest metal surface, using two-step model (black) and single-step model (red). The reference structure is also considered (green) wherein the energy transfer rate is calculated in absence of the metal film. The metal film is (a) gold or (b) silver.

Figure 4.6 | Simulated energy transfer rate and efficiency. Calculated (a) energy transfer rate and (b) energy transfer efficiency versus silver film thickness for the structure that the donor and acceptor dipoles are located on either side of a metal film that its thickness varies from 2 to 100 nm. The distance of the dipoles to the nearest metal surface is selected 2 nm, the donor and acceptor dipoles peak emission wavelength are 520 and 600 nm, respectively. The reference structure is also considered (green) wherein the energy transfer rate is calculated in absence of the metal film.

4.7. Summary

In this chapter, we presented the theoretical models to illustrate the nonradiative energy transfer mechanism between the donor and the acceptor dipoles that are located on either sides of the metal film. Two different models were proposed: single-step and two step model, wherein the single-step model was demonstrated through two different approaches: effective donor and effective acceptor. The simulation results confirmed a very good agreement between the models and predicted the enhanced energy transfer efficiency in presences of the metal film nanostructures.

Chapter 5

Cascaded plasmon-plasmon coupling mediated energy transfer across stratified metal-dielectric nanostructures

In this chapter, we propose and demonstrate the nonradiative energy transfer mechanism between the donor and the acceptor multilayers through layered metallic nanostructures, in which the stratified configuration gives rise to an efficient energy transfer process. This novel approach in NRET, uniquely provides us with the ability to overcome the drawback of high energy absorption losses in a thick metal film by inserting a non-absorbing dielectric layer between two thin metal films. Moreover, a strong plasmon-plasmon near-field coupling through the dielectric spacer layer is proven to highly extend the effective ET distance/efficiency. Alternatively, placing dielectric and metal layers instead of a single thick metal film allows for the SP modes to overlap efficiently through layered configurations. The proposed architecture leads to a remarkable energy transfer efficiency as a result of stronger surface plasmon coupling at the metal-dielectric boundaries.

5.1. Introduction

Energy transfer (ET) from an excited donor dipole to an acceptor may occur either radiatively or nonradiatively. Radiative transfer corresponds to emission and absorption of photons, in which the average distance between the donor and the acceptor should be larger than the donor photoemission wavelength, while nonradiative energy transfer (NRET) needs a distance much shorter than the photoemission wavelength (for dipole-dipole interaction in the range of 1-10 nm) and arises without emission of “real” photons [11, 30, 36, 45, 50, 51, 61, 62]. However, utilizing the NRET mechanism within the moderate separation distance (> 10 nm) between the donors and the acceptors lacks the desired efficiency. Instead, surface plasmon mediated nonradiative energy transfer (SP-NRET) has been demonstrated to increase the NRET efficiency beyond the Förster radius limit.

SP-NRET results from the strong near-field coupling of dipole moment with the surface plasmon modes of the metallic-dielectric interface, which considerably modifies the energy transfer efficiency. SP-NRET offers great potential in numerous applications such as biosensing, light harvesting and light generation [6, 28, 63-65]. In particular, emission enhancement of molecular fluorescence near metallic nanostructures and increased energy transfer through the plasmonic nanostructures have been widely exploited [50, 51, 62, 65]. Furthermore, localized surface plasmon mediated NRET through metal nanoparticles has been demonstrated to effectively increase the Förster radius; and emission enhancement has been obtained in a precisely-designed emitting structure [50].

Since the very first study on SP-NRET through optically thick/lossy metal films [20], several applicable systems have been verified to enhance the efficiency of the process and extend the effective ET range [13, 23, 51, 61]. Despite the fact that SP improves the ET range up to 150 nm through a silver film [46], the mechanism suffers from the significant energy loss due to the absorption by thick metal film.

5.2. Surface plasmon nonradiative energy transfer in plasmonic nanostructures

The mechanism of SP-NRET goes beyond the conventional Förster resonant energy transfer process since the direct interaction of the donor and the acceptor dipoles moments is not effective in SP-NRET. As a matter of fact, the evanescent electric fields coupling of the donor/acceptor excitons to the surface plasmon modes of the metal films plays a crucial role in energy migration. [10-12, 24].

It was well demonstrated in literature that the key factor in designing the structures benefiting an efficient SP-NRET, is to distinguish the difference between the direct quenching/enhancing effect of a plasmonic nanostructure on the donor/acceptor emission and the improved efficiency due to SP-NRET [28, 32, 49, 51]. Therefore, a perceptive understanding of the overall processes is essential to realize an efficient SP-NRET in nanostructures.

Figure 5.1 | Single layer and stratified nanostructures. Architectures of the single layer (a) and stratified (b) plasmonic nanostructures. The donor dipole is placed at one side of the plasmonic layer (single metal film or stratified metal-dielectric layers) and the acceptor dipole is at the opposite side. The surrounding media are isotropic and non-absorbing.

This study aims to apply a stratified structure of metal-dielectric-metal instead of a single metal film to benefit from not only stronger stratified evanescent SP coupling but also the reduction of energy absorption losses. In this chapter, the stratified SP coupling refers to the cross-coupling of an excited SP modes at each of the metal-dielectric interfaces. This electromagnetic coupling arises from an interaction of an excited oscillating dipole moment with the surface modes of metal film. Since the evanescent electric field emission of a dipole acts as an excitation source to derive the surface plasmon modes at the interfaces, the theoretical simulation of electric field enhancement across all layers, presents the capability of the structure to enhance/suppress the SP couplings [10, 22, 23, 32]. The geometry for the single metal film and the stratified structures is depicted in Figure 5.1a and 5.1b, respectively. The donor and the acceptor

dipoles are placed on either side of the metal film in the single layer structure and the stratified layer configuration (metal-dielectric-metal).

The first step of SP-NRET process can be explained through the Sommerfeld's theory of an excited oscillating dipole near an absorbing medium [52]. The excitation of a donor dipole leads to the near-field electromagnetic emission [2, 55, 66] of a dipole moment in which the short range dipole electric field is coupled to the surface modes of the metallic film and the energy of an excited donor dipole is nonradiatively transferred to surface plasmon modes of the metal film [11, 29, 53]. The second step of SP-NRET needs to be describe separately for the single layer and stratified configurations. In the case of single layer structure, the SP modes at the interfaces of each side of the metal film are cross-coupled and the energy is transported to an acceptor dipole.

On the other hand, in stratified structure, the cross-coupling takes place across the SP modes of metal-dielectric and dielectric metal interfaces. We should point out that, while the evanescent interaction of an oscillating dipole with SP modes of the metallic film comprises all the Fourier components, the dipole near-field should be treated differently in comparison with the radiation field (More information is discussed in Chapter 3). Moreover, the exponential dependency of the energy flux on the skin depth in the case of radiation field cannot be applied for the near-field coupling [29]. As a matter of fact, the enhanced electric field at the metal-dielectric interfaces reflects the ability of the plasmonic nanostructure in mediating energy transfer from the donor to the acceptor dipoles (Figure 5.2). The plasmon-mediated nonradiative ET rate is obtained by the classical electrodynamics model [22] expressing the enhancement factor as the ratio of

an induced electric field at the acceptor dipole position in the presence and absence of a plasmonic nanostructure:

$$A_{SPET} = \frac{\gamma_{SP-NRET}}{\gamma_{NRET}} = \frac{|E_{A,W}(\omega_D)|^2}{|E_{A,W/O}(\omega_D)|^2} \quad (5.1)$$

where A_{SPET} is the plasmonic enhancement factor; $E_{A,W}$ and $E_{A,W/O}$ are the induced electric field at the acceptor position with and without the plasmonic nanostructure, respectively; $\gamma_{SP-NRET}$ is the nonradiative ET rate to the acceptor in the presence of the plasmonic structure; and γ_{NRET} is the nonradiative ET rate from the donor to the acceptor.

Figure 5.3 depicts the calculated enhancement factor versus single metal film/stratified metal-dielectric thickness and wavelength for the perpendicular (Figure 5.3 a, c) and the parallel (Figure 5.3 b, d) dipoles (colour map plots). The thickness of single metal film (d_m) in the single layer structure and the metal-dielectric-metal layer thickness ($2d'_m + d'_s$) in stratified configuration, varies from 0 to 100 nm. The distance of the donor and the acceptor dipoles to the nearest metal surface; d_1 and d_2 (Figure 5.1 a, b) are 10 nm.

Figure 5.2 | Electric field distribution. Electric field distribution at the plasmonic resonance wavelength of 380 nm through each layer in stratified (green dotted line) and single layer (red dashed line) structures, and the structure without plasmonic layer (blue solid line) for perpendicular dipole with respect to the surface of the metal layer. The donor dipole is placed in front of the plasmonic layer with the distance of d_1 .

In this simulation the thickness of two metal films (d'_m) and the spacer layer (d'_s) are equally distributed in the stratified configuration, since it has been demonstrated by numerical simulations that this choice results in the maximum enhancement factor (Figure 5.4). The permittivity of the silver metal films was taken from Johnson and Christy [59] dielectric function. In order to fulfil the resonance matching condition in all the metal–dielectric interfaces, the same/similar refractive index of $n=1.7$ was chosen for dielectric layers (the donor, the acceptor and the spacer layers). Noted that the resonance matching condition arises from the most efficient cross-coupling of SP modes

at each interfaces that leads to the highest enhancement factor and can be expressed as a function of the metal and the dielectric layers refractive indexes [10, 11, 28, 29] .

As can be seen in Figure 5.3, the resonance matching condition for perpendicular/parallel dipole orientations and stratified/single layer structures occurs at the wavelength of 380 nm at which the real part of the silver dielectric function equals to the spacer dielectric constant in opposite sign. The maximum enhancement factor in the single layer structure occurs at the silver film thickness of 28 and 22 nm for perpendicular and parallel dipoles, respectively, indicating the optimum silver thickness for the strongest SP cross-coupling (Figure 5.3 a, b). On the other hand, the stratified layer thickness of 61 and 50 nm (including the two metal films and the dielectric film) corresponds to the highest enhancement factor in the stratified configuration for perpendicular and parallel dipoles (Figure 5.3 c, d).

To the best of our knowledge, the physical origins of these optimum thicknesses can be explained through the fact that a very thick metal film suffers from weak overlaps of SP modes at the interfaces due to the long distance between them, while in a very thin metal film the SP modes are not strong enough to efficiently enhance the induced electric fields at the acceptor position through the interfaces. This claim can be verified through an electric field distribution calculation across the layers in which the highest enhancement factor at the metal-dielectric interfaces has been obtained in the structure with an optimized metal film thickness that leads to the maximum enhancement factor at the acceptor position (Figure 5.5).

Figure 5.3 | Enhancement factor. Calculated electric field enhancement factor at the acceptor dipole position as the functions of plasmonic layer thickness and excitation wavelength for simple (c, d) and stratified (e, f) nanostructures. The dipole moment is oriented perpendicular (c, e) and parallel (d, f) with respect to the plasmonic layer surface. The donor/acceptor dipole distance to the nearest plasmonic layer surface is 10 nm and the equation $\mathbf{d}_m = 2 \mathbf{d}'_m + \mathbf{d}'_s$ is applied for the single layer and stratified configurations.

Figure 5.4 | Enhancement factor versus spacer layer thickness. The enhancement factor contour at the acceptor position for three stratified plasmonic layers (a-c) and the single metal film configuration (d), with plasmonic layer/metal film thickness and the excitation wavelength as variables. The plasmonic layer/metal film thickness varies from 0 to 100 nm for stratified and single metal layer structures, and the donor and acceptor dipole distance to the nearest metal film is selected as 5 nm. The donor dipole is perpendicular with respect to the plasmonic layer surface. The thickness of metal nano-films (d'_m) and the spacer layer (d'_s) is as shown: (a) $d'_m = d'_s$, (b) $d'_m = 2d'_s$ and (c) $d'_m = 0.5d'_s$ for the three stratified samples. As can be seen the maximum enhancement factor is obtained in the stratified structure with the distribution of $d'_m = d'_s$.

Figure 5.5 | Electric field distribution for an optimized metal film thickness. Electric field distribution at the plasmonic resonance wavelength of 380 nm through each layer in the single layer (red dashed line) structures, and the structure without plasmonic layer (blue solid line) for perpendicular dipole with respect to the surface of the metal layer. The donor dipole is placed in

front of the plasmonic layer at the distance of 10 nm. The Electric field enhancement with respect to the dipole emission at the metal-dielectric interfaces were shown on the dashed circles for the single layer structure with the silver film thickness of 5 (a), 20 (b) and 50 (c) nm. Donor dipole is placed at the position of 10 nm and the acceptor dipole distance to the nearest metal interface is 10 nm.

Figure 5.6 | Enhancement factor versus donor dipole distance. The enhancement factor contour simulated analytically for the stratified (a) and the single layer (b) nanostructures versus plasmonic layer/metal film thickness and the donor dipole distance to the nearest metal film surface (d_1), at the acceptor position ($d_2 = 5$ nm). The results demonstrate that the increased enhancement factor in the stratified structure compared to the single layer configuration is independent on d_1 . The plasmonic wavelength of 380 nm is chosen for the excitation wavelength and the equal distribution of metal-spacer layers are taken for the stratified nanostructure.

The numerical calculation suggests that if the metal film is too thin, the electric field at the metal-dielectric interfaces cannot be sufficiently enhanced and in the structure with a very thick metal film the interfaces are too far from each other to be able to considerably increase the electric field at the acceptor dipole position. Regardless of the dipole orientation, the maximum enhancement factor is increased up to 3 fold in the stratified configuration compared to the single metal layer structure. Thus, the stratified structure induces higher electric field at the acceptor dipole giving rise to higher SP-NRET efficiency. It is worth mentioning that different choices of d_1 and d_2 (Figure 5.1) lead to the same conclusion that plasmonic effect is enhanced in the stratified configuration (Figure 5.6).

In addition to the fact that the enhancement factor simulation predicts the higher SP coupling in the plasmon-plasmon stratified nanostructure, the nonradiative and radiative decay rates of the donor/acceptor dipoles were taken into account for modelling the overall SP-NRET mechanism in our simulation (Figure 5.7). The plasmonic layer thickness varies from 0 to 100 nm and the donor dipole distance to the nearest metal surface (d_1) is selected as 10 nm.). As can be seen in Figure 5.7, regardless of the comparison method of the plasmonic layer thickness in the single layer and the stratified structure, the donor dipole in stratified plasmonic configuration shows a higher nonradiative decay rate.

Figure 5.7 | Normalized nonradiative rate. The simulation of the normalized nonradiative decay rate (with respect to an intrinsic nonradiative decay rate) for perpendicular (blue line) and parallel (red line) donor dipoles in single layer (dashed line) and stratified (solid line) nanostructures when (a) the metal thickness in the single layer structure is equal to the total metal thickness in stratified structure ($d_m = 2d'_m$) and (b) the metal thickness in the single metal layer structure is equal to the plasmonic layer thickness in stratified structure ($d_m = 2d'_m + d'_s$).

5.3. Experimental develops

5.3.1. Device geometry

The single metal layer and the stratified samples consisting of the donor, the plasmonic nanostructure, and the acceptor layers are fabricated on quartz slides. The thickness of the donor and the acceptor layers are 15 nm for all the sample geometries. The plasmonic nanostructure consists of either a single evaporated silver thin film or stratified layers of silver films and a dielectric layer. The silver films are deposited using thermal evaporation system with a minimum thickness of 20 nm to form homogeneous layers rather than formation of nano-islands [29]. A quenching control layer was deposited between the donor/acceptor and the nearest metal film to maximize the ET rate as the interaction of the oscillating dipole electric field with the SP modes of the metal, highly depends on the dipole distance to the metal surface [61, 62, 67].

The key factor in an efficient nonradiative energy transfer is that the emission spectra of the donor should overlap the absorption spectra of the acceptor, hence several combinations of dyes have been studied in literature [19-21, 46]; the pair of Alq3, Tris (8-hydroxyquinolinato) aluminium and R6G, Rhodamine 6G is one the most efficient pair for our purpose.

The absorption and emission spectra for the donor, the acceptor, and the spacer layers are depicted in Figure 5.8. Alq3 was used as the donor with the emission peak at 525 nm which overlaps with the absorption peak of R6G as the acceptor. TcTa, Tris (4-carbazoyl-9-ylphenyl) amine, was used as the spacer layer between the two silver films and the quenching control layer between the donor/acceptor and the silver film.

Consequently, the structures for the stratified (Figure 5.8 c) and the single metal layer (Figure 5.8 b) samples are:

- *Stratified: Quartz substrate / Alq3 (15nm) / TcTa (nm) / Ag (nm) / TcTa (nm) / R6G (15nm)*
- *Single layer: Quartz substrate/ Alq3 (15nm) / Ag (nm) / R6G (15nm)*

Their respective control samples (Figure 5.8 d, e) have been obtained by replacing the donor layer (Alq3) with spacer layer (TcTa):

- *Stratified control sample: Quartz substrate / TcTa (15nm) / TcTa (nm) / Ag (nm) / TcTa (nm) / R6G (15nm)*
- *Single layer control sample: Quartz substrate/ TcTa (15nm) / Ag (nm) / R6G (15nm)*

Figure 5.8 | Emission/Absorption spectrum. Absorption (dashed line) and photoluminescence (solid line) spectra for the donor (a): Alq₃ (green), the spacer: TcTa (blue), and the acceptor: R6G (red). The vertical arrow indicates excitation laser wavelength for PL measurements. The single layer (b) and stratified structures (c), and their respective control samples (d, e).

5.3.2. Sample fabrication and measurement setups

The quartz substrates were cleaned using an ultrasonic bath with detergent, deionized water, acetone and isopropyl alcohol sequentially for 20 min and then dried by Nitrogen gas. The silver films and organic nanolayers were deposited using thermal evaporation system under the pressure of 4×10^{-4} Pa. The silver deposition rate was controlled ($0.1 \text{ \AA}/\text{s}$) to gain smooth surface and prevent an unwanted roughness. Similarly, all the organic layers, Alq3, TcTa, and R6G were thermally evaporated with a rate of $0.5 \text{ \AA}/\text{s}$. The substrates were quartz slides.

The linear steady state photoluminescence spectra of the samples were recorded using Shamrock SR-303i spectrograph that is integrated with Andor's CCD camera spectroscopy detector systems. The excitation source was a diode laser with a wavelength of 405 nm. The excitation was applied from the donor side and the PL intensities were collected from the acceptor side in all the samples (Figure 5.9 a).

The fluorescence lifetime measurements were carried out using a time correlated single photon counting system with an excitation laser at 375 nm. The band pass filter with a full width at half-maximum of 50 nm and central wavelength of 520 nm is used to record the decay rates of the samples at the donor emission. The time-resolved emission data were fitted with two-exponential approximation by Fluo-fit decay analysis software (Pico Quant Technologies, Germany). In the time-resolved system the pulse duration is 40 to 90 ps, repetition rate is 20 MHz, the CW- equivalent power is 0.3-2.5 mW and the collection N.A is 0.75 (Figure 5.9 b).

Figure 5.9 | Optical setups for photoluminescent and time-resolved fluorescence measurements. The schematic illustration of PL intensity measurements setup (a) and time-resolved fluorescence system (b). In the PL measurement system, the samples are excited by 405 nm laser from a donor side and the resultant intensities are collected from the acceptor side. The UV filter in both systems is used to bypass collection of excitation source from the substrate

5.4. Photoluminescence and time resolved characterizations

Room-temperature steady-state photoluminescence (PL) spectra for the single layer, the stratified and the control samples with the plasmonic layer thickness of 60 and 90 nm ($d_m = 2 d'_m + d'_s = 60$ and 90 nm), are shown in Figure 5.10. Noted that for all the samples, a 405 nm excitation laser source was applied from the donor site (spacer site in control samples) and the PL intensities were collected from the acceptor side. From the control samples PL spectra (red line), it can be verified that the direct excitation of the acceptor with the laser source has a negligible effect on the acceptor excitation since the acceptor PL intensities with the peak emission wavelength of 585 nm are distinctly small compared to acceptor emission in corresponding single layer and stratified samples (blue line in Fig. 5.10).

As a matter of fact, the significant presence of the acceptor emission in the donor-single layer-acceptor and the donor-stratified layers-acceptor samples is the direct effect of SP-NRET from the donor to the acceptor site, demonstrating the role of the plasmonic structure as the energy mediator.

In other words, from the two sources of excitation that are available for the acceptor layer; the external laser source and the SP-NRET from donor layer, the latter one has the major contribution in the acceptor excitation. Furthermore, it can be clearly seen from Figure 5.10 that the acceptor emission is significantly increased in the stratified structures compared to the corresponding single layer samples.

Figure 5.10 | PL intensity. PL intensity from the stratified (a, c) and single layer (b, d) structures for single /stratified layer-acceptor (red) and donor-single/stratified layer-acceptor (blue) samples. In the single layer structure the thickness of silver film and in the stratified samples the metal-spacer-metal thickness is 60 (c, d) and 90 nm (a, b). The excitation source is 405 nm. The stratified samples show the higher SP-NRET efficiency and absolute photoemission compared to the single layer structures.

The ratio of the acceptor emission in the presence of the donor layer (I_{AD}) to the acceptor emission in the absence of the donor (I_A) for the single layer structures with $d_m = 60$ and 90 nm is 11.25 and 4.94 (Figure 5.10 b, d), respectively; while this ratio for the stratified samples with $d'_m = 20$ and 30 nm is increased to 38.4 and 44.4

(Figure 5.10 a, c), respectively. It is worth noticing that the higher PL intensity in the stratified structures distinctly confirms the reduced absorption as a result of introducing the spacer layer between the metal films.

5.5. Results and discussions

In order to measure the SP-NRET efficiency for the single layer and the stratified nanostructures, since the ET process takes place at two steps, both the donor and the acceptor photoluminescence intensities should be reflected in energy transfer efficiency calculation to fully cover the effects of each step on the donor and the acceptor PL intensities.

Notably, the method described in equation 5.2 provides an accurate SP-NRET efficiency measurement as a result of its dependency on the donor emission in the presence of the acceptor (quenched donor PL intensity) and the acceptor emission in the presence of the donor (sensitized acceptor PL intensity)[30].

It is worth mentioning that the conventional methods for measuring NRET efficiency may not be essentially effective for multi-step ET process as they involve an extra correction factor definition due to the fact that these methods are mainly based on the ratio of the donor PL intensity quenching in the presence and the absence of the acceptor [20, 46]. Therefore, taking into account both the donor and the acceptor PL intensities, the ET efficiency can be expressed through the quenched donor and the sensitized acceptor intensities method as

$$\eta_{ET} = \frac{(I_{AD} - I_A)/\Phi_A}{(I_{AD} - I_A)/\Phi_A + I_{DA}/\Phi_D} = \left(1 + \frac{\Phi_A}{\Phi_D} \frac{I_{DA}}{I_{AD} - I_A}\right)^{-1} \quad (5.2)$$

where I_{AD} and I_A are the acceptor PL intensities in the presence and the absence of donor, respectively; I_{DA} is the donor PL intensity in the presence of acceptor; and Φ_A and Φ_D are the acceptor and the donor intrinsic quantum yields, respectively. Since the ET mechanism is a unidirectional process from the donor to the acceptor through the plasmonic nanostructure, the excitation of the acceptor and accordingly its energy relaxation could not lead to the donor excitation.

Therefore, the donor PL intensity is the result of an external excitation that is modified through its vicinity to the plasmonic nanostructure, while the acceptor emission is obtained according to the sum of an external excitation (laser source) and the SP-NRET. As a result, in order to study the effect of SP-NRET on the acceptor emission, the acceptor photoluminescence caused by the laser excitation source should be extracted from the overall acceptor emission ($I_{AD} - I_A$). After the spectral decomposition of the donor and the acceptor photo emission from the mixed emission spectra, the terms I_{DA} and I_{AD} can be defined as the area under the donor and the acceptor spectra, respectively.

For the purpose of the comparison of SP-NRET efficiency in the single layer and stratified configurations, we consider two cases: (1) the thickness of plasmonic nanostructure in the stratified configuration is equal to the silver film in single layer structure ($d_m = 2 d'_m + d'_s$), which we used above; and (2) the total thickness of silver films in the stratified samples is equal to the thickness of silver film in the single layer structure which stands for the same energy absorption losses in plasmonic layer ($d_m =$

$2 d'_m$). Table 5.1 shows that regardless of the comparison method, the SP-NRET efficiency in the stratified samples is clearly higher than that in the single layer structures.

For instance, in the stratified sample with $d'_m = 30 \text{ nm}$ the average experimental efficiency is obtained 26.46%, which is 1.78 and 3.11 times greater than the single layer structures with 60 and 90 nm silver film thickness, respectively. In the case of stratified structure, the optimized thickness of the spacer layer was determined to obtain the highest efficiency.

Figure 5.11 | SP-NRET acceptor emission versus spacer layer thickness. The normalized PL spectra with respect to the donor emission peak, for the stratified samples with $d'_m = 20 \text{ nm}$. The spacer layer thickness (d'_s) varies from 10 to 40 nm. As can be seen that the highest acceptor emission is obtained at a spacer thickness of 20 nm, which is in good agreement with the numerical simulation.

In the case of stratified structure with $d'_m = 20 \text{ nm}$, by means of varying the spacer layer thickness from 0-40 nm, the maximum SP-NRET efficiency happens at $d'_s = 20$

nm (Figure 5.11). As can be seen in Figure 5.12 a, the maximum SP-NRET efficiency occurred at the spacer thickness of 20 and 30 nm for stratified nanostructures with each silver film thickness of $d'_m = 20$ and 30 nm, respectively, which agrees well with the theoretical simulation (Figure 5.4).

Table 5.1 | Experimental and theoretical steady state efficiency of SP-NRET. The stratified layer thickness in stratified structure equals to $2 d'_m + d'_s$; e.g. in the stratified structure with the plasmonic layer thickness of 70 nm and $d'_m = 20$ nm, the spacer layer thickness is $d'_s = 30$ nm. The plasmonic layer thickness in single layer sample equals to d_m . The errors on fitting parameters in steady state efficiency of SP_NRET are estimated to be approximately 8%.

Structure	Stratified / Single layer thickness (nm)	SP-NRET efficiency (%) (Experimental)	SP-NRET efficiency (%) (Theoretical)
Stratified	50	18.15 ± 1.03	24.69
	$d'_m = 20$ nm		
	60	21.74 ± 0.75	27.81
	70	18.64 ± 0.74	25.58
	80	17.27 ± 0.91	23.11
	70	19.06 ± 0.78	25.54
	$d'_m = 30$ nm		
	80	22.38 ± 1.20	27.96
Single layer	90	26.46 ± 1.87	29.71
	100	25.59 ± 1.14	24.56
	40	15.46 ± 0.80	20.07
	60	14.68 ± 1.41	17.66
	90	8.55 ± 0.95	10.56

Figure 5.12 | Spacer optimization and time resolved spectroscopy. (a) SP-NRET efficiency in the stratified nanostructures with $d'_m = 20$ and 30 nm versus the spacer layer thickness. The highest SP-NRET efficiency is obtained at the thickness of the spacer layer equals to the silver films for each set. (b) Time resolved photoluminescence decay curves with two-exponential decay model at the donor emission wavelength for the donor-only layer (Alq3), the single layer structures with $d_m = 60$ and 90 nm and the stratified configurations with $d'_m = 20$ and 30 nm. Faster decay rates is observed in the stratified samples compared to the single layer structures. In the stratified structures, the thickness of silver layers and the spacer layer are deposited equally ($d'_m = d'_s$).

Regardless of the fact that the photoluminescence characterization of the samples verify the presence of SP-NRET in our structures, time-resolved spectroscopy method has been also known as an unequivocal demonstration of ET mechanism. In simple donor-acceptor structures, if the lifetime of the donor is significantly longer than that of the acceptor, the donor lifetime decreases in the presence of nonradiative energy transfer from the donor to the acceptor. As a matter of fact, ET process gives rise to an additional nonradiative decay channel for the donor molecule that raises the overall decay rates and consequently reduces the donor lifetime. However, in the plasmonic nanostructures the modification of the donor lifetime should be interpreted differently as the presence of the acceptor molecule may not considerably modify the donor lifetime[20, 46].

More specifically, in our structure the distance between the donor and the acceptor layers is large enough to prevent any direct nonradiative energy transfer from the donor dipole to the acceptor dipole and the modification of the donor decay rate occurs due to the ET from the excited donor molecule to the SP modes at the metal surface (the first step of SP-NRET).

Temporal evolution of spectrally resolved donor emission was collected for all the samples using an appropriate bandpass filter to bypass the acceptor emission. The time resolved PL for the donor-only, single layer and stratified nanostructures at the donor emission peak wavelength are shown in Figure 5.12 b. Donor-only sample exhibits a decay lifetime of 13.5 ns that is in good agreement with previous studies[68, 69]. In the case of single metal film layer and stratified films, since the relaxation of the excited donor molecules occurs in front of different local photonic environments for each of the

molecules, a more complex temporal behaviour has been expected from the decay curves.

Two exponential fitting was employed for amplitude average lifetime approximation of the single layer and the stratified nanostructures. The amplitude averaged decay lifetime of the donor in single metal film layer sample with silver film thickness of 60 and 90 nm were obtained 1.95 and 1.96 ns, respectively. In stratified structures the measured lifetime decreases down to 0.85 and 0.89 ns for $d'_m = 20$ and 30 nm, respectively. Notably, the significant reductions of donor lifetime in the single layer and stratified structures confirm the presence of very large nonradiative decay channels as a result of SP modes on metal surface.

Moreover, shorter donor lifetime in stratified structures compares to single layer sample demonstrates faster nonradiative ET rate from donor layer to the SP modes, which arises from the capability of the stratified layers in enhancing the SP modes coupling and consequently increasing the decay rates of the donor. As mentioned before, our experimental observations show that the presence/ absence of the acceptor layer has negligible contribution in the donor temporal behaviour (Figure 5.13).

As a result, it is important to emphasize that the temporal behaviour of the donor emission is only the evidence of ET to SP modes while for the comprehensive study of SP-NRET mechanism, the effect of SP cross-coupling (which is expressed by enhancement factor) should be also taken in to account. More detailed results on time-resolved measurements and simulations for single layer and stratified structures are presented in Table 5.2. Noted that the theoretical calculation were performed base on

the modification of both radiative and nonradiative decay channels to estimate all the decay rates.

Through numerical simulation of the donor dipole induced electric field at the acceptor position, we show that the stratified plasmonic nanostructure leads to a higher enhancement factor compared to the single layer configuration. Since the SP-NRET mechanism is highly dependent on the plasmon-induced electric field at the metal-dielectric interfaces [11], introducing an extra interface in the stratified plasmonic nanostructure amplifies the structure capability to enhance the electric field.

We consider this factor as the ability of plasmonic nanostructure in transferring the nonradiative energy from the donor to the acceptor. In order to simulate the overall process of SP-NRET from the excited donor dipole to the acceptor dipole through the plasmonic nanostructure, we developed a model based on CPS-Kuhn theory, which expresses the decay rate constant of an excited dipole through the radiative and nonradiative components due to the effect of the absorbing medium [11]. The context of this model was derived from the classical electrodynamics theory of a nano-antenna near earth that was modified to define the decay rates of an oscillating dipole in adjacent of the metallic nanostructure [11, 29, 52, 53, 56, 70]. However it has been shown through considering accurate overlap function of a guest emission and a host absorption, that the classical and quantum approaches can be treated equivalently [53].

Figure 5.13 | Time resolved characterization. Time resolved photoluminescence decay curves with two-exponential decay model at the donor emission wavelength for stratified samples with (D-Plasmonic-A) and without (D-Plasmonic) the acceptor layer, with (a) $d'_m = 20\text{nm}$ and (b) $d'_m = 30\text{nm}$. In the stratified structures for each configuration, the thicknesses of silver layers and the spacer layer are deposited equally ($d'_m = d'_s$).

Table 5.2 | Time resolved analysis. The errors on fitting parameters in time resolved spectroscopy are estimated to be approximately 6%.

Structure	Stratified/Single layer thickness (nm)	t_1 (ns)	t_2 (ns)	A_1	A_2	t_{avg} (ns)	t_{avg} (ns) (Theoretical)
Stratified	60 ($d'_m = 20$ nm)	0.73 ± 0.05	3.86 ± 0.15	7.98E6	18655	0.85	0.95
	90 ($d'_m = 30$ nm)	0.78 ± 0.11	3.85 ± 0.24	1.35E7	43264	0.89	0.99
Single layer	40	1.52 ± 0.28	6.98 ± 0.48	38522	3085	2.05	2.04
	60	1.48 ± 0.12	6.85 ± 0.51	30514	2986	1.95	2.12
	90	1.41 ± 0.17	6.90 ± 0.36	36368	3310	1.96	2.13

The SP modes at the metallic nanostructure is first considered as the primary acceptor site for the donor dipole to calculate the nonradiative ET transfer rate. Next, the induced electric field of the donor dipole at the acceptor dipole position is taken as the enhancement factor for ET rate to excite the secondary acceptor. Similar numerical calculation was applied to the excited acceptor dipole to separately derive the radiative and nonradiative decay rates. Note that, to evaluate the theoretical results for experimental verification, further modification is needed as the theory analysis is performed for single donor dipole energy transfer to the single acceptor dipole through the plasmonic layer, while in the experiment, thin film form of donor and acceptor was used.

To model and quantify the multilayers of the donor /acceptor in the simulation, the 15 nm donor/acceptor thin films was taken as 15 layers of donor/acceptor dipoles stacked on each other (the dye dipole diameter ~ 1 nm). Consequently, the two-

dimensional dipole arrayed structure was applied at each step of ET calculation [23]. Another important assumption is that the homo transfer between the donor/acceptor dipoles was neglected and only the hetero transfer of the donor and the acceptor was considered.

The simulation results showing in Table 5.1 are obtained for the isotropic distribution of the donor/acceptor dipole. As can be seen from this table, the theoretical and experimental results are in good agreement confirming higher SP-NRET efficiency enhancement in the stratified nanostructures compared to the single layer samples. The slight inconsistency in SP-NRET efficiency from experiments and theory can be explained through the following assumption that we have considered in our theoretical calculations: first, the smooth surface approximation in the model, while in reality the surface roughness of silver as a result of thermal deposition is inevitable which may introduce high scattering; second, the two-dimensional assembly model for the donor and the acceptor layers can't be precisely realized in experimental samples. We assumed in our calculation that dipoles arrays are uniformly stacked on each other however, the random distribution of the donor/acceptor dipoles is more prone to take place.

Figure 5.14 | Time resolved characterization (experimental and theoretical analysis). (a) Time resolved photoluminescence decay curves with two-exponential decay model at the donor emission wavelength for the single metal layer samples with the silver film thickness of 10 - 90 nm. (b) The theoretical calculation of the lifetime (dashed line) and experimental results.

5.6. Summary

In summary, we show that the stratified plasmonic coupling to enhance the SP-NRET in metal-dielectric nanostructures. Both experimentally and theoretically, we demonstrated that the stratified plasmonic layer leads to the higher ET efficiency compared to the single metal film nanostructure. Our findings show that multi-layer plasmonic configurations enhance the induced electric field of the emitting donor molecule because of surface plasmon near-field coupling created at the interfaces.

Chapter 6

Spectral tunability and enhancement of radiative emission by metal-dielectric stratified plasmonic nanostructures

Plasmonic nanostructures have been widely known for their notable ability to enhance the spontaneous emission of an electric dipole in their vicinity. Due to the availability of large density of states at the metallic surface, the radiative and nonradiative decay channels are dramatically modified. However, the enhancement cannot be realized for any desired emissive dipole as the existing plasmonic resonance frequency is limited to the well-known plasmonic materials. Despite the fact that recent studies in metamaterials structures demonstrate a promising approach of tuning Purcell factor across the emission wavelength, the structures still lack an efficient radiative emission besides the complexity of its fabrication.

In this chapter, we demonstrate theoretically and experimentally, that the cascaded metal-dielectric nanostructure results in a tunable resonance frequency approach to obtain a maximum radiative decay rate for any desired dipole peak emission wavelength. Thanks to the effective cascaded plasmonic modes coupling across the

metal-dielectric interfaces, the proposed design uniquely illustrate the ability to optimize the plasmonic nanostructure for 100% radiative transmission and 3 fold radiative emission enhancement.

6.1. Introduction

In recent years, planar plasmonic nanostructures have obtained considerable attentions due to their crucial role in the theoretical comprehension of surface enhanced fluorescent [55] (SEF) along with their wide applications in plasmonic wave-guided mode nanostructures [58], Raman scattering spectroscopy [14, 71, 72], colour filters [8, 25], light emitting and light harvesting devices [16, 26, 27, 41-43]. It has been well understood that the excitation of the surface plasmon (SP) modes at the surface of the metal gives rise to an optical behaviour modification of a molecule in the vicinity of metal surface due to the large enhancement of local electromagnetic field [10, 11, 34, 73].

More specifically, near field coupling of SP modes of metal surface with the evanescent emission of light emitters, brings into an enhanced spontaneous emission and large Purcell factor [74-77]. This effect offers manipulating the radiative and nonradiative decay rates of an emitter near metallic nanostructures as a result of large plasmonic density of states (DOS) available at the metal-dielectric interface [4, 31, 33, 56, 73]. However, despite the fact that several studies have reported the significant enhancement of fluorescence spontaneous emission rate, mostly the radiative decay rate

contribution in total relaxation rate has been suppressed by extremely large nonradiative decay rate [77, 78].

Moreover, the excitation enhancement has also been playing a considerable role in an increasing the fluorescence intensity [76, 79-81]. In a planar nanostructures, the constructive interference between incoming and reflected excitation electromagnetic waves results in an excitation field enhancement and consequently raised the fluorescence emission while the quantum yield is not improved. On the other hand, it is worth mentioning that the radiative emission enhancement is also effected by the spectral overlap between the SP modes frequency and the emitter molecule emission spectra [74]. Such spectral overlap is essential to derive an efficient SP coupling and since it is governed by limited existing plasmonic materials such as silver and gold, the radiative decay rates modification has been narrowed by restricted frequencies.

From the above discussion, in order to realize the structure benefiting from an enhanced radiative emission, it is therefore critical not only to enhance the radiative decay rate independent of excitation pump but also to be able to adjust the resonance coupling frequency at any desired emission wavelength.

We present herein the theoretical and experimental demonstration of surface plasmon modes ability to tune the maximum radiative decay rate frequency of an emitting dipole in vicinity of a stratified metal-dielectric-metal nanostructure. This effect arises from an efficient SPs coupling at the metal-dielectric interfaces that leads to the highest electric field enhancement at the dipole position in an optimized cascaded nanostructure. To the best of our knowledge, the tunability of the radiative decay rate of an emitting dipole across the visible spectra has not been reported yet.

Furthermore, the results show ~100% transmission of dipole emission peak through an optimized structure. The design principle allows modifying the structure to obtain a maximum transmission efficiency at any desired frequency. The current approach uniquely provides the ability to get the highest plasmonic modes outcoupling to the far field emission at the interfaces by adjusting variable parameter including dielectric layer thickness and refractive index.

6.2. Theoretical calculation of radiative rate enhancement in stratified structures

Figure 6.1 presents the schematic view of a proposed configuration, in which a thin film of an emissive layer (Tris (8-hydroxyquinolino) aluminum, Alq3) was deposited on metal-dielectric-metal stratified plasmonic structure. The stratified structure consists of an optimized thickness of TPBi (2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)) that is sandwiched between two silver (Ag) films. The thickness of TPBi is determined through numerical calculation to achieve a maximum transmission/radiative efficiency at any desired emission frequency, whereas the SP modes outcoupling leads the highest radiative emission.

Figure 6.1 | Problem schematic. Schematic configuration of metal-dielectric-metal stratified structure deposited on quartz substrate with Alq3 as an emissive layer on top of plasmonic structure. Silver films thickness is 20 nm and spacer layer (TPBi) thickness varies from 60 to 200 nm to reach a resonance condition.

In numerical calculation, an emitting dye molecule was modelled as a Hertzian dipole located at 5 nm distance from a metal-dielectric stratified nanostructure ($d_1 = 5 \text{ nm}$). Parallel and perpendicular dipole moment orientations with respect to the surface of the silver film, were considered in the calculation. The permittivity function of silver film was taken from Johnson and Christy [59] dielectric function and the emissive /spacer layer refractive index was considered 1.7 that is typical for organic semiconductors.

We adopted and developed the energy flux method presented by Chance, Prock and Silbey (CPS model) [11, 29, 53], in which a precise separation of decay channels is provided to distinctly study the effect of SPs modes on each of the decay rates. Predominately the radiative and nonradiative decay rates of an oscillating dipole is altered due to the absorbing surface modes of silver-dielectric interface. Following the

CPS model the normalized radiative decay rate of an emitting dipole in front of an absorbing plasmonic nanostructure can be obtained as

$$\hat{\gamma}_r^\perp(\omega) = q - \frac{3}{2}q \operatorname{Im}\left(\int_0^1 R^\perp e^{-2l_d \hat{d}_1} \frac{u^3}{l_d} du\right) \quad (6.1)$$

$$\hat{\gamma}_r^\parallel(\omega) = q + \frac{3}{4}q \operatorname{Im}\left(\int_0^1 [R^\perp + (1 - u^2)R^\parallel] e^{-2l_d \hat{d}_1} \frac{u^3}{l_d} du\right) \quad (6.2)$$

where q is an intrinsic quantum yield of an emitting dipole, $\hat{d}_1$ is a normalized dipole distance to the nearest metal surface, $l_d \equiv -i\sqrt{1 - u^2}$, u is the integral variable and $R^\parallel$ and $R^\perp$ are nearfield reflection coefficients which are evaluated by defining the Hertz vectors at each layer and applying appropriate boundary conditions at metal-dielectric interfaces for parallel and perpendicular dipoles. More details on Hertz function calculations can be found in Chapters 3 and 4. It is worth mentioning that the nearfield reflection coefficient is a function of metal films/spacer layer thicknesses and refractive indexes, which accordingly allows us to modify the radiative rates by adjusting these variable parameters as long as the experimental limitations are not violated. Since the nano-islands formation and consequently high roughness are inevitable in deposition of silver film with thickness of less than 20 nm [19, 29], for both silver films in a cascaded plasmonic nanostructure a 20 nm thickness was chosen. Noted that this choice results in an efficient option to avoid an unnecessary metal film absorption in thicker configuration.

Figure 6.2 | Radiative decay rate calculation. Radiative decay rate of an emitting dipole in front of stratified structure normalized to the maximum rate, versus emission peak wavelength for 60, 80 100 120 140 and 160 nm spacer layer thickness.

Taking in to account the mentioned practical considerations and for the sake of the simplicity, we establish our calculation based on the spacer layer thickness modification. Figure 6.2 represents the normalized radiative decay rate of an isotropic dipole ($\hat{\gamma}_r^{iso}(\omega) = \hat{\gamma}_r^{\perp}(\omega) + 2/3 \hat{\gamma}_r^{\parallel}(\omega)$) with respect to the maximum rate, versus wavelength for the stratified structure with the spacer layer thickness varies from 60 to 160 nm. One can see that the resonance condition (maximum radiative decay rate) for a desired emission frequency is attainable by modifying the spacer layer thickness. For instance, the maximum radiative decay rate at a dipole peak emission wavelength of 525 nm occurs in a cascaded nanostructure with the spacer layer thickness of 100 nm, which is altered to 140 nm for an emitting dipole with a peak emission wavelength of 600 nm. Such spectral tunability that arises from the engineering of density of states and an

efficient outcoupling of surface mode to the far field emission in the stratified structure, can be also verified through electric field enhancement across the layers (Figure 6.3 a-d). Two-dimensional full-wave simulation method (see Appendix) was used to illustrate the field distribution for an emitting dipole in stratified structure with the spacer layer thickness of 20, 60, 100 and 140 nm. The initially excited dipole is placed at the center of top half-space and its emission peak wavelength is assigned 525 nm.

Figure 6.3 | Electric field map. Calculated electric field distribution ($|E_z|$) calculated by COMSOL simulation tool in stratified structure with spacer layer thickness of 20 nm (a), 60 nm (b), 100 nm (c) and 140 nm (d).

The vertical component of the electric field was monitored across all metallic and dielectric layers to perfectly illustrate the SP coupling modification as a function of

spacer layer thickness. Interestingly, substantial electric field enhancement at the dipole position and across all the layers has been observed in the stratified structure with $TPBi=100$ nm that is a distinct consequent of dipole near field resonance coupling with the far field modes of an optimized stratified structure. In the other words, the constructive interferences give rise to the highest electric field oscillation at the dipole position and the strongest SP mode coupling at each of the metal-dielectric interfaces. Confirming the corresponding results from radiative decay rates calculations, an excellent agreement is achieved from electric field distribution to allocate a remarkable potential of stratified structure in tuning the decay rates.

Next, we focus on the effects of cascaded nanostructure and optimized choice of a spacer layer thickness on the radiative emission power of a dipole. Two regions of interest are considered in calculations, the upper free space (Figure 6.4 a) and the outer most space (Figure 6.4 b). The normalized radiative power is defined as a ratio between radiative power of an emitting dipole in front of a cascaded structure and the dipole radiation which is placed in vicinity of quartz substrate.

Figure 6.4 a shows the normalized radiative emission for an isotropic dipole versus peak emission wavelength and spacer layer thickness. As can be seen in this figure, the normalized radiative power is highly dependent on the thickness of spacer layer ($TPBi$), leading to the precise control on emission intensity that both the radiative power enhancement and attenuation is achievable for all the dipole emission wavelength by adjusting the spacer thickness. For the Alq3 dipole with the peak emission wavelength at 525 nm the highest radiative enhancement factor of 3.2 fold is obtained at the spacer

layer thickness of 105 nm which is consistent with the maximum radiative decay rate results in Figure 6.2.

Figure 6.4 | Radiative Power calculation. Calculated radiative power for an isotropic emitting dipole placed at the distance of $d_1 = 5 \text{ nm}$ from the stratified structure, versus peak emission wavelength and the spacer layer thickness, wherein the radiative power was calculated from a, the emissive layer and b, the substrate side of the samples.

The transmission power efficiency is also obtained as the ratio between the transmitted radiative power through two absorbing metal films and the spacer layer in stratified structure, and the transmitted dipole power in proximity of quartz substrate through nonabsorbing medium (Figure 6.4). The theoretical calculation offers more than 100% transmission at an optimum spacer layer thickness.

The consistency between the results presented in Figure 6.3 and Figure 6.4, demonstrates the ability of stratified plasmonic nanostructure in engineering the radiative channels at any desired emission wavelength. Noted that the effect of an external excitation field wasn't considered in these calculations and the emission enhancement only results from a dipole field modification due to the surface modes variation at the metallic structure.

6.3. Experimental results

To experimentally investigate the theoretical results, we have designed the experimental samples based on the optimum spacer thickness that was obtained from the maximum radiative power enhancement calculation for an emission wavelength of 525 nm (Alq3 peak emission wavelength). Furthermore, two control samples with a single silver layer of 20 and 40 nm were also prepared to address the comparison between the effect of single metal film structure and stratified configuration on emissive layer radiation intensity. All the organic and metallic layers were deposited using thermal evaporation system under the pressure of 4×10^{-4} Pa. In order to obtain smooth and continues surface of silver film the deposition rate of silver was controlled

at a rate of $0.1 \text{ \AA}^{\circ}/\text{s}$. The silver film surface topography was characterized using atomic force microscopy (AFM) which confirms the acceptable flatness across the metal surface (Figure 6.5).

The excitation source was a continuous diode laser with the emission wavelength of 405 nm, which overlaps with the absorption spectra of Alq3 while it does not excite the spacer layer (Figure 6.6). The excitation was applied from the Alq3 side and the photoluminescence (PL) intensity was measured from either Alq3 (radiative power enhancement measurement) or quartz substrate side (transmission measurement). The linear steady state photoluminescence spectra of the samples were recorded using Shamrock SR-303i spectrograph that is integrated with Andor's CCD camera spectroscopy detector systems. More details on PL measurement setup can be found in Figure 6.7.

Figure 6.5 | AFM image. Topographic image of measured surface profiling of silver film stratified structures by atomic force microscopy (AFM) that shows the acceptable flatness.

Figure 6.6 | Emission/Absorption spectrum. Absorption (dashed line) for the emissive layer (Alq3) and the spacer layer (TPBi) and photoluminescence (solid line) spectra for Alq3. The vertical arrow indicates excitation laser wavelength for PL measurement.

Figures 6.8a and b show the measured PL intensities for the emissive layer on substrate (reference sample), stratified and single layer structures, in which the intensity measurements were carried out from the emissive layer and substrate sides of the samples, respectively (indicated by the arrows at the schematic view of structures). From Figure 6.8a one can see that both the stratified and the single layer structures show an enhancement in radiative emission compared to the reference sample. Thanks to the most efficient SP coupling across the metal-dielectric interfaces in the stratified structure, 3 fold radiative emission enhancement was observed from the emissive layer which is almost 2.5 times greater than the enhancement obtained from the single metal film structures (Figure 6.8a, black and red lines). Such enhancement arises from the

efficient alignment of an emitter peak emission spectra with the DOS in the optimized stratified structure (TPBi = 100 nm), while in single metal film configuration the coupling tunability is not available due to the fixed silver film SP mode spectra.

Figure 6.7 | Optical setups for photoluminescence measurement. Optical setups for photoluminescence intensity measurements. The schematic illustration for radiative emission enhancement (a) and transmission (b) measurement. In the transmission measurement system, the samples were excited by 405 nm laser from Alq3 side and the resultant intensities are collected from the outer most silver layer, while in radiative emission measurement setup both the excitation and collection were applied from the Alq3 side. The UV filter was used to bypass collection of excitation source from the substrate.

Figure 6.8 | Experimental PL intensity measurements. Photoluminescence intensity measurements radiated from an emissive layer in front of stratified structure (green), single layer configuration with the metal thickness of 20nm (red) and 40nm (black) and the Alq3 on the quartz substrate (blue).

Moreover the almost 100% transparency of an optimized stratified structure at the Alq3 peak emission wavelength can be verified through Figure 6.8b, wherein the single layer structures with the silver film thickness of 20 and 40 nm show 35% and 10% transparency, respectively. As a result, in absence of an efficient SP resonance coupling,

only 10-12% transmission of dye molecule is expected from the stratified structure with two 20 nm-thick metal films (Figure 6.9), while an optimized thickness of TPBi would significantly support the surface modes at the Ag/TPBi and TPBi/Ag interfaces and results in full transmission at the specific resonance frequency. It is important to note that the narrower Alq3 emission spectra with the full-width at half maximum of 50 nm in front of stratified configuration, indicates the filter-like behavior of the plasmonic structure and its ability to filter any wide spectra to a bright emission.

Figure 6.9 | Simulated normalized transmission. The calculated transmission through a stratified nanostructure for an emitting dipole with a peak emission wavelength of 525 nm using COMSOL 2D simulation. The spacer layer thickness varies from 20 nm to 500 nm. The off-resonance points with the transparency ~ 10 %, are shown with the dashed circles. 92%, 75% and 64% transparency are obtained at the first (spacer = 100 nm), second (spacer = 260 nm) and third (spacer = 400 nm) resonance points, respectively.

Besides the effect of decay rates modification on emission enhancement, the extinction coefficient of the emitting molecule may profit the excitation field enhancement. The standing waves that are formed from the reflection of the excitation incident field at the interfaces, have the ability to boost the dye molecule excitation rate. Consequently, in order to quantitatively evaluate the experimental results, the radiative enhancement factor (REF) is defined considering the excitation enhancement factor besides the radiative decay rate in the calculations

$$REF = \frac{I_{stratified}}{I_0} = \frac{P_{stratified}}{P_0} A_{excitation} \quad (6.3)$$

where $I_{stratified}$ and I_0 are the measured PL intensities from stratified and reference samples, respectively, $P_{stratified}$ and P_0 are the calculated emission power in stratified and reference structures, respectively, and $A_{excitation}$ is the excitation enhancement factor that is calculated at the dipole position for the laser emission wavelength of 405 nm. Figure 6.10 a and b present REF that were obtained by the theoretical calculation (solid line), 2D full-wave simulation (open circle) and the experimental measurements (square) in the stratified structure at the Alq3 peak emission wavelength of 525 nm versus the spacer layer thickness varied from 30 to 180 nm.

From Figure 6.10 a dependency of REF on the spacer layer thickness can be verified wherein the PL intensities were collected from emissive layer side. One may notice that REF can be even smaller than unity (TPBi=60 nm) however in most of the points the enhancement is greater than one. This behavior emphasizes the destructive/constructive role of the interferences in the stratified configurations as a function of spacer layer

thickness and indicates the significance of an optimized design to achieve the resonance matching point between emission wavelength and geometrical properties of the plasmonic structure. Noted that the effective excitation cross section at the dipole position as well as the decay rate enhancement has been put into account and reflected in the REF calculation presented in Figure 6.10. Accordingly, the maximum REF calculated in Figure 6.10a is 3.5 while from considering only the effect of radiative decay rate it has obtained 3.2 (Figure 6.4 a) which confirms the neglectable role of excitation cross section in our plasmonic configuration.

It is also worth mentioning that, the emitted electromagnetic field from the dipole source would undergo different circumstances in each of our intensity collection methods (REF and Transmitted REF, Figure 6.7), therefore as can be seen in Figure 6.10 a and b, the resultant REF curve in transparency measurement setup (Figure 6.10 b) shows a very distinguishable resonance enhancement compared to the one in Figure 6.10 a. In fact the transmitted electromagnetic field through the absorbing and non-absorbing layers in stratified structure at the emission peak emission wavelength, experienced a transparent medium at the resonance point in which the intensity of dipole emission in other off-resonance frequencies extremely suppressed (Figure 6.11).

Figure 6.10 |Theoretical and experimental REE and transmitted REE measurements.

Representative values of radiative enhancement factor (REF) that were derived from theoretical calculation (solid line), COMSOL simulation (circle) and experimental measurements (square) based on equation 3, when the photoluminescence spectra were collected from the emissive layer (a) and quartz substrate (b) sides of samples.

Figure 6.11 | Theoretical and experimental PL measurements. The theoretical calculation (dashed line) and experimental measurement (solid line) for the transmission efficiency measurement setup. The thickness of the spacer layer (TPBi) is varied from 60 to 140 nm.

Although, a very good agreement between theoretical and experimental results in Figure 6.4 and 6.8 demonstrates the effect of stratified structure on radiative decay rate enhancement, to distinctly address the negligible excitation contribution in radiative emission enhancement, we have designed a new batch of samples in which all the effective parameters including PL spectroscopy measurement system, laser excitation source and the stratified structure remained unchanged but the emissive layer. Alq3 was replaced with DCM, 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran, an organic dye molecule that peaks around $\lambda = 660 \text{ nm}$. Since all the optical properties are identical in both batches of samples, the enhancement should be observed

at the stratified structure with the spacer layer thickness of 100 nm, if it dominantly arises from an enhanced excitation electric field intensity. Our experimental measurements show that in consistent with the theoretical calculation, the maximum enhancement occurs in the structure with the spacer layer thickness of 160 nm, demonstrating the dominant effect of radiative decay rate enhancement in stratified structures rather than excitation field (Figure 6.12).

Figure 6.12 | DCM transmitted REE. The experimental measurement transmitted PL intensity for the stratified structure with DCM as the emissive layer. The thickness of the spacer layer (TPBi) is varied from 100 to 200 nm.

6.4. Summary

We have presented the experimental and theoretical demonstration of the stratified plasmonic nanostructure capability to tune and enhance the radiative emission rate. It was well understood that the spontaneous emission of a dipole in front of a metallic structure affected tremendously as a result of an enhancement in plasmonic density of states. By exploiting this effect in a cascaded metal-dielectric-metal configuration, it was verified that the radiation enhancement reaches the maximum in a stratified structure with an optimized choice of the spacer layer thickness.

The radiative decay rate calculation based on CPS energy flux model, showed that the resonance matching condition in which the highest radiative rate is derived, which highly relies on the spacer layer thickness. In fact, the modification of spacer layer provided an efficient spectral overlap between an emitter molecule spectra and the surface plasmon mode of the stratified structure. 3 fold radiation enhancement and 100% transmission efficiency, resulted from the stratified structure with the spacer layer thickness of 100 nm for an emitting dipole with the peak emission wavelength of 525 nm. Theoretical calculations were consistent with the experimental results, demonstrating the leading role of the decay rate improvement over the negligible contribution of excitation enhancement in the proposed stratified nanostructures. Exploiting this effect in light emitting devices, bio sensors and surface-enhance Raman spectroscopy may lead to the structures with high radiated intensity at any desires emission frequency.

6.5. Appendix: COMSOL simulation

The commercial software, COMSOL Multiphysics was used to perform 2 dimensional full-wave simulation. A Cartesian domain was created around the layered structure and a scattering boundary condition was applied to pass the electromagnetic wave without any reflection. An electric point dipole with the peak emission wavelength of 525 nm was located at the distance of 5 nm to the nearest metal surface. The thickness of TPBi varied from 20 to 200 nm with the sweeping length of 10 nm to simulate the effect of spacer layer thickness on transmission/radiative emission enhancement. Two 20 nm thick silver film were placed on either side of the TPBi layer and the permittivity of all layer were selected the same as those that were used in theoretical calculation. The quartz substrate with the refractive index of 1.45 was placed beneath the stratified structure and the semi-infinite air medium was considered to be located on top of Alq3 emissive layer.

The radiative power were calculated by integrating the total power which is radiating out of the desired domain; the transmitted power through the stratified structure was obtained by integration at the far field in quartz domain (P_t), while the radiative emission from the emissive layer was obtained by integrating over the boundaries in the air medium at the far field (P_{rad}). The reference structure was also modelled by replacing the plasmonic stratified structure with non-absorbing dielectric medium; $P_{t,ref}$ and $P_{rad,ref}$ were calculated at the corresponding medium. As a result the transmission and the radiative emission enhancement were respectively obtained as

$$\eta_t = \frac{P_t}{P_{t,ref}} \quad (6.4)$$

$$\eta_{rad} = \frac{P_{rad}}{P_{rad,ref}} \quad (6.5)$$

For both the dipole polarization, the radiated power was obtained and it was extended to an isotropic (*iso*) one by applying $P^{iso} = 1/3 P^\perp + 2/3 P^\parallel$,

Chapter 7

Conclusions and recommendations

7.1. Conclusions

In this dissertation, we have studied the effects of the planar plasmonic nanostructures on the radiative and nonnative decay rates of an oscillating dipole. A full theoretical model for the behavior of an emitting molecule in the vicinity of planar plasmonic nanostructure was presented to compute the radiative and nonradiative decay rates, radiative emission enhancement, electric field enhancement factor and nonradiative energy transfer rate/efficiency. The simulations were performed for the two most applicable plasmonic materials: silver and gold metal films. Also, we have applied and developed the energy flux method from the conventional single layer of the metallic nanostructure to the layered metal-dielectric-metal configuration, in which a remarkably enhanced energy transfer efficiency was obtained as a result of stronger surface plasmon coupling at the metal-dielectric boundaries as evidenced by the enhanced electric field enhancement factor.

We have proposed two different theoretical models to illustrate the surface plasmon mediated nonradiative energy transfer in planar metallic structures, wherein the donor and acceptor dipoles are placed on either side of the metal film. The first model was called two-step in which we assisted the theory of surface plasmon enhanced nonradiative energy transfer along with the energy flux method to comprehensively describe the energy transfer mechanism in two successive steps: energy migration from donor to surface modes of metallic structure and then surface plasmon coupling and transferring the energy to the acceptor dipole. The other proposed model was the one-step model in which we simplified the overall processes by defining the new concept of effective donor/acceptor. We have simulated the models for different practical cases and showed that the proposed models are in good agreement and demonstrated the effect of enhanced energy transfer efficiency in presence of the plasmonic nanostructures.

Based on our theoretical model, we have designed the experimental samples and setups to measure the nonradiative energy transfer efficiency in planar structures; conventional single metal film and our proposed configuration of stratified metal-dielectric nanostructures. We have demonstrated the nonradiative energy transfer mechanism between the donor and the acceptor through the multi-layered metallic nanostructures – stratified configuration, in which we have shown that an efficient energy transfer can be realized. This novel approach in nonradiative energy transfer uniquely provided us with the ability to overcome the drawback of high energy absorption losses in a thick metal film by inserting a non-absorbing dielectric layer between two thin metal films. Moreover, a strong plasmon-plasmon near-field coupling through the dielectric spacer layer was proven to highly extend the effective energy transfer distance/efficiency. The proposed architecture has been demonstrated through

theoretical modeling and experiment. Consistent with theoretical and numerical results, experimental measurements confirm at least 50% plasmon resonance energy transfer enhancement in the donor-metal-dielectric-metal-acceptor compared to the donor-metal-acceptor structure.

Moreover, we presented the theoretical and experimental demonstration of engineering surface plasmon mode to tune the maximum radiative decay rate frequency of an emitting dipole in a vicinity of a stratified metal-dielectric-metal nanostructure. This effect arises from an efficient SP coupling at the metal-dielectric interfaces that leads to the highest electric field enhancement at the dipole position in an optimized cascaded nanostructure. The design principle allows modifying the structure to obtain a maximum transmission efficiency at any desired frequency. The current approach uniquely provides the ability to obtain the highest plasmonic mode outcoupling to the far field emission at the interfaces by adjusting variable parameter including dielectric layer thickness and refractive index. Thanks to the effective cascaded plasmonic modes coupling across the metal-dielectric interfaces, the proposed design uniquely illustrate the ability to optimize the plasmonic nanostructure for 100% radiative transmission and 3 fold radiative emission enhancement.

7.2. Recommendations for future works

Here are our suggested works and studies that can be perused based on our experimental and theoretical experiences obtained through this dissertation:

- The effect of dimensionality

One of the very important assumptions that have been taken into account in our theoretical modeling of surface plasmon mediated nonradiative energy transfer, is that we have treated the effective donor/acceptor as a point-like dipole in the single-step model. Since the combination of donor dipole and the metallic layer or similarly the metallic layer and the acceptor dipole, is more complicated than a point-like dipole and involves the effect of dimensionality (it is, in fact, a two-dimensional structure), an extra equations and mathematical modifications are needed to fully cover this effect in the proposed model. We should mention that although the single-step model and the two-step models are proven to be in very good agreement and also our experimental observations followed the same results, the dimensionality effect should be considered in the modeling to cover all the effective parameters.

- The effect of orientation factor

Kappa-squared or the orientation factor is one of the significant factors in the Förster theory of energy transfer between donor and acceptor dipoles, which basically depends on the donor emission transition dipole moment and the acceptor absorption transition dipole moment. In most of the studies, the averaged value of $2/3$ has been considered for this parameter. Noted that this assumption is based on the fact that both the donor and acceptor sites are modeled as the dipoles. Once again we should stress that in our

theoretical model this important assumption is not valid for some of the cases which introduce the error in our modeling. Therefore the study of the effect of the orientation factor in more complex structure, two-dimensional configurations, and plasmonic nanostructures may be useful.

- Energy transfer in plasmonic cavities and nanoantennas

The plasmonic nanoantennas structures consist of the silver nanocubes that are deposited on a very thick silver film. The nanocubes and the silver film are separated by a dielectric medium. It has been studied by many groups [74, 76] that by adjusting the variable parameters including the dielectric medium thickness and nanocubes size, the dramatic enhancement of the absorption and spontaneous emission can be achieved. This effect arises from the availability of large optical density of states and enhanced local electric field at the plasmonic cavity between nanocubes and the metal film. As a result, exploiting this structure in nonradiative energy transfer problem may lead to energy transfer efficiency enhancement.

- Energy transfer in hyperbolic metamaterials

Hyperbolic metamaterials (HMMs) have recently obtained considerable attention due to their unique optical properties. HMMs have been widely applied to enhance the spontaneous emission rate of an emitting molecule which is placed in their vicinity. This happens due to the indefinite photonic density of states that are available in HMMs. Therefore these structures can be a very good candidate to be applied to enhance the energy transfer efficiency. Placing the donor-acceptor pair close to the HMMs may lead to enhance the energy transfer efficiency.

Author's Publications

1. Golmakaniyoon, S.; Hernandez-Martinez, P. L.; Demir, H. V.; Sun, X. W., "Cascaded plasmon-plasmon coupling mediated energy transfer across stratified metal-dielectric nanostructures" Scientific Reports, 2016, 6.
2. Golmakaniyoon, S.; Hernandez-Martinez, P. L.; Demir, H. V.; Sun, X. W., "Spectral Tunability and Enhancement of Dye Molecule Radiative Emission by Metal-Dielectric-Metal Stratified Plasmonic Nanostructure", preparation for submission.
3. Golmakaniyoon, S.; Demir, H. V.; Sun, X. W., "Theory of surface plasmon mediated nonradiative energy transfer in planar plasmonic nanostructures", preparation for submission.
4. Golmakaniyoon, S.; Demir, H. V.; Sun, X. W. In Nonradiative energy transfer in a layered metal-dielectric nanostructure mediated by surface plasmons, SPIE Nanoscience+ Engineering, 2015; pp 95470T-95470T-6.
5. Golmakaniyoon, S.; Hernandez-Martinez, P. L.; Demir, H. V.; Sun, X. W., "Surface Plasmon-Enhanced Radiative Emission through Cascaded Metal-Dielectric Nanostructures", ICMAT, 2017.
6. Golmakaniyoon, S.; Demir, H. V.; Sun, X. W., "Theory of Plasmon-Mediated Energy Transfer in Planar Metallic Nanostructures", ICMAT, 2017.

References

1. Akselrod, G.M., et al., Probing the mechanisms of large Purcell enhancement in plasmonic nanoantennas. *Nature Photonics*, 2014. 8(11): p. 835-840.
2. Bourg, N., et al., Direct optical nanoscopy with axially localized detection. *Nature Photonics*, 2015. 9(9): p. 587-593.
3. Chanda, D., et al., Coupling of plasmonic and optical cavity modes in quasi-three-dimensional plasmonic crystals. *Nature communications*, 2011. 2: p. 479.
4. Jia, H., H. Liu, and Y. Zhong, Role of surface plasmon polaritons and other waves in the radiation of resonant optical dipole antennas. *Scientific reports*, 2015. 5.
5. Rose, A., et al., Control of radiative processes using tunable plasmonic nanopatch antennas. *Nano letters*, 2014. 14(8): p. 4797-4802.
6. Shi, X.-B., et al., Surface Plasmon Polariton Enhancement in Blue Organic Light-Emitting Diode: Role of Metallic Cathode. *Applied Physics Express*, 2012. 5(10): p. 102102.
7. Xu, T., et al., Localizing surface plasmons with a metal-cladding superlens for projecting deep-subwavelength patterns. *Applied Physics B*, 2009. 97(1): p. 175-179.
8. Xu, T., et al., Plasmonic nanoresonators for high-resolution colour filtering and spectral imaging. *Nature communications*, 2010. 1: p. 59.

9. Andrews, D.L., A unified theory of radiative and radiationless molecular energy transfer. *Chemical Physics*, 1989. 135(2): p. 195-201.
10. Barnes, W., Fluorescence near interfaces: the role of photonic mode density. *journal of modern optics*, 1998. 45(4): p. 661-699.
11. Chance, R., A. Prock, and R. Silbey, Molecular fluorescence and energy transfer near interfaces. *Adv. Chem. Phys*, 1978. 37(1): p. 65.
12. Gersten, J. and A. Nitzan, Spectroscopic properties of molecules interacting with small dielectric particles. *The Journal of Chemical Physics*, 1981. 75(3): p. 1139-1152.
13. Marocico, C. and J. Knoester, Effect of surface-plasmon polaritons on spontaneous emission and intermolecular energy-transfer rates in multilayered geometries. *Physical Review A*, 2011. 84(5): p. 053824.
14. Barnes, W.L., A. Dereux, and T.W. Ebbesen, Surface plasmon subwavelength optics. *Nature*, 2003. 424(6950): p. 824-830.
15. Scalora, M., et al., Transparent, metallo-dielectric, one-dimensional, photonic band-gap structures. *Journal of Applied Physics*, 1998. 83(5): p. 2377-2383.
16. Schuller, J.A., et al., Plasmonics for extreme light concentration and manipulation. *Nature materials*, 2010. 9(3): p. 193-204.
17. Fang, N., et al., Sub-diffraction-limited optical imaging with a silver superlens. *Science*, 2005. 308(5721): p. 534-537.
18. Zhang, X. and Z. Liu, Superlenses to overcome the diffraction limit. *Nature materials*, 2008. 7(6): p. 435-441.

19. An, K.H., M. Shtein, and K.P. Pipe, Surface plasmon mediated energy transfer of electrically-pumped excitons. *Optics express*, 2010. 18(5): p. 4041-4048.
20. Andrew, P. and W. Barnes, Energy transfer across a metal film mediated by surface plasmon polaritons. *Science*, 2004. 306(5698): p. 1002-1005.
21. Andrew, P. and W.L. Barnes, Förster energy transfer in an optical microcavity. *Science*, 2000. 290(5492): p. 785-788.
22. Govorov, A.O., J. Lee, and N.A. Kotov, Theory of plasmon-enhanced Förster energy transfer in optically excited semiconductor and metal nanoparticles. *Physical Review B*, 2007. 76(12): p. 125308.
23. Hernández-Martínez, P.L., A.O. Govorov, and H.V. Demir, Förster-Type Nonradiative Energy Transfer for Assemblies of Arrayed Nanostructures: Confinement Dimension vs Stacking Dimension. *The Journal of Physical Chemistry C*, 2014. 118(9): p. 4951-4958.
24. Hua, X., J. Gersten, and A. Nitzan, Theory of energy transfer between molecules near solid state particles. *The Journal of chemical physics*, 1985. 83(7): p. 3650-3659.
25. Diest, K., et al., Tunable Color Filters Based on Metal– Insulator– Metal Resonators. *Nano letters*, 2009. 9(7): p. 2579-2583.
26. Atwater, H.A. and A. Polman, Plasmonics for improved photovoltaic devices. *Nature materials*, 2010. 9(3): p. 205-213.

27. Gifford, D.K. and D.G. Hall, Emission through one of two metal electrodes of an organic light-emitting diode via surface-plasmon cross coupling. *Applied Physics Letters*, 2002. 81(23): p. 4315-4317.
28. Heidel, T., et al., Surface plasmon polariton mediated energy transfer in organic photovoltaic devices. *Applied Physics Letters*, 2007. 91(9): p. 093506.
29. Chance, R., A. Prock, and R. Silbey, Comments on the classical theory of energy transfer. *The Journal of Chemical Physics*, 1975. 62(6): p. 2245-2253.
30. Medintz, I. and N. Hildebrandt, *FRET-Förster Resonance Energy Transfer: From Theory to Applications*. 2013: John Wiley & Sons.
31. Guclu, C., et al., Radiative emission enhancement using nano-antennas made of hyperbolic metamaterial resonators. *Applied Physics Letters*, 2014. 105(12): p. 123101.
32. Guzatov, D.V., et al., Plasmonic enhancement of molecular fluorescence near silver nanoparticles: theory, modeling, and experiment. *The Journal of Physical Chemistry C*, 2012. 116(19): p. 10723-10733.
33. Lakowicz, J.R., Radiative decay engineering 5: metal-enhanced fluorescence and plasmon emission. *Analytical biochemistry*, 2005. 337(2): p. 171-194.
34. Lakowicz, J.R., et al. Advances in surface-enhanced fluorescence. in *Biomedical Optics 2004*. 2004. International Society for Optics and Photonics.
35. Maier, S.A., *Plasmonics: fundamentals and applications*. 2007: Springer Science & Business Media.

36. Valeur, B. and M.N. Berberan-Santos, *Molecular fluorescence: principles and applications*. 2012: John Wiley & Sons.
37. Pines, D., Collective energy losses in solids. *Reviews of modern physics*, 1956. 28(3): p. 184.
38. Ritchie, R., Plasma losses by fast electrons in thin films. *Physical Review*, 1957. 106(5): p. 874.
39. Kretschmann, E. and H. Raether, Notizen: radiative decay of non radiative surface plasmons excited by light. *Zeitschrift für Naturforschung A*, 1968. 23(12): p. 2135-2136.
40. Otto, A., Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection. *Zeitschrift für Physik*, 1968. 216(4): p. 398-410.
41. Hobson, P.A., et al., Surface Plasmon Mediated Emission from Organic Light-Emitting Diodes. *Advanced Materials*, 2002. 14(19): p. 1393-1396.
42. Okamoto, K., et al., Surface-plasmon-enhanced light emitters based on InGaN quantum wells. *Nature materials*, 2004. 3(9): p. 601-605.
43. Ozbay, E., Plasmonics: merging photonics and electronics at nanoscale dimensions. *science*, 2006. 311(5758): p. 189-193.
44. Nie, S. and S.R. Emory, Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. *science*, 1997. 275(5303): p. 1102-1106.
45. Andrews, D.L. and D.S. Bradshaw, Virtual photons, dipole fields and energy transfer: a quantum electrodynamical approach. *European journal of physics*, 2004. 25(6): p. 845.

46. Collini, E., et al., Photophysics and dynamics of surface plasmon polaritons-mediated energy transfer in the presence of an applied electric field. *Journal of the American Chemical Society*, 2012. 134(24): p. 10061-10070.
47. Golmakaniyoon, S., et al., Cascaded plasmon-plasmon coupling mediated energy transfer across stratified metal-dielectric nanostructures. *Scientific Reports*, 2016. 6.
48. Dulkeith, E., et al., Fluorescence quenching of dye molecules near gold nanoparticles: radiative and nonradiative effects. *Physical review letters*, 2002. 89(20): p. 203002.
49. Fujiki, A., et al., Enhanced fluorescence by surface plasmon coupling of Au nanoparticles in an organic electroluminescence diode. *Applied Physics Letters*, 2010. 96(4): p. 043307.
50. Lunz, M., et al., Surface plasmon enhanced energy transfer between donor and acceptor CdTe nanocrystal quantum dot monolayers. *Nano letters*, 2011. 11(8): p. 3341-3345.
51. Ozel, T., et al., Observation of selective plasmon-exciton coupling in nonradiative energy transfer: donor-selective versus acceptor-selective plexcitons. *Nano letters*, 2013. 13(7): p. 3065-3072.
52. Sommerfeld, A., *Partial differential equations in physics*. Vol. 1. 1949: Academic press.

53. Chance, R., A. Prock, and R. Silbey, Lifetime of an emitting molecule near a partially reflecting surface. *The Journal of Chemical Physics*, 1974. 60(7): p. 2744-2748.
54. Purcell, E.M., Spontaneous emission probabilities at radio frequencies. *Physical Review*, 1946. 69: p. 681.
55. Lakowicz, J.R., et al., Radiative decay engineering: 2. Effects of silver island films on fluorescence intensity, lifetimes, and resonance energy transfer. *Analytical biochemistry*, 2002. 301(2): p. 261-277.
56. Anger, P., P. Bharadwaj, and L. Novotny, Enhancement and quenching of single-molecule fluorescence. *Physical review letters*, 2006. 96(11): p. 113002.
57. Novotny, L. and B. Hecht, *Principles of nano-optics*. 2012: Cambridge university press.
58. Jun, Y.C., et al., Nonresonant enhancement of spontaneous emission in metal-dielectric-metal plasmon waveguide structures. *Physical Review B*, 2008. 78(15): p. 153111.
59. Johnson, P.B. and R.-W. Christy, Optical constants of the noble metals. *Physical Review B*, 1972. 6(12): p. 4370.
60. Golmakaniyoon, S., H.V. Demir, and X.W. Sun. Nonradiative energy transfer in a layered metal-dielectric nanostructure mediated by surface plasmons. in *SPIE Nanoscience+ Engineering*. 2015. International Society for Optics and Photonics.

61. Breshike, C.J., R.A. Riskowski, and G.F. Strouse, Leaving Förster Resonance Energy Transfer Behind: Nanometal Surface Energy Transfer Predicts the Size-Enhanced Energy Coupling between a Metal Nanoparticle and an Emitting Dipole. *The Journal of Physical Chemistry C*, 2013. 117(45): p. 23942-23949.
62. Yun, C., et al., Nanometal surface energy transfer in optical rulers, breaking the FRET barrier. *Journal of the American Chemical Society*, 2005. 127(9): p. 3115-3119.
63. Kumar, A., et al., Efficiency enhancement of organic light emitting diode via surface energy transfer between exciton and surface plasmon. *Organic Electronics*, 2012. 13(1): p. 159-165.
64. Seker, U.O.S., T. Ozel, and H.V. Demir, Peptide-mediated constructs of quantum dot nanocomposites for enzymatic control of nonradiative energy transfer. *Nano letters*, 2011. 11(4): p. 1530-1539.
65. Yates, C., et al., Surface plasmon-polariton mediated emission from phosphorescent dendrimer light-emitting diodes. *Applied physics letters*, 2006. 88(16): p. 161105.
66. Axelrod, D., Evanescent excitation and emission in fluorescence microscopy. *Biophysical journal*, 2013. 104(7): p. 1401-1409.
67. Persson, B. and N. Lang, Electron-hole-pair quenching of excited states near a metal. *Physical Review B*, 1982. 26(10): p. 5409.

68. Garbuzov, D., et al., Photoluminescence efficiency and absorption of aluminum-tris-quinolate (Alq 3) thin films. *Chemical Physics Letters*, 1996. 249(5): p. 433-437.
69. Zhang, X., et al., Tris-(8-hydroxy-quinoline) aluminium/zirconium phosphate: a novel hybrid assembly with strong luminescence and prolonged lifetime. *Chemical Communications*, 2011. 47(22): p. 6359-6361.
70. Wasey, J. and W. Barnes, Efficiency of spontaneous emission from planar microcavities. *Journal of Modern Optics*, 2000. 47(4): p. 725-741.
71. Willets, K.A. and R.P. Van Duyne, Localized surface plasmon resonance spectroscopy and sensing. *Annu. Rev. Phys. Chem.*, 2007. 58: p. 267-297.
72. Xu, H., et al., Spectroscopy of single hemoglobin molecules by surface enhanced Raman scattering. *Physical review letters*, 1999. 83(21): p. 4357.
73. Gryczynski, I., et al., Radiative decay engineering 4. Experimental studies of surface plasmon-coupled directional emission. *Analytical biochemistry*, 2004. 324(2): p. 170-182.
74. Lu, D., et al., Enhancing spontaneous emission rates of molecules using nanopatterned multilayer hyperbolic metamaterials. *Nature nanotechnology*, 2014. 9(1): p. 48-53.
75. Zhang, J., et al., Metal-enhanced fluoroimmunoassay on a silver film by vapor deposition. *The Journal of Physical Chemistry B*, 2005. 109(16): p. 7969-7975.
76. Muskens, O., et al., Strong enhancement of the radiative decay rate of emitters by single plasmonic nanoantennas. *Nano letters*, 2007. 7(9): p. 2871-2875.

77. Shimizu, K., et al., Surface-enhanced emission from single semiconductor nanocrystals. *Physical review letters*, 2002. 89(11): p. 117401.
78. Gontijo, I., et al., Coupling of InGaN quantum-well photoluminescence to silver surface plasmons. *Physical Review B*, 1999. 60(16): p. 11564.
79. Biteen, J.S., et al., Enhanced radiative emission rate and quantum efficiency in coupled silicon nanocrystal-nanostructured gold emitters. *Nano letters*, 2005. 5(9): p. 1768-1773.
80. Munechika, K., et al., Spectral control of plasmonic emission enhancement from quantum dots near single silver nanoprisms. *Nano letters*, 2010. 10(7): p. 2598-2603.
81. Le Moal, E., et al., Enhanced fluorescence cell imaging with metal-coated slides. *Biophysical journal*, 2007. 92(6): p. 2150-2161.