Novel Optical Properties Of Metal Nanostructures Based On Surface Plasmons

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NOVEL OPTICAL PROPERTIES OF METAL NANOSTRUCTURES BASED ON SURFACE PLASMONS

by

HAINING WANG
B.S. Shandong University, China, 2005

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the College of Science at the University of Central Florida Orlando, Florida

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Major Professor: Shengli Zou
ABSTRACT

Surface plasmons have been attracted extensive interests in recent decades due to the novel properties in nanometer sized dimensions. My work focused on the novel optical properties of metal nanostructures based on surface plasmons using theoretical simulation methods. In the first part, we investigated metal nanofilms and nanorods and demonstrated that extremely low scattering efficiency, high absorption efficiency and propagation with long distance could be obtained by different metal nanostructures. With a perforated silver film, we demonstrated that an extremely low scattering cross section with an efficiency of less than 1% can be achieved at tunable wavelengths with tunable widths. The resonance wavelength, width, and intensity are influenced by the shape, size and arrangement pattern of the holes, as well as the distance separating the holes along the polarization direction. The extremely low scattering could be used to obtain high absorption efficiency of a two-layer silver nanofilm. Using the discrete dipole approximation method, we achieved enhanced absorption efficiencies, which are close to 100%, at tunable wavelengths in a two-layer silver thin film. The film is composed of a 100 nm thick perforated layer facing the incident light and a 100 nm thick solid layer. Resonance wavelengths are determined by the distances between perforated holes in the first layer as well as the separation between two layers. The resonance wavelengths shift to red with increasing separation distance between two layers or the periodic distance of the hole arrays. Geometries of conical frustum shaped holes in the first layer are critical for the improved absorption efficiencies. When the hole bottom diameter equals the periodic distance and the upper diameter
is about one-third of the bottom diameter, close to unit absorption efficiency can be obtained. We examined the electromagnetic wave propagation along a hollow silver nanorod with subwavelength dimensions. The calculations show that light may propagate along the hollow nanorod with growing intensities. The influences of the shape, dimension, and length of the rod on the resonance wavelength and the enhanced local electric field, $|E|^2$, along the rod were investigated. In the second part, a generalized electrodynamics model is proposed to describe the enhancement and quenching of fluorescence signal of a dye molecule placed near a metal nanoparticle (NP). Both the size of the Au NPs and quantum yield of the dye molecule are crucial in determining the emission intensity of the molecule. Changing the size of the metal NP will alter the ratio of the scattering and absorption efficiencies of the metal NP and consequently result in different enhancement or quenching effect to the dye molecule. A dye molecule with a reduced quantum yield indicates that the non-radiative channel is dominant in the decay of the excited dye molecules and the amplification of the radiative decay rate will be easier. In general, the emission intensity will be quenched when the size of metal NP is small and the quantum yield of dye molecule is about unity. A significant enhancement factor will be obtained when the quantum yield of the molecule is small and the particle size is large. When the quantum yield of the dye molecule is less than $10^{-5}$, the model is simplified to the surface enhanced Raman scattering equation.
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CHAPTER 1: INTRODUCTION

1.1 Surface Plasmons

Surface plasmons (SPs)\textsuperscript{1-6} are defined as the coherent oscillations of conduction electrons at the interface between two materials, which have dielectric constants (real part) with opposite sign. In simple case, SPs can be induced at the interface of a dielectric and a metal film. When SPs couple with photons, the surface plasmon polaritons (SPPs) can be obtained. The SPPs can propagate along the metal surface and is a TM-polarized wave (Transverse Magnetic), in which its magnetic field is vertical to the incident wave and parallel to the plane of interface, as shown in Figure 1-1(a)\textsuperscript{7}. By solving Maxwell’s equation we can obtained the boundary condition as

\[
\frac{k_{x1}}{\varepsilon_1} + \frac{k_{z2}}{\varepsilon_2} = 0 \quad (1.1)
\]

and

\[
k_{x1}^2 + k_{z1}^2 = \varepsilon_i \left(\frac{\omega}{c}\right)^2 \quad i = 1, 2 \quad (1.2)
\]

where \(k_x\) and \(k_z\) indicate the wave vector parallel or perpendicular to the interface, \(\varepsilon\) is dielectric constants, \(\omega\) is the angular frequency of the light, \(c\) denotes the speed of light, and 1 or 2 indicates each medium. By solving these equations we can get that

\[
k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad (1.3)
\]
The effective surface plasmon wavelength $\lambda_{sp}$ can be calculated by

$$\lambda_{sp} = \frac{2\pi}{k_x}$$  \hspace{1cm} (1.4)

If we assume medium 2 is dielectric, like air or glass, then $\varepsilon_2 > 0$. To satisfy Equation (1.1), we should have $\varepsilon_1 < 0$, which indicates the SPs could be excited at the metal/dielectric interface. However, SPs will lose energy during propagating along the surface of metal due to the absorption of the metal. We can define the propagation length, $L$, as the distance when SPs intensity decreases by a factor of $1/e$, and $L$ can be obtained from the imaginary part of $k_x$ by

$$L = \frac{1}{2 \text{Im}(k_x)}$$  \hspace{1cm} (1.5)

Surface plasmon resonance (SPR) usually appears on a metal film when the frequency of incident light matches the natural frequency of surface electrons oscillation. For a nanometer sized metal structure, the localized surface plasmon resonance (LSPR) could be obtained, as shown in Figure 1-1(b). Both SPR and LSPR are very sensitive to the material size, shape, and surrounding environment. As a result, they can be utilized to design chemical sensors and biosensors. SPR and LSPR can also lead us to control light at sub-wavelength dimension beyond the diffraction limit, and miniaturization of optical devices could be achieved based on them, for example, to achieve light focusing, splitting, filter, imaging, and waveguides at nanometer size dimension. Silver or gold materials are usually used to obtain SPR or LSPR at the visible spectral region.
Raman scattering and fluorescence are two important phenomenon in the nature, and have wide and significant applications in science. In experiment they are different but inside the mechanism they are both related with the vibration energy states of the molecules. In this section I will give a brief introduction for them.

The Raman scattering is the inelastic scattering of a photon by a molecule. When the photons are scattered by a molecule, most photons are elastic scattered, which means the
scattering photons have the same frequency with the incident photons and is called the Rayleigh scattering. A very small portion of photons have inelastic scattering which means the frequency of the scattered photons is different from the incident ones and is called Raman scattering. The reason can be explained as following. When incident photons reach a molecule, the molecule can absorb the energy from the photons and be excited to a higher energy state. The molecule will then lose the energy and drop back to ground energy state, but the emitted energy could be different from the excited energy when the molecule drops back to a different vibration energy state other than the initial one. The different scattering frequency includes Stokes scattering where the scattering frequency is smaller than the incident frequency, and Anti-Stokes scattering where the scattering frequency is larger than the incident frequency, as shown in Figure 1-2. The Rayleigh scattering usually has the highest intensity since most molecules will get back to the original vibrational energy state. The Stokes scattering has higher peak than anti-Stokes scattering since initially there are more molecules staying in ground vibrational energy state than higher energy state.
Fluorescence is the emitting light from a substance which absorbed light. When fluorescence occurs, the molecule is firstly absorbing the energy from the incident light and excited to a higher electronic energy state. The molecule stays at the excited stated for a certain time, and relaxes to ground state by emitting photons which is called radiative decay. Some of the relaxing energy will be released in the form of non-radiative decay like thermal energy. Therefore the wavelength of emission light is usually longer than the incident wavelength. There are two important parameters to describe the fluorescence, which are the lifetime and quantum yield. The lifetime indicates the average time the molecules stay in excited energy state before emitting light. The decay of the molecule concentration in excited energy state \([S1]\) can be treated as first-order reaction.

\[
[S1] = [S1]_0e^{-rt}
\]  

(1.6)
where $\Gamma$ is the decay rate. The lifetime is defined as the time when $[S1]$ decreases by a factor of $1/e$.

The fluorescence quantum yield describes the efficiency of the fluorescence process. It’s defined as the ratio of emitted photons number during the fluorescence process to the absorbed photons number during the absorbing process.
CHAPTER 2: LITERATURE REVIEW

2.1 The Properties of Surface Plasmon

The existence of surface plasmons (SPs) was demonstrated by Ritchie in 1957. SPs have attracted extensive interest by wide range of scientists in recent decades. Due to the novel properties of SPs, it could help people in kinds of perspectives, from achieving new structure at nanometer sized dimension to designing solar cells with high efficiency, from miniaturizing optical devices beyond the diffraction limit to designing new chemical sensors or biosensors. The SPs and localized SPs have very sensitive properties to the material, shape, size or environment.

2.1.1 Nanoparticles

The resonance wavelength of a silver or gold spherical nanoparticle significantly depends on the particle size. The resonance wavelength has red shift as the particle becomes larger. A gold nanoparticle with 9 nm diameter has a resonance wavelength at 517 nm. The peak shifts to 575 nm when its diameter increases to 99 nm. That’s the reason why the gold nanoparticles with different size in solution have different colors. El-Sayed et.al. also showed that the absorption peak of a spherical gold nanoparticle doesn’t change much at the temperature of 18 or 72°C.10

Mirkin and co-workers showed a method to analyzing combinatorial DNA array using gold nanoparticle probes.11,12 Mirkin group also showed that the nanoparticles could be used as detectors in biodiagnostics based on optical, electrical or magnetic relaxation detection.13 For example, with the existence of complementary target DNA, the oligonucleotide-functionalized
gold nanoparticles will get aggregated with each other, which will result in the change of red solution to blue one. As a result, the process of gold particle aggregation can be observed using a UV-vis spectroscopy to detect the presence of DNA.

Maier et. al. demonstrated that the electromagnetic energy can transport from a localized source with subwavelength dimension to a detector for a distance of 500 nm in plasmon waveguides which are consisted of closely spaced silver nanoparticles.\textsuperscript{14}

Van Duyne et. al. reviewed how the single nanoparticle and nanoparticle arrays can be used as biosensing. The localized surface plasmon resonance has significantly sensitive properties by shape and size of particle as well as the environment, therefore it can be applied to detect the binding of molecules and changes about the conformation of molecules. There are several challenges in current study, for example, to increase the sensitivity to the limit of single molecule detection, to combine other molecular identification techniques with LSPR, and to develop practical sensors for wide range detection.\textsuperscript{15}

Zou demonstrated that the extinction spectra can have very narrow lineshapes by using one-dimensional silver nanoparticle array. Extremely narrow extinction peak could be produced at the wavelength equals to twice of particle spacing when a one-dimensional array of silver nanoparticles is arranged parallel to incident wavevector and perpendicular to incident polarization direction.\textsuperscript{16}
Metal nanoparticles are also used to achieve surface enhanced Raman scattering. The enhancement factor is proportional to $|E|^4$ of the local electric field. Metal nanoparticles can generate highly enhanced electric field around them, where is called the ‘hot spots’. The Raman scattering could be extremely enhanced if the molecules are put in the hot spots. Kneipp and co-workers achieved the detection of Raman scattering of single molecule for the first time by measuring the scattering spectrum of a single molecule of crystal violet in the solution of colloidal silver.\textsuperscript{17} Nie et. al. reported that the Raman scattering of a single molecule of rhodamine 6G could be enhanced to a factor of $10^{14}$ to $10^{15}$ when adsorbed on silver nanoparticle.\textsuperscript{18}

Optical properties of metallic core shell particles had been investigated extensively\textsuperscript{19-29}. Halas group showed that a plasmon resonance wavelength could be obtained from 600 to over 1000 nm for gold-coated Au$_2$S particle when the ratio of the radius of core to the radius of particle is changed from 0.6 to 0.9.\textsuperscript{21}

Sensing applications of a single metallic core shell particles and particle arrays had been demonstrated\textsuperscript{26,30,31}.

West and co-workers demonstrated that gold nanoshell could be used to for thermal ablative therapy for cancer.\textsuperscript{32} Gold nanoshells are tuned to have strong absorption for near infrared light at the wavelength of 820 nm. Human breast carcinoma cells incubated with nanoshells were detected to have photothermally induced morbidity by illumination of NIR light.
2.1.2 Nanofilms

Ebbesen and co-workers demonstrated that extraordinary optical transmission could be obtained through subwavelength hole arrays in a silver nanofilm. The highest transmission efficiency could be larger than one when it’s normalized with the holes area. Their pioneering work stimulated extensive interests in the investigations of the optical properties of perforated metal films.

Chang et. al. investigated isolated and periodic holes in gold nanofilm by theoretical calculation using 3-D finite-difference time-domain method, and proved that enhanced transmission efficiency is related with surface plasmon polaritons and localized surface plasmon polaritons.

Thin films with reduced scattering and improved absorption efficiencies have applications in many fields such as solar cells. There are many different approaches in the design of films with reduced reflectivity, which include monolayer interference coating, coating with gradient refractive index. Monolayer interference coating requires the film thickness to be about a quarter of the incident wavelength, so the reflective light has opposite phase with incident light and they could be cancelled with each other to decrease the reflection light.

The reflection coefficient $R$ obeys to Fresnel’s equation when a reflection occurs at the interface of two medium and for normal incident light $R$ could be express as
\[ R = \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2 \]  

(2.1)

where \( n_1 \) and \( n_2 \) are the indices of refraction of two medium. Fresnel’s equation shows that small reflection could be obtained when the refraction index of two mediums are close to each other. As a result, the gradient refractive index structure is designed to reduce the reflection. However, it’s difficult to find the materials with suitable index of refraction, especially for the materials with refractive index of smaller than 1.4. For example, we can’t find dense materials with extremely low refractive index of, like 1.10 or 1.20, in the nature.\(^{50}\) Schubert et. al. demonstrated that the small refractive index of 1.08 could be obtained by silica nanorod array dielectric films.\(^{51}\) By using a graded-index coating film which has three layers of TiO\(_2\) nanorod and two layers of SiO\(_2\) nanorod, they shows that very low reflection of as small as 0.1\% could be achieved.\(^{50}\)

Moths’ eyes have the similar property that their surfaces are covered with a natural nanostructure film which can eliminate reflections. This property allows moths to see well in dark, as well as no reflection of light to give their location away to predators.\(^ {52}\) As a result, moth eye structures or porous films\(^ {53-57}\) are utilized to reduce the effective index of refraction of the surface and minimize the surface scattering\(^ {48-50,58-61}\). Minot showed that a single layer antireflection glass film could effectively reduce the reflection from 8\% to 0.5\% for the wavelength from 0.35 to 2.5 \( \mu \text{m} \).\(^ {62}\) Jiang and co-workers showed that the anti-reflection coatings with subwavelength dimension on the substrates of single-crystalline silicon could be obtained
and the inverted pyramid array structure could reduce the reflection from 40% to 10% at the wavelength region from 600 to 800 nm.\textsuperscript{53}

2.1.3 Nanorods

Understanding light propagation along a path with subwavelength dimensions over a substantial long distance may open new opportunities for the design of waveguide\textsuperscript{63-72} and subwavelength imaging\textsuperscript{73-82} devices. Due to the diffraction limit, light may only propagate along a subwavelength path with a pre-designed structure. Various metal nanostructures have been demonstrated to achieve relatively long distance propagation of light beyond the diffraction limit.

Light propagation along a metal nanoparticle chain with a propagation distance over several hundred nanometers had been proposed and experimentally demonstrated\textsuperscript{14,16,83-91}.

Law et al. demonstrated individual nano-ribbons of crystalline oxide could be used as optical waveguides at subwavelength dimension and the propagation distance can reach several hundred microns. But the dimension of the nanoribbons is still relatively large which is about several hundred nanometers.\textsuperscript{92}.

Nanowire waveguide based on small organic molecule was reported by Zhao et al.\textsuperscript{93} They use 2,4,5-triphenylimidazole molecule to fabricate nanowire which could have light propagation distance to several tens of microns.
Zou et al. proposed that silver nanoparticle chain structures can be used as waveguide to propagate light over several hundred microns and the propagation direction could be perpendicular to the incident wavevector. The nanoparticle chain is partially illuminated and the particle spacing is similar to the wavelength. The other part of the chain is non-illuminated and the particle spacing is approximately half of the wavelength.\(^91\)

K. Kempa et al.\(^{94,95}\) demonstrated light propagation along a nanocoaxial cable of carbon nanotube-\(\text{Al}_2\text{O}_3\)-Cr structure with inner diameter 100 nm and outer diameter 300 nm, and showed that the light might propagate over 6 microns along the cable.

Silveirinha and co-workers theoretically investigated that subwavelength imaging at infrared frequencies using an array of metallic nanorods with a resolution of \(1/10\) of wavelength and over a propagation distance of \(0.6\) of wavelength.\(^96\) They also experimentally demonstrated that imaging at microwave regions could be achieved using the metallic nanorods array to obtain a propagation distance of \(3.5\) times larger and a resolution of \(15\) times less than the wavelength.\(^97\)

The early research proved that nanostructure materials could focus incident wave and be used as a lens. But there are two major restrictions, one is that they can only transfer the image to a short distance in the region of near field, and the other is that they can only be used at specific wavelength, which means color imaging couldn’t be achieved. S. Kawata\(^{98}\) proposed a lens made of silver nanorods, which could be useful in the development of color imaging techniques with subwavelength resolution in the visible wavelengths\(^{99}\).
2.2 Fluorescence Quenching and Enhancement

The energy transfer between fluorophore molecules and metal nanostructures has attracted significant interest in recent years. These research not only advances our fundamental understanding of the mechanism for the energy transfer between fluorophores and metal nanostructures, but also provides solid bases for applications such as bio-sensors. The fluorescence signal from a molecule is influenced by a nearby metal particle in two ways, one is the energy transferred from the dye molecule to nanostructure in the form of radiative decay and non-radiative decay, the other is the enhanced local electric field by the metal structure at both excitation and emission wavelengths. The detailed mechanism is still under controversy.

2.2.1 Experiment work

2.2.1.1 The enhancement of fluorescence by metallic nanostructures

In the previous literature, both enhanced and quenched fluorescence signal of dye molecule placed near metal nanoparticles have been reported. Enhanced fluorescence has been experimentally demonstrated by using various types of metallic structures. Spherical nanoparticles, for example core-shell nanoparticles, nanorods, bowtie structures, or tips.

Ginger et. al. demonstrated that fluorescent dyes attached to silver nanoprisms by DNA linker of ~5.5nm distance could have enhanced fluorescence signal, and the brightest
fluorescence is usually obtained near nanoparticles with LSPR peaks that are only slightly blue-shifted from the dye emission peak.\textsuperscript{107}

Bakker and co-workers showed that pairs of elliptical nanoparticles can be used to form antennae which has resonance peak in visible wavelength region, and they can be used to enhance the fluorescence of 100 times at different wavelength.\textsuperscript{108}

Acuna et. al. introduced self-assembled nanoantennas by linking DNA origami structures with one or two gold nanoparticles. They investigated the influence of nanoparticle size and number on the fluorescence enhancement and compared with numerical calculation. When a dye molecule is placed in the 23 nm gap of 100 nm gold nanoparticles, a maximum enhancement factor of 117 could be obtained.\textsuperscript{101}

Halas group demonstrated that an enhancement factor of ~40 could be obtained for the near-infrared fluorophore IR800 by the influence of Si/Au core/shell nanoparticles with 63 nm core radius and 78 nm shell radius.\textsuperscript{112}

Gerritsen et. al. investigated the properties of metal core/silica shell nanoparticles on fluorophore and obtained a highest enhancement factor of 12.5 for cascade yellow molecule when the core diameter is 47.2 nm and the averaged dye-metal core distance is 68 nm.\textsuperscript{113}
Fu and co-workers showed that a dye-labeled single stranded DNA could be conjugated to a biotin end-capped gold nanorod when the length of rod is 80 nm and diameter is 13 nm. A remarkable increase in fluorescence of single fluorophore was observed with a factor of 40.\textsuperscript{115}

Hecht et. al. observed the enhanced fluorescence of a single fluorophore at a gold tip and the enhancement factor of the fluorescence signal of ~5.7 was obtained. The enhancement is suggested to be due to the resonance plasmon excitation, since they didn’t observed the enhancement of fluorescence using Pt/Ir tips.\textsuperscript{117}

Moerner group reported that an enhancement factor of up to 1340 could be obtained for a single molecule placed between a gold bowtie nanoantenna. The quantum yield of the fluorophore molecule is very low of ~2.5%. The electromagnetic simulations proved that the enhancement is due to the significantly absorption as well as the increasing of radiative emission rate.\textsuperscript{116}

Chou group designed a new disk-coupled dots-on-pillar antenna array structure and optimized the spacer, and showed that an enhancement factor of 2970 and $4.5 \times 10^6$ for area-average and single-molecule placed at a hot spot could be achieved for the fluorescence signal of ICG dye molecule\textsuperscript{120}.

2.2.1.2 The quenching of fluorescence by metallic nanostructures

In the meanwhile, fluorescence quenching has also been reported by many groups\textsuperscript{121-126}. 

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Liu and co-workers used rigid DNA as the spacer to separate the dye molecules away from the gold nanoparticles with controlled 1:1 ratio which could achieve precise determination of the influence of gold nanoparticles at different distance on the fluorescence intensity. The fluorescence quenching of dye molecules Cy3 and Cy5 was obtained with gold nanoparticle of 5 or 10 nm diameter. The experiment results have good agreement with the calculation using our proposed model which will be discussed in Chapter 5.\textsuperscript{121}

Klar et. al. carried out time-resolved fluorescence experiments of lissamine dye molecules which are chemically attached to gold particles with different sizes and investigated the radiative and non-radiative decay rates. With a nanoparticle as small as 1 nm radius, a fluorescence quenching was observed.\textsuperscript{123} The same group also showed that a hybrid system of Cy5 molecules linked to gold particles with 6 nm radius using ssDNA could reduce the fluorescence in the distance range between 2.2 and 16.2 nm. The different distance between the Cy5 molecule and the nanoparticle surface could be tuned by the different surface coverage of ssDNA.\textsuperscript{124}

Acuna and co-workers investigated the influence of a metallic particle of 10 nm diameter at different distance on the quenching of fluorescence. The distance between molecule and nanoparticle could be controlled by using the self-assembled DNA structures.\textsuperscript{125}

Novotny and co-workers showed experimentally and theoretically a continuous transition from fluorescence enhancement to quenching for a single nile blue molecule placed close to a
gold spherical nanoparticle. The continuous transition could be obtained by varying the distance from the metal particle to the dye molecule.\textsuperscript{126}

**2.2.2 Theoretical work**

There has been many theoretical works for the calculation of energy transfer between a molecule and metal structures\textsuperscript{127-130}.

Förster resonance energy transfer (FRET) is commonly employed to describe the mechanism of energy transfer between dipoles. It shows that the energy transfer rate between two dipoles separated by a distance $d$ is proportional to $1/d^6$. FRET is limited to detectable distance of smaller than 10 nm since the Förster distance is generally in the range of 3-6 nm.\textsuperscript{127}

Strouse and co-workers proposed the surface energy transfer theory to describe the energy transfer rate from a dipole to a metal surface with a distance larger than 10 nm where the energy transfer rate is proportional to $1/d^4$.\textsuperscript{128}

Nitzan and co-workers developed a theoretical model to compute the surface enhanced Raman scattering and enhanced or quenching fluorescence from molecule adsorbed on a rough surface of silver. They showed that the enhancement factor can be obtained from the electric field at excitation and emission frequency, the population relaxation rate, and the thermalization rate. They found that silver film can enhance the normal Raman scattering as much as $10^5$, The resonance Raman scattering by $10^3$, and fluorescence by 10 for molecules with high quantum yield. For molecules with low quantum yield, the factor is less than 0.1.\textsuperscript{131}
Lakowicz proposed a radiating plasmon model to describe the fluorophores near metal surface, which showed that the fluorescence besides the metal could be obtained using the optical properties of the different structures of metal. For example, the incident energy is consumed by absorption of the metal, and far-field radiation is generated from the light scattering. The model showed consistence with a wide range of experiments, and could provide a potential guidance to design metal-dye molecule configuration to achieve desirable properties.132
CHAPTER 3: METHODS

3.1 Introduction

Maxwell’s equations are the foundation of the classic electrodynamics theory and describe how electric and magnetic fields are generated and altered by each other. In 1908, Gustav Mie demonstrated how to calculate light scattering by small spherical particles using Maxwell’s electromagnetic theory for the first time.\textsuperscript{133} The Mie theory successfully explained the color changing of gold colloids with different size of gold particles. Many numerical methods have been demonstrated to calculate the optical properties of metal nanostructures. In this chapter I will discuss several computational methods, which are general Mie theory\textsuperscript{133,134}, T-matrix method\textsuperscript{135-141}, discrete dipole approximation method\textsuperscript{142-148}, and coupled-dipole method.

3.2 Mie Theory

General Mie theory\textsuperscript{133,134} is an analytical solution to the optical properties of a single spherical particle. For a spherical particle with core-shell structure which is illuminated by plane electromagnetic wave, we can use the vector spherical harmonics to describe the electromagnetic fields in the shell, core and out of the particle and the incident light.

We can express the incident plane wave as

$$E_i = E_0 \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (M^{(i)}_{\alpha \beta} - iN^{(i)}_{\alpha \beta}), \quad (3.1)$$
\[ H_i = \frac{-k}{\omega \mu} \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (M^{(1)}_{eln} + iN^{(1)}_{oIn}), \tag{3.2} \]

where the electromagnetic fields within the core, shell and outside the particle can be obtained as

\[ E_1 = \sum_{n=1}^{\infty} E_n (c_n M^{(1)}_{oIn} - id_n N^{(1)}_{oIn}), \tag{3.3} \]

\[ H_1 = \frac{-k}{\omega \mu_i} \sum_{n=1}^{\infty} E_n (d_n M^{(1)}_{eln} + ic_n N^{(1)}_{oIn}), \tag{3.4} \]

\[ E_{sh,j} = \sum_{n=1}^{\infty} E_n (f_{n,j} M^{(1)}_{oIn} - ig_{n,j} N^{(1)}_{oIn} + \nu_{n,j} M^{(2)}_{oIn} - i\omega_{n,j} N^{(2)}_{oIn}), \tag{3.5} \]

\[ H_{sh,j} = \frac{-k_j}{\omega \mu_j} \sum_{n=1}^{\infty} E_n (g_{n,j} M^{(1)}_{eln} + if_{n,j} N^{(1)}_{oIn} + w_{n,j} M^{(2)}_{eln} + i\nu_{n,j} N^{(2)}_{oIn}), \tag{3.6} \]

\[ E_s = \sum_{n=1}^{\infty} E_n (ia_n N^{(3)}_{oIn} - b_n M^{(3)}_{oIn}), \tag{3.7} \]

\[ H_s = \frac{k}{\omega \mu} \sum_{n=1}^{\infty} E_n (ib_n M^{(3)}_{oIn} + a_n N^{(3)}_{oIn}), \tag{3.8} \]

where \( k \) and \( k_j \) are the wave vectors in the environment and \( j^{\text{th}} \) shell, \( \omega \) refers to the angular frequency of the light, \( \mu \) and \( \mu_j \) represent the permeabilities of the environment and \( j^{\text{th}} \) shell, \( n \) denote the degree of the functions, \( a, b, c, d, g, f, w, v \) are expansion coefficients, \( E_1, H_1, \) are the
electromagnetic fields in the core and $E_s$, $H_s$ are the scattered ones. $E_{sh,j}$ and $H_{sh,j}$ represent fields within the $j^{th}$ shell. $E_0$ denotes the magnitude of incident electric field $E_i$ is expressed as

$$E_n = i^n \frac{E_0 (2n + 1)}{n(n + 1)}.$$  \hspace{1cm} (3.9)

Vector functions $M$ and $N$ are

$$M_{0ln} = \cos \phi \pi_n (\cos \theta) z_n (\rho) \hat{e}_\theta - \sin \phi \pi_n (\cos \theta) z_n (\rho) \hat{e}_\phi, \hspace{1cm} (3.10)$$

$$M_{eln} = -\sin \phi \pi_n (\cos \theta) z_n (\rho) \hat{e}_\theta - \cos \phi \pi_n (\cos \theta) z_n (\rho) \hat{e}_\phi, \hspace{1cm} (3.11)$$

$$N_{0ln} = \sin \phi n(n + 1) \sin \theta \pi_n (\cos \theta) \frac{z_n (\rho)}{\rho} \hat{e}_r + \sin \phi \pi_n (\cos \theta) \frac{[\pi_n (\rho)]}{\rho} \hat{e}_\theta + \cos \phi \pi_n (\cos \theta) \frac{[\pi_n (\rho)]}{\rho} \hat{e}_\phi, \hspace{1cm} (3.12)$$

$$N_{eln} = \cos \phi n(n + 1) \sin \theta \pi_n (\cos \theta) \frac{z_n (\rho)}{\rho} \hat{e}_r + \cos \phi \pi_n (\cos \theta) \frac{[\pi_n (\rho)]}{\rho} \hat{e}_\theta - \sin \phi \pi_n (\cos \theta) \frac{[\pi_n (\rho)]}{\rho} \hat{e}_\phi, \hspace{1cm} (3.13)$$
superscripts appended to the functions $M$ and $N$ are the kinds of spherical Bessel function $Z_n$: (1) represents $j_n(\rho)$ and (3) refers to the first kinds of $h_n(\rho)$. (2) indicates $j_n(\rho)$ for $N$ functions and $y_n(\rho)$ for $M$ functions, the dimensionless $\rho = kr$ with $r$ the radius of the shell and $k$ the wave vector. $\theta$ and $\phi$ are the spherical polar angles. The functions

$$\pi_n = \frac{P^1_n}{\sin \theta}, \quad \tau_n = \frac{dP^1_n}{d\theta},$$

(3.14)

$P^1_n$ is the associated Legendre functions of the first kind with order 1 and degree $n$.

The expansion coefficients could be expressed with boundary conditions at every interface.

$$E_{\theta}^{\text{in}} = E_{\theta}^{\text{out}}, \quad E_{\phi}^{\text{in}} = E_{\phi}^{\text{out}},$$

$$H_{\theta}^{\text{in}} = H_{\theta}^{\text{out}}, \quad H_{\phi}^{\text{in}} = H_{\phi}^{\text{out}},$$

(3.15)

where the superscripts $\text{in}$ and $\text{out}$ denote the electromagnetic fields inside and outside the interface surface.

$P^1_n$ is the associated Legendre functions of the first kind with degree $n$ and order 1.
The extinction and scattering cross sections are calculated with equation

\[ C_{\text{sca}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2) \]  \hspace{1cm} (3.16)

\[ C_{\text{ext}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}(a_n + b_n) \]  \hspace{1cm} (3.17)

The absorption cross section \( C_{\text{abs}} \) could be calculated from \( C_{\text{ext}} - C_{\text{sca}} \). The extinction, scattering, and absorption efficiencies are obtained by dividing the cross sections with the physical cross section of the particle.

### 3.3 T-matrix Method

T-matrix method is an accurate and low-cost method for the computation of spectra of an array of spherical nanoparticles with arbitrary radius and position. It was proposed by Waterman\(^{135}\) in 1971. Mishchenko, Mackowski and coworkers\(^{136-141}\) made significant improvement to the method. We briefly introduce the theory here.

For an array of spherical particles, the scattered electric field \( E_s \) is the sum of the electric field from each sphere \( E_{s,i} \),

\[ E_s = \sum_{i=1}^{N} E_{s,i} , \]  \hspace{1cm} (3.18)
where \( N_s \) is the number of sphere. \( E_{s,i} \) can be represented with vector spherical harmonics,

\[
E_{s,i} = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} \sum_{p=1}^{2} a_{mnp}^i h_{mnp}(r_i),
\]

(3.19)

where \( m \) and \( n \) are the degree and order for the spherical harmonics \( h_{mnp} \), \( a_{mnp}^i \) is the expansion coefficient for particle \( i \), \( p \) is the mode of scattered electric field, with \( p=1 \) means transverse magnetic mode (TM) and \( p=2 \) means transverse electric mode (TE). If the expansion coefficient is truncated to \( n=N_i^j \),

\[
ad_{mnp}^i - d_{nlp} = \sum_{j=1}^{N_s} \sum_{l=1}^{N_i} \sum_{k=-l}^{l} \sum_{q=1}^{2} H^{ij}_{mnpklq} a_{klq}^i = -d_{nlp}^i p_{mnp}^i,
\]

(3.20)

where \( H^{ij}_{mnpklq} \) denotes the Hankel-function-based addition coefficients, \( a_{nlp}^i \) are the TM and TE Mie coefficients, and \( p_{mnp}^i \) are the coefficients of the incident wave at the origin of the \( i \)th sphere.

Then \( a_{mnp}^i \) can be transferred to a T matrix,

\[
a_{mnp}^i = \sum_{j=1}^{N_s} \sum_{l=1}^{N_i} \sum_{k=-l}^{l} \sum_{q=1}^{2} T^{ij}_{mnpklq} p_{klq}^j.
\]

(3.21)
To describe all the spheres as a whole, we need describe the electric field based on a single coordinate origin. We can have the expansion coefficient for the scattered field expressed as

\[ d_{mp}^0 = \sum_{i=1}^{N_s} \sum_{l=1}^{N_l} \sum_{k=-l}^{l} \sum_{q=1}^{2} J_{mpklq}^{0i} a_{klq}^i, \]  

where \( J_{mpklq}^{0i} \) are addition coefficient. Then we can have

\[ d_{mp}^0 = \sum_{i=1}^{N_s} \sum_{l=1}^{N_l} \sum_{k=-l}^{l} \sum_{q=1}^{2} T_{mpklq}^{0} P_{klq}^{0}, \]  

Finally the orientation-averaged extinction cross section of the array of particles can be obtained as

\[ C_{ext} = \frac{2\pi}{k^2} \text{Re} \left( \sum_{n=1}^{N_s} \sum_{m=-n}^{n} \sum_{p=1}^{2} T_{mpmp}^{0} \right). \]  

### 3.4 Discrete Dipole Approximation Method

Mie theory and T-matrix method can be utilized for the computations of optical properties of a single or array of spherical particles. Many new calculation methods had been developed for the investigations of optical properties for particles with arbitrary shape\textsuperscript{146-148}, such as Discrete Dipole Approximation (DDA)\textsuperscript{142-144,149-154}, Finite Difference Time Domain
(FDTD)\textsuperscript{155-158}, and Extended Boundary Condition (EBCM)\textsuperscript{159-161} methods. The review for the comparison between these computational methods by Wriedt et al.\textsuperscript{162} shown that the DDA method needs less computation time and generates more accurate results. The DDA method was first proposed by Purcell and Pennypacker\textsuperscript{142}, and had been developed and improved by Draine and Flatau groups\textsuperscript{143-145}. For the DDA method, there are also many available computational codes, such as DDSCAT\textsuperscript{142-144}, ZDD\textsuperscript{149-151} and ADDA\textsuperscript{152-154}. The comparison of these different codes is reported by Antti Penttila et al\textsuperscript{163}. In this chapter, some of the calculations are carried out with the modified DDSCAT computational code developed by Draine et al.\textsuperscript{143,145}. The detailed information about the DDSCAT code could be found in Draine’s papers\textsuperscript{143,144}. We will discuss a brief introduction of the method in the following paragraphs.

In the DDA method, the target particle with arbitrary shape is divided into $N$ polarizable cubes. The positions and polarizabilities of each cube is denoted with $r_i$ and $\alpha_i$. By solving the electrodynamics properties of the dipole array when the incident light is applied to the target, the optical properties can be obtained after the localized electric field and polarization at each cube position are calculated.

The polarization of each dipole is caused by the incident wave and the retarded fields which are caused by all the other dipoles, and could be obtained as:

$$
P_i = \alpha_i E_{loc,i}, \quad i=1,2,\ldots,N \tag{3.25}
$$
where $E_{\text{loc},i}$ is the localized electric field which equals to the retarded plus incident electric fields where the retarded part comes from all the other dipoles. At specific wavelength $\lambda$ of incident light, the local electric field is expressed as:

$$E_{\text{loc},i} = E_{\text{inc},i} + E_{\text{retard},i} = E_0 \exp(ik \cdot r_i) - \sum_{j=1}^{N} A_{ij} \cdot P_j, \quad i=1,2,\ldots,N,$$

(3.26)

where $E_0$ means the amplitude of the incident light, $k=2\pi/\lambda$ is the wave vector of incident light with the wavelength $\lambda$. $A$ is the interaction matrix and can be shown as:

$$A_{ij} \cdot P_j = k^2 \exp(ikr_{ij}) \frac{r_{ij} \times (r_{ij} \times P_j)}{r_{ij}^3} + \exp(ikr_{ij})(1 - ikr_{ij}) \frac{r_{ij}^2 P_j - 3 r_{ij} \cdot (r_{ij} \cdot P_j)}{r_{ij}^3}$$

(i=1,2,\ldots,N, j=1,2,\ldots,N, j\neq i),

(3.27)

where $r_{ij} = r_i - r_j$ denotes the vector of distance between the two dipoles $i$ and $j$. From the previous three equations, we can obtain

$$(\alpha_i^{-1}) P_i + \sum_{j=1}^{N} A_{ij} \cdot P_j = E_{\text{inc},i}, \quad i=1,2,\ldots,N.$$  

(3.28)

It can be expressed as a $3N$ linear equation as
\[ A'P = E, \]

and the matrix’s diagonal elements are \( \alpha_j^{-1} \) which comes from the polarizability, and the off-diagonal elements are symmetric. After solving this equation we can obtain the polarization and local electric field of each cube.

The extinction and scattering cross section can be calculated from the dipole and local electric field as:

\[
C_{\text{ext}} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \text{Im}(E_{\text{inc},j}^* \cdot P_j), \quad (3.29)
\]

\[
C_{\text{sca}} = \frac{k^4}{|E_0|^2} \int d\Omega \left| \sum_{j=1}^{N} (P_j - \hat{n} \cdot P_j) \exp(-i\mathbf{k} \cdot r_j) \right|^2, \quad (3.30)
\]

where \( \hat{n} \) is the unit vector along each direction of scattering, and \( \Omega \) is the integration angle in the space. The absorption cross section is calculated with \( C_{\text{ext}} - C_{\text{sca}} \).

The unit of the extinction, scattering and absorption cross section obtained here is the unit of area, the corresponding efficiencies of particles or films are calculated from dividing the cross sections with the physical areas of the nanoparticles or films.
3.5 Coupled Dipole Method

For spherical nanoparticle or nanoparticle arrays, the coupled-dipole approximation method could be applied to get an more simple solution to the calculation. When the wave vector of incident light is vertical to the long axis of a nanoparticle array, and if we assume induced polarization at every particle has same value, a simple analytical solution to Equation (3.29) can be obtained. The polarization of each particle can be expressed from the polarizability as:

\[
P = \frac{\alpha_s E_0}{1-\alpha_s S} = \frac{E_0}{1/\alpha_s - S} \tag{3.32}
\]

and the extinction cross section of every particle could be calculated as

\[
C_{ext} = 4\pi k \text{ Im} \left( \frac{P}{E_0} \right) = 4\pi k \text{ Im} \left( \frac{1}{1/\alpha_s - S} \right) \tag{3.33}
\]

where \( S \) denotes the sum of retarded dipoles

\[
S = \sum_{j \neq i} \left[ \frac{(1-ikr_{ij})(3cos^2\theta_{ij}-1)e^{i\alpha r_{ij}}}{r_{ij}^3} + \frac{k^2sin^2\theta_{ij}e^{i\alpha r_{ij}}}{r_{ij}} \right] \tag{3.34}
\]

The polarizability in Equation (3.32) is

\[
\alpha_s = \frac{3a_1}{2k^3} \tag{3.35}
\]
where $k$ represents the wave vector of the incident light, $a_1$ means expansion coefficients from the Mie theory which can be obtained from

$$a_1 = \frac{\mu m^2 j_1(mp)[\rho j_1(\rho)]' - \mu_j j_1(mp)[mpj_1(mp)]'}{\mu m^2 j_1(mp)[\rho h_1(\rho)]' - \mu_j h_1(mp)[mpj_1(mp)]'}$$

(3.36)

In this expression, $m$ denotes the ratio of the refractive indices in and out of the particle, $\rho = kr$, where $r$ denote particle radius, $j_1, h_1$ denote the usual spherical Bessel functions, and $\mu_i, \mu_o$ are the magnetic permeabilities in and out of the particle respectively.
CHAPTER 4: TRAPPING AND PROPAGATING LIGHT AT SUBWAVELENGTH DIMENSION WITH SILVER NANOSTRUCTURES

4.1 General Introduction

In this chapter I will discuss the novel optical properties of different metal nanostructures using theoretical methods.

The first part is the extremely low scattering cross section of a perforated silver film. With a perforated silver nanofilm, we demonstrated that an extremely low scattering efficiency of less than 1% can be achieved at tunable wavelength with tunable widths. The resonance wavelength, width, and intensity are influenced by the shape, size and arrangement pattern of the holes, as well as the distance separating the holes along the polarization direction.

The second part discusses an effective and tunable light trapping thin film. Using the discrete dipole approximation method, we demonstrated that the enhanced absorption efficiencies, which are close to 100%, at tunable wavelengths in a two-layer silver thin film. Resonance wavelengths are determined by the distances between perforated holes in the first layer as well as the separation between the two layers. Geometries of conical frustum shaped holes in the first layer are critical for the improved absorption efficiencies.

The last part talks about the gain and loss of propagating electromagnetic wave along a hollow silver nanorod. We examined the electromagnetic wave propagation along a hollow silver nanorod with subwavelength dimensions. The calculations show that light may propagate along
the hollow nanorod with growing intensities. The influences of the shape, dimension, and length of the rod on the resonance wavelength and the enhanced local electric field, $|E|^2$, along the rod were investigated.

### 4.2 Extremely Low Scattering Cross Section of a Perforated Silver Film

#### 4.2.1 Introduction

Ebbesen’s pioneering work on the extraordinary optical transmission through subwavelength hole arrays\textsuperscript{33} stimulated extensive interests in the investigations of the optical properties of perforated metal films\textsuperscript{34-38}. The increased transmission could be resulted from decreased scattering or decreased absorption of the metal films, but there’s not much work to investigate the corresponding mechanism. In this section, I will report how the scattering spectra are affected by the perforated metal film structure.

Figure 4-1 shows a schematic of the simulation. In the simulations, the incident wave is parallel to the X direction, and polarization direction is along the Z axis. The film is arranged in the YZ plane. The film thickness is kept to be 100 nm in all the simulations. The silver’s dielectric constants are obtained from the handbook of Palik.\textsuperscript{164} Periodic boundary condition\textsuperscript{165} is applied to the DDA method.
Figure 4-1: Schematic of a perforated film. t represents the thicknesses of the film, d is the diameter of the holes in the film and P denotes the periodic distance of the squarely arranged hole arrays.

4.2.2 Results and Discussion

4.2.2.1 The Influence of Hole Diameter

We start with a silver film perforated with cylindrical holes arranged in a square lattice of 400 nm separation. The diameter of the hole is changed from 100, 200, to 300 nm. As shown in Figure 4-2(a), when the holes is separated by a fixed distance of 400 nm, the resonance dip becomes more prominent with the expansion of hole diameter. The width of the resonance dip also broadens correspondingly. For a perforated film with the diameter of holes to be 100 nm, the scattering cross section at the resonance wavelength of 470 nm drops only by 33% compared with that of a solid film with same thickness. When the diameter of hole is changed to 300 nm, the resonance wavelength is red shifted as 570 nm and scattering efficiency of the film drops
significantly to less than 1%. The corresponding absorption spectra of the same films are shown in Figure 4-2(b). Figure 4-2(b) shows that absorption peaks can be observed at the same wavelength associated with the remarkably low scattering efficiency. The enhanced absorption indicates that surface plasmon does play a role in the scattering reduction of the film.

![Figure 4-2: Scattering (a) and absorption (b) spectra for a 100 nm thick silver film with cylindrical holes arranged in a square lattice of 400 nm distance with different diameters (d) (A) d=100 nm, (B) d=200 nm, (C) d=300 nm.](image)

**4.2.2.2 The Influence of Hole Shape and Orientation**

The shape and orientation of the holes will play important roles on the scattering spectrum of the film. We investigated the perforated film when rectangular holes of different aspect ratios are arranged in a square lattice with a 400 nm distance. The area of the holes is fixed to be 67600 nm$^2$ which is approximately equivalent to the area of a cylindrical hole of 300 nm diameter. The shapes of the rectangular holes are chosen to be 220×320 nm$^2$, 240×290 nm$^2$, 35
and 260×260 nm². The holes are arranged with their short or long edge along the polarization direction of the incident light. Figure 4-3(a) shows that extraordinarily low scattering cross section can always be achieved for films with holes of different shapes and orientations. The resonance wavelength appears at short wavelength when the long edge of the rectangle is along the polarization direction, and shifts to longer wavelength with the decrease of edge length along the polarization direction. For example, when the 220×320 nm² rectangular holes are arranged with its long edge (320 nm) along the polarization direction, the reduced scattering dip appears at resonance wavelength of 475 nm. The resonance wavelength is shifted to 750 nm when the short edge (220 nm) is arranged along the polarization direction. The dip width widens with the drop of the edge length along the polarization direction.

Figure 4-3: Scattering (a) and absorption (b) spectra of a 100 nm thick silver film with rectangular holes of 400 nm distance and different shapes; (A) 220×320 nm², (B) 240×290 nm², (C) 260×260 nm², (D) 290×240 nm², (E) 320×220 nm². (The latter number is the edge length of hole parallel to the polarization direction.)
The corresponding absorption spectra of the perforated films are displayed in Figure 4-3(b), which shows the absorption spectra vary with the same trend but a less magnitude in comparison with the scattering spectra.

4.2.2.3 The Excited Electric Field

To understand the mechanism leading to the reduced scattering of the film, we calculate the electric fields, $|E|^2$, around holes. The electric field contour plots at the resonance wavelength of 595 nm for films with 260×260 nm$^2$ holes are displayed in Figure 4-4. Figure 4-4(a) shows the electric field contour plot in the YZ plane with a 5 nm distance away from the film surface and facing the incident wave. Figure 4-4(b) displays the electric field contour plot in the XZ plane through a hole center. The enhanced local electric field indicates that surface plasmons are excited at the resonance wavelength with a reduced scattering efficiency. The highest enhanced electric field, $|E|^2$, of 46 is obtained. Figure 4-4(b) shows that the enhanced electric fields are locally confined around the hole area.
Figure 4-4: The electric field, $|E|^2$, contour plots at resonance wavelength of 595 nm in the YZ (a) and XZ (b) planes for a film with 260×260 nm$^2$ rectangular holes.

### 4.2.2.4 The Influence of Each Edge of the Rectangular Hole

To further study the influence of the hole shape on scattering spectra of the film, we fix the edge length of the rectangular holes perpendicular to the polarization direction to be 260 nm and vary the other edge length from 65 to 325 nm. The holes are arranged in a square lattice with a 400 nm periodic distance. The scattering spectra are shown in Figure 4-5(a) which indicates that remarkably low scattering efficiencies can always be obtained when the edge length along the polarization direction is changed from 65 to 325 nm. The resonance wavelength is blue-shifted from 850 to 490 nm when the edge length is varied from 65 to 325 nm. The simulations show that the lowest scattering efficiency grows to larger than 10% when the edge length is decreased to 50 nm.
The effect of the edge length perpendicular to the polarization direction is explored by keeping the parallel edge length to be 260 nm and varying the perpendicular edge length from 65 to 325 nm as shown in Figure 4-5(b). The change in the perpendicular edge length has a more significant influence on the scattering intensity of the film. For holes with a 325 nm edge length perpendicular to the polarization direction, a broad resonance dip with the lowest scattering efficiency of less than 1% can be obtained at the wavelength of 680 nm. As the decreasing of the edge length, the resonance wavelength is shifted to shorter wavelength, the resonance width narrows, and the lowest scattering efficiency increases substantially. When the edge length is decreased to be 65 nm, the resonance dip at 375 nm wavelength becomes very weak.

Figure 4-5: Scattering spectra of a 100 nm thick silver film with rectangular holes of 400 nm distance and different edge lengths; (a) Holes with the same edge length (260 nm) perpendicular to the polarization direction and different parallel lengths; (b) holes with the same parallel edge length (260 nm) and different perpendicular lengths. (A) 65 nm, (B) 130 nm, (C) 195 nm, (D) 260 nm, (E) 325 nm for both (a) and (b).
4.2.2.5 The Influence of Periodic Distance

In the above simulations, the holes are always arranged in a square lattice and their center to center distance is fixed to be 400 nm. To investigate the influence of the distance between holes on the scattering efficiency and resonance wavelength, we arrange holes in a rectangular lattice. The dimension of the rectangular holes is kept to be 260×260 nm². We firstly fix the distance perpendicular to the polarization direction (Dᵥ) between holes to be 400 nm and change the parallel distance (Dₚ) from 300 to 500 nm. Figure 4-6(a) shows the resonance wavelength is very sensitive to the hole spacing along the polarization direction. When Dₚ is 300 nm, the lowest scattering efficiency can be found at the wavelength of 455 nm. When Dₚ is expanded to be 500 nm, the resonance wavelength is shifted to 695 nm. The depth and width of the resonance dip are varied slightly. The observed distance dependence of resonance wavelength is caused by the propagation direction of the surface plasmon on the metal film. The excited surface plasmon around each hole propagates along the polarization direction and the hole distance along the polarization direction is crucial in determining the resonance wavelength.

We further fix the hole spacing along the polarization direction (Dₚ) to be 400 nm and vary the distance along the perpendicular direction (Dᵥ). Figure 4-6(b) shows the resonance wavelength is not very affected by the perpendicular distance but the depth of the resonance dip can be altered dramatically. With the increasing of Dᵥ, the resonance dip evolves shallow due to the weaker coupling between holes and less hole area on the film.
Figure 4-6: Scattering spectra for a 100 nm thick silver film with square holes of the same area and different spacings: (a) Holes with a fixed 400 nm distance perpendicular to the polarization direction and different parallel distances. (A) 300 nm, (B) 400 nm, (C) 500 nm; (b) Holes with a fixed 400 nm parallel distance and different perpendicular distances: (A) 300 nm, (B) 400 nm, (C) 500 nm, (D) 600 nm, (E) 800 nm.

4.2.3 Summary

In summary, we investigate the reduced scattering of a perforated silver film. Extraordinarily low scattering cross sections with efficiency close to zero at tunable wavelengths with tunable width are demonstrated. The resonance wavelength, width, and intensity are influenced by the size, shape and arrangement pattern of holes. For the holes of the same area, rectangular holes with short edge length (larger than 100 nm) along the polarization direction generate more significant scattering reduction. The resonance wavelength shifts to red with the decrease of the edge length along the polarization direction, and also shifts to red with the increase of hole distance along the polarization direction.
4.3 Light Trapping Thin Films

4.3.1 Introduction

In the previous section, I showed that extremely low scattering efficiencies can be obtained using a perforated silver film. The enhanced absorption was observed at wavelengths associated with the reduced scattering; however the enhancement of absorption is limited due to the enhanced transmission of the film. In this section, I will demonstrate near unity absorption efficiency could be obtained using a two-layer silver film.

4.3.2 Results and Discussion

The schematic of a two-layer film is displayed in Figure 4-7. The film is arranged in the YZ plane. The incident light propagates parallel to X direction and the polarization direction is along the Z axis. The film is composed of a perforated silver layer facing the incident wave and a solid layer with a separation L from the first layer. The second layer is utilized to completely block the transmitted light and enhance the film absorption efficiencies using Fabry-Perot effect. The structure of the first layer is designed to minimize the scattering efficiency of the incident wave and prohibit escape of the trapped light between the two layers. And the thicknesses of two layers (t₁ and t₂) are fixed at 100 nm. The distance between the two layers, L, is varied from 150 nm to 250 nm. The perforated holes are arranged in a square lattice with a periodic distance, P, ranging from 400 to 500 nm. The diameters of the asymmetric holes d₁ and d₂ are also varied.
Figure 4-7: Schematic of the two-layer film. L refers to the distance between the two layers, \( t_1 \) and \( t_2 \) represent the thicknesses of the two layers, \( d_1 \) and \( d_2 \) are the two diameters of the asymmetric holes in the first layer and \( P \) denotes the periodic distance of the squarely arranged hole arrays.

4.3.2.1 The Enhanced Absorption due to Second Layer

We first compare the optical spectra of a one-layer perforated film with a two-layer film in which the first layer has the same configuration as that of the one layer film. The thicknesses of both layers are fixed at 100 nm. The hole arrays are arranged in a square lattice with a periodic distance of 400 nm, the diameters of the asymmetric holes are \( d_1 = 400 \) nm and \( d_2 = 115 \) nm. As shown in Figure 4-8(a), there are two resonance dips in the scattering spectrum of the one layer
film due to the coupling between holes which is similar to what was observed in previous section. The two resonance wavelengths shifts from 444 and 570 nm to 460 and 582 nm, respectively, when the second solid layer is included with a separation $L$ of 150 nm from the first layer. Interestingly, the scattering efficiencies are remarkably reduced to close to zero at the two resonance wavelengths. Figure 4-8(b) shows that the corresponding absorption efficiency is improved from 85% for the one layer film to 97% in the two layer film at around the wavelength of 450 nm and the efficiency is increased from 59% to 99% at the wavelength of 580 nm.

Figure 4-8: (a) Scattering and (b) absorption spectra of a one-layer and two-layer silver films. The structure of the one-layer film is the same with that of the first layer in the two-layer film with a 100 nm thickness, $d_2=115$ nm and $d_1=400$ nm hole arrays with a periodic distance 400 nm. The distance between the two layers, $L$, in the two-layer film is 150 nm.
4.3.2.2 The Influence of Hole Diameter

We firstly explore the effect of hole geometries on the optical properties of the two-layer films. The thicknesses of both layers are kept to be 100 nm, the periodic distance of the hole arrays in the first layer is 400 nm. The hole diameter $d_1$ is fixed at 400 nm, which equals to the periodic distance, $L$, and $d_2$ is varied from 20 to 210 nm. Figure 4-9(a) shows that the scattering efficiency and resonance wavelength are changed only slightly for the resonance peaks located at around 450 nm. The resonance wavelength at 498 nm is shifted to 626 nm when $d_2$ is increased from 20 nm to 210 nm and the scattering efficiency also changes dramatically. The scattering efficiency at the wavelength of 498 nm is 17% when $d_1$ is 20 nm. The close to zero scattering efficiency is observed at the wavelength of 582 nm when $d_1$ is increased to 115 nm which is about one third of $d_2$. Increasing $d_2$ from 20 nm to 115 nm allows more light penetrating through the first layer and subsequently leads to a reduced scattering efficiency of the film. When $d_2$ is further increased to 210 nm, more reflected light from the second layer may escape from the film and the scattering efficiencies become larger. The scattering efficiency at the wavelength of 626 nm reaches 19% when $d_2$ becomes 210 nm. Figure 4-9(b) shows that the absorption efficiency close to one can be observed at the wavelength of 582 nm associated with the zero scattering efficiency for $d_2 = 115$ nm.
Figure 4-9: (a) Scattering and (b) absorption spectra of a two-layer silver film with 100 nm thicknesses for both layers (t₁ and t₂) and a 150 nm separation (L). The hole diameter, d₁, and the periodic distance, P, are fixed at 400 nm, d₂ is varied from 20 to 210 nm.

4.3.2.3 The Influence of Periodic Distance

To further understand the mechanism leading to the increased absorption efficiencies and the variation of the resonance wavelength, we change the periodic distance of the hole arrays and the separation between the two layers. Figure 4-10(a) and (b) are the scattering and absorption spectra of films with different periodic distance. The separation between the two layers, L, is kept at 150 nm, and the thicknesses of the two layers are fixed as 100 nm. When the periodic distance is varied from 400 to 500 nm, the hole diameter d₁ is kept to be the same as the periodic distance and d₂ is taken to be about one third of d₂ which is optimized value for the enhanced absorption efficiencies. Figure 4-10(a) and (b) show that two resonance wavelengths at 460 and 582 nm shift monotonically red to 550 and 720 nm when the periodic distance is increased from 400 to 500 nm. The results indicate that both resonance wavelengths are sensitive to the periodic
distance change while the resonance wavelength at longer wavelength is more sensitive to the geometrical change of holes as shown in Figure 4-9. Figure 4-10 also shows that a higher order peak at 440 nm wavelength appears when the periodicity is changed to 500 nm.

Figure 4-10: (a) Scattering and (b) absorption spectra of a two-layer silver film with 100 nm thicknesses for both layers ($t_1$ and $t_2$) and a 150 nm separation (L). The periodic distance and the hole diameters (P, $d_1$, and $d_2$) are increased from (400 nm, 400 nm, and 115 nm) to (500 nm, 500 nm, and 180 nm).

4.3.2.4 The Influence of Two-layer Separation

The dependence of the optical spectra of the film on the separation distance between the two layers, L, is examined by varying L from 150 to 250 nm. In the calculations, the hole diameters are set to be $d_1= 400$ nm and $d_2=115$ nm, and the periodic distance is fixed at 400 nm. The thicknesses of the two layers are still fixed to be 100 nm. Figure 4-11 shows that when L is increased from 150 to 250 nm, the resonance wavelength at 460 nm shifts slightly to shorter
wavelengths which indicates that that resonance peak is dominantly determined by the periodic distance of hole arrays not by the separation between the two layers. The resonance wavelength at 582 nm for L=150 nm is shifted to 596 nm for L=200 nm and further shifts to 648 nm when L=250 nm. Please note that a small peak with an efficiency of 44% appears at 490 nm wavelength when L=200 nm and the peak efficiency grows to close to 100% and red shifts to 536 nm when L=250 nm.

Figure 4-11: (a) Scattering and (b) absorption spectra of a two-layer silver film with different separations (L) ranging from 150 to 250 nm. The hole diameters d₁= 400 nm and d₂=115 nm and the periodic distance is fixed at 400nm.

4.3.2.5 The Excited Electric Field

We examined the excited electric field of the film when the absorption efficiency is close to 100%. Figure 4-12 shows the electric field, |E|^2, contour plots of a two-layer film in XZ plane through the center of holes. Both layers have the thickness of 100 nm and 250 nm separation.
The periodic distance between holes is 400 nm and the diameters of holes are set to be \( d_1 = 400 \) nm and \( d_2 = 115 \) nm. The resonance wavelength for unity absorption appears at 652 nm. Figure 4-12 clearly shows that the light is trapped between the two layers and the electric field with a factor of over 10 could be achieved inside the film.

![Electric field contour plots](image)

Figure 4-12: Electric field contour plots of a two-layer silver film with and 100 nm thickness and 250 nm separation at resonance wavelength of 652 nm. The hole diameters \( d_1 = 400 \) nm and \( d_2 = 115 \) nm and the periodic distance is fixed at 400 nm.

**4.3.3 Summary**

Using a two-layer silver film composed of a perforated and a solid layer, we show that total absorption efficiencies can be obtained at tunable wavelengths. The absorption efficiency is determined by the geometries of the perforated holes. Total absorption efficiencies can be achieved when the top diameter \( (d_2) \) of the hole is about one third of the bottom diameter \( (d_1) \), which equals to the periodic distance. The resonance wavelength may be changed by varying the
periodic distance of squarely arranged hole arrays as well as the separation distance between the two layers. The discoveries may have applications of photovoltaic devices and anti-reflection thin films.

4.4 Propagating Electromagnetic Wave along a Hollow Silver Nanorod

4.4.1 Introduction

The design of new subwavelength-dimension waveguides or imaging devices needs to control light at nanometer dimensions. It’s not easy to control light at subwavelength dimensions due to the diffraction limit. In this part I will discuss the light could propagate along a hollow silver nanorod with growing intensity for relatively long distance.

4.4.2 Results and Discussion

In the simulations, the incident wave vector was along X axis and the direction of polarization was along Z axis. The silver nanorod was arranged along the X axis (wavevector direction). The silver dielectric constants were taken from the handbook of Palik\textsuperscript{164}. The grid length in the DDA calculations was 5 nm. Schematics of hollow silver rods with different structures are displayed in Figure 4-13.
Figure 4-13: Schematics of hollow silver rods with different shapes.

4.4.2.1 The Influence of Shell Thickness

We started with hollow silver rods with cylindrical cross sections. The length of the rod was kept at 5 μm and the outer diameter was initially set at 100 nm. The extinction spectra of the hollow rods with different thicknesses of 10 nm, 20 nm, or 30 nm are displayed in Figure 4-14(a). Figure 4-14(a) shows that the resonance wavelength blue shifted with increasing shell thickness. When the thickness was 10 nm, the resonance peak appeared at 570 nm wavelength. The resonance wavelength shifted to 500 nm and 475 nm when the thickness increased to 20 nm and 30 nm, respectively. The resonance extinction intensity dropped slightly. Figure 4-14(b) shows the influence of outer diameter on the extinction spectra of the rods. In the calculations, the length of the rods was 5 μm and the shell thickness was fixed at 10 nm. Figure 4-14(b) shows
that the resonance wavelength red shifted with increasing outer diameter. The resonance wavelength shifted from 570 nm to 815 nm when the outer diameter was increased from 100 nm to 200 nm. The resonance extinction efficiency dropped with increasing outer diameter due to the increasing physical cross section of the rods.

![Figure 4-14: (a) Extinction spectra of cylindrical hollow silver nanorods with 5 μm length, 100 nm outer diameter, and different thicknesses (t). (b) Extinction spectra of cylindrical hollow silver nanorods with 5 μm length, 10 nm thickness, and different outer diameters (d).](image)

For hollow silver rods with a square cross section, the influence of the shell thickness and the edge length of the square cross section on the extinction spectra showed the same trend as that of cylindrical rods. The resonance wavelength red shifted with decreasing shell thickness or increasing cross section. The resonance wavelength showed up at 685 nm for a rod with edge length of 100 nm and shell thickness of 10 nm, and was blue shifted to 515 nm when the shell thickness grew to 30 nm.
4.4.2.2 The Excited Electric Field along the Rod

The electric field, $|E|^2$, distribution along the nanorods at the resonance wavelength is displayed in Figure 4-15. In the calculations, the electric field was calculated in the XZ plane through the center of the rod. The contour plot for a cylindrical rod with 5 μm length, 100 nm diameter, and 10 nm thickness at the resonance wavelength 570 nm is displayed in Figure 4-15(a), which describes the evolution of the intensity of electric field increased along the propagation direction. The highest enhanced electric field, $|E|^2$, at the end of the rod was 906. The enhanced electric field declined with increasing shell thickness. The $|E|^2$ dropped from 906 to 603 when the shell thickness increased from 10 nm to 30 nm. For hollow rods with the same shell thickness, the highest enhanced electric field at the rod end varied slightly with its outer diameter. The electric field contour plot for a 5 μm long rod with a square cross section is displayed in Figure 4-15(b). The edge length and shell thickness of the rod were 100 nm and 10 nm, respectively. Figure 4-15(b) indicates that rods with a square cross section generated more enhanced electric fields along the rod in comparison with the cylindrical rods. The highest electric field, $|E|^2$ at the end of the square rod was 1712 at the resonance wavelength of 685 nm.
Figure 4-15: (a) The electric field, $|E|^2$, contour plot of a cylindrical hollow silver nanorod with 5 μm length, 100 outer diameter and 10 nm shell thickness at resonance wavelength of 570 nm. The highest $|E|^2$ at the end of the rod was 906. (b) The electric field contour plot of a square hollow silver nanorod with the length of 5 μm, edge length of 100 nm and thickness of 10 nm at resonance wavelength of 685 nm. The highest $|E|^2$ at the end of the rod was 1712.

4.4.2.3 The Influence of Each Edge

To further understand the structural dependence of the propagating electromagnetic wave, we calculated the extinction spectra and electric field of silver rods with rectangular cross sections. In the simulations, the length and shell thickness of the rods were kept at 5 μm and 10 nm, respectively. The edge length perpendicular to the polarization direction ($d_Y$) was fixed at
100 nm and the parallel edge length \((d_Z)\) was varied from 30 nm to 80 nm. Figure 4-16(a) shows that the extinction efficiency grew from 193 to 343 when \(d_Z\) increased from 30 to 50 nm and dropped with further increasing \(d_Z\). The resonance wavelength blue shifted initially from 720 nm to 620 nm when \(d_Z\) increased from 30 to 50 nm and shifted to red when \(d_Z\) was further increased from 50 nm to 80 nm. The resonance wavelength appeared at 645 nm when \(d_Z\) was changed to 80 nm. The initial blue shift was due to the weakened coupling between the two perpendicular edges as they were separated. When the separation was larger than 30 nm (the separation distance equals the edge length subtracting the two shell thicknesses), the coupling between the two perpendicular edges became very weak and the two parallel edges played a more important role in determining the resonance wavelength. Longer edge results in light coupling at longer wavelength, which shows that the resonance wavelength shifted to red.

The influence of perpendicular edge length \((d_Y)\) on the extinction spectra is shown in Figure 4-16(b). In the simulations, \(d_Z\) was fixed at 100 nm and \(d_Y\) was varied from 40 nm, 60 nm, 80 nm, to 100 nm. Figure 4-16(b) shows that the resonance wavelength monotonically red shifted with increasing \(d_Y\). The resonance wavelength was shifted from 595 nm to 705 nm when \(d_Y\) grew from 40 nm to 100 nm.
Figure 4.16: (a) Extinction spectra of rectangular hollow silver nanorods with 5 µm length, 10 nm thickness, 100 nm edge length along the Y direction (dY) and different edge lengths along the Z axis (dZ). (b) Extinction spectra for rods with 100 nm edge length along the Z axis (dZ) and different edge lengths along the Y axis (dY).

4.4.2.4 The Excited Electric Field along Rectangular Silver Rod

The electric field contour plots around the rectangular rods with 5 µm length, a fixed dY=100 nm, and different dZ at corresponding resonance wavelength are shown in Figure 4.17. The contour plot was in the XZ plane through the center of the rod. Figure 4.17(a) shows that when dZ = 40 nm, the propagating electric field was confined inside the rod with enhancement factors over 300 at most of the host spots. The highest enhanced electric field, |E|^2, at the end of the rod was 764. Figure 4.17(c) displays the corresponding contour plot in the YZ plane 5 nm away from the rod end. For the rod with 80 nm parallel edge length, light propagated along the outer surface of the rod with enhanced electric fields, |E|^2, over 100 as displayed in Figure 4.17(b). Figure 4.17(d) indicates the corresponding electric field contour plot in the YZ plane 5 nm...
away from the rod end. Interestingly, the highest enhanced electric field, $|E|^2$, at the end of the rod was $1079$, which was larger than the enhancement factor obtained in the rod with the $40$ nm parallel edge length. We also examined the influence of $d_Y$ on the light propagation along the rod. The decreasing $d_Y$ reduced the intensity of the propagating electromagnetic wave and generated a higher enhanced electric field at the end of the rod.

Figure 4-17: Electric field contour plots of rectangular hollow silver nanorods with $5 \mu m$ length, $10$ nm thickness, $100$ nm perpendicular edge length ($d_Y$), and different parallel edge lengths ($d_Z$) at corresponding resonance wavelength. (a) $d_Z=40$ nm in the XZ plane; (b) $d_Z=80$ nm in the XZ plane; (c) $d_Z=40$ nm in the YZ plane; (d) $d_Z=80$ nm in the YZ plane.
4.4.2.5 The Influence of Rod Length

In the above simulations, the length of the rods was fixed at 5 μm. The rod length also plays an important role in light propagating. We fixed the rod thickness and cross section at 10 nm and $100 \times 60 \text{ (d}_x \times \text{d}_z \text{) nm}^2$ respectively, and varied the rod length from 1 μm to 5 μm in the following simulations. Figure 4-18 shows that the resonance extinction efficiency grew with increasing rod length and the resonance wavelength red shifted slightly. The larger extinction efficiency indicates that more light around the rod was coupled by the rod as the rod becomes longer.

![Figure 4-18: Extinction spectra of rectangular hollow silver nanorods with 10 nm thickness, a $100 \times 60 \text{ (d}_x \times \text{d}_z \text{) nm}^2$ cross section, and different lengths (h). (A) h=1 μm; (B) h=2 μm; (C) h=3 μm; (D) h=4 μm; (E) h=5 μm.](image-url)
The electric field contour plots of rods at corresponding resonance wavelength are expressed in Figure 4-19. The contour plot was in XZ plane through the rod center. The calculations show that the highest electric field, $|E|^2$, at the end of the rod was 362 for a rod with 1 μm length. The $|E|^2$ was amplified to 667 when the length was extended to 3 μm and increased to 729 when the rod length was changed to 5 μm. Both the increasing extinction efficiency in Figure 4-18 and increasing electric field in Figure 4-19 proves that more light was coupled in the rod as the rod become longer.

Figure 4-19: Electric field, $|E|^2$, contour plots along rectangular hollow silver rods with $100 \times 60$ $(d_1 \times d_2)$ nm$^2$ cross section and different lengths (h) at corresponding resonance wavelength. (a) h=1 μm; (b) h=3 μm; (c) h=5 μm.
4.4.3 Summary

We investigated the extinction spectra and the electromagnetic wave propagation for hollow silver rods with different structures. Simulations indicate that light may propagate with growing intensities along a hollow silver nanorod. Nanorods with square and rectangular cross sections showed more efficient wave propagations in comparison with cylindrical rods. For rods with a fixed 10 nm thickness and 100 nm parallel edge length ($d_Z$), the resonance wavelength shifted monotonically to red with increasing perpendicular edge length ($d_Y$). The $d_Z$ played a more important role in the light propagation in comparison with $d_Y$. For a rectangular nanorod with a fixed $d_Y=100$ nm, the resonance wavelength initially blue shifted when $d_Z$ was increased from 30 to 50 nm and shifted to red with further increasing $d_Z$. The propagating electromagnetic wave was confined inside the hollow rods with higher intensities when $d_Z$ was less than 50 nm. Light traveled along the outer surface of the rods with lower enhanced local electric fields when $d_Z$ was larger than 50 nm. For rods with the same 10 nm thickness and $100 \times 60$ ($d_Y \times d_Z$) nm$^2$ cross section, the enhanced local electric field, $|E|^2$, at the end of the rods increased from 362 to 667 when the rod length was increased from 1 $\mu$m to 3 $\mu$m, and grew to 729 when the rod length became 5 $\mu$m. Therefore, we have shown that light propagated better along hollow square and rectangular nanorods (only for those with edge separations larger than 10 nm), and the dimension that affected the propagating intensities the most was along the parallel edge length of the rod.

4.5 Conclusion

Light could be controlled by silver nanostructures at sub-wavelength dimensions. By using a perforated silver nanofilm, extremely low scattering efficiency of less than 1% could be
obtained at resonance wavelength due to the coupling of light by the periodic holes in the film, which also results in enhanced absorption efficiency but the enhancement is limited due to the enhanced transmission. Therefore we make an improvement by using a two-layer silver nanofilm to achieve almost 100% absorption efficiency. The light could be trapped between the two layers at the resonance wavelength. Light can also propagate along a silver hollow nanorod to a distance as long as 5 μm. The silver nanorod could couple more light into it during the light propagating along it and significantly enhanced electric field could be obtained at the end of the rod. These works could lead to potential application for optical devices at sub-wavelength dimensions.
CHAPTER 5: A GENERALIZED ELECTRODYNAMICS MODEL FOR THE SURFACE ENHANCED RAMAN SCATTERING AND ENHANCED/QUENCHED FLUORESCENCE CALCULATIONS

5.1 Introduction

Surface-enhanced Raman scattering (SERS) has obtained extensive interests from different disciplines. An enhancement of Raman scattering, which is approximately proportional to $|E|^4$ of the local electric field, can be achieved when molecules are placed close to a particle surface. The enhancement factor as high as $10^{10}$ to $10^{14}$ had been experimentally demonstrated\textsuperscript{17,18}. However, the influence of metal nanostructures on the fluorescence signal is still under investigating and the detailed mechanism is controversy. In this chapter, I will discuss a proposed generalized electrodynamics model to describe the surface enhanced Raman scattering and enhanced or quenched fluorescence of a dye molecule near a metal nanoparticle.

5.2 Model and Method

In this chapter we propose an electrodynamics model to demonstrate that either enhancement or quenching could be obtained for the fluorescence signal of a dye molecule when it is placed adjacent to a metal nanoparticle (NP). The model gives a generalized perspective for surface-enhanced Raman scattering and enhanced or quenched fluorescence of various kinds of molecules and metals by electrodynamics method. The NP size and the quantum yield of the dye molecule are two crucial parameters for the enhancement or quenching of the fluorescence signal. In the calculation, the molecule and the metal NP were treated as oscillating dipoles and they were described by Lorentz model. The Fourier transform was carried out to obtain the dipole
moment and local electric field at frequency domain. The coupled-dipole method was then adopted to calculate the emission (scattering) spectra of the system. The properties of the molecule are similar to those of a Cy3 dye molecule and the properties of the metal NP are close to those of gold.

For an excited molecule, it will decay by two channels, one is called radiative decay which will emits photons and the other is through a non-radiative decay channel in which the energy is converted to thermal energy (phonon energy). The quantum yield, $\eta$, of the molecule is defined by

$$ \eta = \frac{k_r}{k_r + k_{nr}}, \quad (5.1) $$

where $k_r$ and $k_{nr}$ refer to the radiative and non-radiative decay constants of the molecule, respectively. When a metal NP is placed nearby the molecule, the pseudo radiative rate constant of the molecule will be modified which is denoted by $k_t$. We call it pseudo radiative rate constant since part of the energy in the newly defined radiative decay channel ($k_t$) will be transferred to the metal NP. A portion of the transferred energy will be absorbed by the metal NP and become its thermal energy and only the rest will be emitted eventually as detectable photons. In this regard, the relative ratio between the absorption and scattering cross sections of the metal NP will determine the percentage of the energy to be converted to thermal energy or photonic energy and plays a crucial role in the quenching or enhancement effect of the metal NP to the dye.
molecule. We define the altered radiative rate constant of the system including the dye molecule and the metal NP as $k_r'$. The modified quantum yield $\eta'$ of the system can be expressed as

$$\eta' = \frac{k_r'}{k_t + k_{nr}} = \frac{f_r \times k_r}{f_t \times k_r + k_{nr}},$$  \hspace{1cm} (5.2)

where $f_r = k_r'/k_r$ is the enhancement factor of the radiative rate constant of the system including the dye molecule and the metal NP relative to that of an isolated dye molecule and $f_t = k_t/k_r$ is the enhancement factor of the pseudo radiative rate constant of the molecule itself in the complex system including the dye molecule and the metal NP in comparison to the radiative rate constant of an isolated dye molecule. Since the total energy is conserved, the number of dye molecule at the excited energy state can be assumed to be the same. The fluorescence signal ratio of the molecule due to the presence of a metal particle at the emission wavelength $q_{em}$ can be calculated by

$$q_{em} = \frac{\eta'}{\eta} = \frac{f_r \times (k_r + k_{nr})}{f_t \times k_r + k_{nr}} = \frac{f_r}{f_t \times \eta + 1 - \eta}$$ \hspace{1cm} (5.3)

In the simulation, $f_r$ is proportional to the intensity of electric field $|E|^2$ of the metal NP at the molecule position at the emission wavelength$^{168}$. Since the excitation rate of the molecule may also be amplified by a factor of $|E|^2_{ex}$, due to the enhanced local electric field of the metal NP at the excitation wavelength, the detectable fluorescence signal enhancement factor can be calculated by
We may find that Equation (5.4) is simplified to \( |E|^2_{ex} \cdot f_r \) which is the equation to calculate the surface enhanced Raman scattering \(^{168}\), when the quantum yield, \( \eta \), of the dye molecule is extremely small. The lifetime ratio of the dye molecule with or without the metal particle can be readily derived as

\[
\frac{\tau'}{\tau} = \frac{k_r + k_{nr}}{k'_r + k_{nr}} = \frac{1}{f_r \times \eta + 1 - \eta}
\]  

where \( \tau' \) and \( \tau \) are the lifetimes of the dye molecule with or without the presence of the nearby metal particle.

In the calculations, the molecule and the metal NP were treated as oscillating dipoles using Lorentz model. The displacement of electrons at different times can be obtained using equation

\[
\omega_0^2 x + \gamma \dot{x} + \ddot{x} = \frac{e E_{loc}}{m}, \quad (5.6)
\]

where \( \omega_0 \) and \( \gamma \) are resonance and damping angular frequency of the dye molecule or metal NP, respectively, \( x \) is displacement of electrons at each time, \( e \) and \( m \) are charge and mass of electrons, respectively, and \( E_{loc} \) denotes the local electric field at the dipole position. For the dye
molecule, the $E_{\text{loc}}$ includes the incident light and the scattered light from the metal NP, while the $E_{\text{loc}}$ at the metal NP position only includes the scattered light from the molecule.

The dipole moment, $P$, of the dye molecule or metal NP at each time can be obtained by

\[ P = \rho V e_x \varepsilon_0 , \quad (5.7) \]

where $\rho$ and $V$ are the electron density and volume of the particle, respectively, and $\varepsilon_0$ is the vacuum permittivity. The dipole moment and local electric field at frequency domain can be obtained after a Fourier transform. Then the coupled-dipole method\textsuperscript{169} was adopted to calculate the extinction, absorption and scattering cross section of a single particle or a system including a metal NP and a dye molecule.

\[
C_{\text{ext}} = \frac{k}{|E_0|^2} \sum_{j=1}^{N} \text{Im}(E_{\text{inc},j} \cdot P_j), \quad (5.8)
\]

\[
C_{\text{abs}} = \frac{k}{|E_0|^2} \sum_{j=1}^{N} \text{Im} \left( P_j \cdot E_{\text{loc},j} - \frac{2k^3}{3\cdot4\pi} P_j \cdot P_j^* \right), \quad (5.9)
\]

\[
C_{\text{sca}} = \frac{k^4}{(4\pi)^2|E_0|^2} \int d\Omega \left| \sum_{j=1}^{N} \left[ P_j - \hat{n}(\hat{n} \cdot P_j) \right] \exp(-ik\hat{n} \cdot r_j) \right|^2 , \quad (5.10)
\]

where $k=2\pi/\lambda$ is the wave vector at a wavelength of $\lambda$, $\hat{n}$ is unit vector along the scattering direction, and $d\Omega$ denotes the solid angle element, $E_0$ is the amplitude of the incident light, $E_{\text{inc},j}$ and $E_{\text{loc},j}$ represent the incident and local electric field for particle $j$, respectively. $r_j$
and $P_j$ denote the coordinate and dipole for particle $j$, respectively. The efficiencies can be calculated by dividing the calculated cross sections over the physical area of the particle.

The radiative decay rate constants defined in Equation (5.1) - (5.5) are represented using the scattering cross section of the dye molecules or metal NPs. To reduce the numerical errors in the calculations, we computed the scattering cross section of the whole system using Eq. (10), and the scattering cross section of the molecule itself by $C_{ext}C_{abs}$ when a metal particle is placed adjacent to it.

5.3 Results and Discussion

The schematic of a dye molecule and a metal NP is shown in Figure 5-1. A dye molecule is illuminated by the incident light and the scattered light represents the emission of an excited fluorophore. A metal NP is placed close to the dye molecule which is excited by the emitted (scattered) light from the dye molecule. The coupling between the dye and the metal NP is treated with the coupled dipole method and the dipole excitations of both elements are described by Lorentz model as discussed in the previous paragraph. In the calculations, the excitation wavelength is set at 550 nm while the emission wavelength is fixed as 570 nm and the quantum yield of molecule is chosen as 0.16. Those parameters are close to a Cy3 molecule. For the metal particle, we use an electron density of $0.80 \times 10^{28}$ m$^{-3}$ and a damping frequency of $5 \times 10^{14}$ rad$^{-1}$ which is close to a Au metal NP. The resonance wavelength of the metal NP is set at 540 nm.
5.3.1 Validation of the Model

We first confirmed the validation of our proposed model by comparing the scattering and absorption spectra of a gold NP from coupled dipole calculation and from our proposed model. In the coupled dipole calculation, the dielectric constants of the gold NP is derived from Drude model using the same parameters which are adopted in the proposed model. Figure 5-2 indicates the scattering and absorption spectra of a gold NP of a radius of 10 or 20 nm calculated from both methods. The figure shows that the scattering and absorption spectra obtained from our proposed model have good agreement with those calculated from coupled dipole method. This proved the validation of the proposed model and code.
Figure 5-2: The scattering and absorption spectra of a gold NP with a radius (r) of 10 or 20 nm calculated from the proposed model in comparison with the calculation from coupled-dipole (CD) method.

Table 5-1 shows the electric field, $|E|^2$, at varying distance from 2 to 10 nm beside a metal particle with a radius of 10 nm along X axis. The results are obtained from the coupled-dipole method and proposed model, respectively. The results show that the calculated electric field from the proposed model agrees well with that from the coupled-dipole method, which proves our model and code give the correct electric field.
Table 5-1: Electric field, $|E|^2$, beside a metal particle with 10 nm radius at varying distance along X axis calculated from coupled-dipole (CD) method and the proposed model at the wavelength of 287 nm.

<table>
<thead>
<tr>
<th>Distance/nm</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD</td>
<td>16.732</td>
<td>6.787</td>
<td>3.125</td>
<td>1.585</td>
<td>0.869</td>
</tr>
<tr>
<td>model</td>
<td>17.243</td>
<td>6.991</td>
<td>3.220</td>
<td>1.636</td>
<td>0.896</td>
</tr>
</tbody>
</table>

Table 5-2: Comparison of $f_r$ and $|E|^2$ of two metal particles at different wavelength. The radii of two particles are 3 and 10 nm respectively. The first particle is illuminated and put in origin. The second one is put in dark at X, Y or Z axis. The distance between two particles is 15 nm.

| Wavelength/nm | $f_r$ | $|E|^2$ |
|---------------|-------|---------|
| x             | 260   | 0.18874 | 0.21171 |
| y             | 260   | 1.83548 | 1.83864 |
| z             | 260   | 1.83565 | 1.93089 |
| x             | 287   | 4.57711 | 6.12174 |
| y             | 287   | 1.80542 | 1.78183 |
| z             | 287   | 1.80551 | 2.42943 |
| x             | 300   | 6.01365 | 6.24006 |
| y             | 300   | 0.5078  | 0.42893 |
| z             | 300   | 0.50767 | 0.79033 |
We also examined the relationship of the enhancement factor of the scattering efficiency of a particle when there’s another particle put beside it and the enhanced electric field of the second particle. The results are shown in Table 5-2. When there is another metal particle put beside one particle, the scattering efficiency of the first particle will be enhanced. Table 5-2 shows that the enhancement factor equals to the enhanced electric field of the second particle at the position of the first one.

5.3.2 Enhancement and Quenching of Fluorescence

Figure 5-3(a) shows the fluorescence ratio of a dye molecule placed near a metal NP at varying distance in comparison to that of an isolated dye molecule. The results were averaged over different orientations relative to the wave vector and polarization directions of incident light. When the radius of the metal NP is 10 nm, the fluorescence signal of the dye molecule was quenched due to that the energy transfer from dye molecule to metal NP is dominant by the form of non-radiative decay. Theoretical calculations had been experimentally proved in the previous report\textsuperscript{121}. When the distance between the molecule and the metal NP is larger than 50 nm, the effect of the metal NP to the molecule becomes very weak and the signal ratio reaches to 1. However, when a larger metal NP with a radius of 20 nm was placed near the molecule, the fluorescence signal of the dye molecule is enhanced to 3 times when the metal NP is placed 5 nm away from the molecule. The enhancement factor reaches to 15 when a metal NP with a 30 nm radius was used. The alternative enhancement and quenching effect of the metal NP to the fluorescence signal of the dye molecule can be explained as following. For a metal NP, its cross section of scattering is proportional to $R^6$ while cross section of absorption is changing
proportional to $R^3$ when the particle radius, $R$, varies. The different $R$ dependence of the cross sections indicates that the scattering cross section will increase much more significantly than that of the absorption when the particle radius is increased. For the presentation clarity of figures, we show scattering and absorption efficiencies in Figure 5-3(c) and (d) which are obtained by dividing the cross sections over $2\pi R^2$ where $R$ is the particle radius. For a small particle of 10 nm radius as shown in Figure 5-3(c) and (d), the scattering efficiency is much smaller in comparison with the absorption efficiency. The scattering efficiency of a metal particle with a 10 nm radius is only $6.84 \times 10^{-3}$ and the absorption efficiency is 1.48 at resonance wavelength of 570 nm. Most of the transferred energy from the dye molecule to the metal NP will be absorbed by the metal NP in the form of non-radiative decay and only small portion is eventually scattered (emitted) as photons, which results in a quenched signal. For a large particle of 30nm radius, the scattering efficiency of the metal NP is 0.554 and the absorption efficiency is 3.93 at the emission wavelength. The ratio of the scattering efficiency over the absorption efficiency is much larger than that of a 10 nm radius metal particle. Consequently, more transferred energy from the excited dye molecule to the metal nanoparticle will decay through the radiative channel and becomes detectable photonic signal which leads to an enhancement of the fluorescence signal.
Figure 5-3: (a) Fluorescence signal ratio and (b) lifetime ratio of a dye molecule placed near a metal NP with different radii in comparison to those of an isolated dye molecule. (c) The scattering and (d) the absorption spectra of a metal NP with different radii.

Figure 5-3(b) shows the fluorescence lifetime ratio of a dye molecule placed besides a metal NP with different radii at varying distance in comparison to that of an isolated dye molecule. Figure 5-3(b) shows that when the distance is short, a small sized metal NP results in a shorter lifetime than a larger sized metal NP. When the distance increases, the lifetime ratio of the dye molecule is higher when a metal NP of 10 nm radius is placed near the molecule relative to a 30 nm radius particle. Since the lifetime ratio of the dye molecule as shown in Equation (5.5)
is only related to the pseudo radiative decay rate constant \( (f_t) \) of the molecule and the non-radiative decay constant of an isolated dye molecule, Figure 5-3(b) displays the effect of the absorption cross section of a metal particle is more important in altering \( f_t \) of the dye molecule than the scattering cross section of the metal NP.

**5.3.3 The Influence of Electron Density and Damping Frequency**

To further understand the proposed mechanism, we numerically change the electron density \( \rho \) and damping frequency \( \gamma \) of the metal NP to adjust the energy transfer efficiency between the dye molecule and the metal NP. Figure 5-4(a) shows the fluorescence signal ratio of a dye molecule placed near a metal NP in comparison to that of an isolated dye molecule when the electron density of the metal NP is changed from \( 0.8 \times 10^{28} \) to \( 1.6 \times 10^{28} \) and \( 3.2 \times 10^{28} \) m\(^{-3}\). Figure 5-4(a) shows that the fluorescence signal is enhanced with a higher factor with increasing electron density of the metal NP. A larger electron density means more electrons in the particle which has a similar effect as increasing particle radius, which results in larger scattering cross section of the metal nanoparticle. While a decreased damping frequency leads to reduced absorption cross section. When the damping frequency is decreased from \( 5 \times 10^{14} \) to \( 4 \times 10^{14} \) or \( 3 \times 10^{14} \) rad\(^{-1}\), the ratio between the absorption and scattering cross sections of the metal particle will increase, which will also give a more enhanced fluorescence signal, as shown in Figure 5-4(b).
5.3.4 The Influence of Quantum Yield

We have showed the fluorescence signal ratio of a dye molecule placed near a metal NP at different conditions. Equation (5.3) shows that the quantum yield $\eta$ of the molecule is also crucial in calculating the quenching/enhancement factor of the dye molecule placed near a metal NP. From Equation (5.3) we can find that, when $\eta$ is close to 1, the equation will be reduced to $f_r/f_t$. Since $f_r$ represents the radiative decay rate constant (total emission) enhancement while $f_t$ includes both the emitted energy and the absorbed energy by the metal NP and is always larger than $f_r$, the fluorescence will always be quenched if we did not consider the excitation rate enhancement at the excitation wavelength. However, if $\eta$ is extremely small, Equation (5.3) is simplified to $f_r$, which is proportional to the enhanced local electric field $|E|^2$ of the metal NP at the emission wavelength at the position of the molecule. Equation (5.4) is simplified to the equation used to calculate the surface-enhanced Raman scattering which has an enhancement.
factor proportional to $|E|^4$. It is worth to note the enhancement of the Raman signal at emission wavelength is due to the change of the relative decay rate constants between the radiative and non-radiative channels which does not violate the energy conservation of the system. The effect of quantum yield to the fluorescence quenching and enhancement is shown in Figure 5-5. When a metal NP with a 20 nm radius is placed 5 nm away from the molecule, the signal ratio is enhanced as 516 times if the quantum yield $\eta$ is set at $1 \times 10^{-5}$. However, when $\eta$ is set to be 1, the signal ratio is reduced to 1.2. Similar results will be obtained while the distance is changed as 10 nm. As the distance further increasing as 80 nm, the enhancement/quenching factor will be close to 1 no matter of the quantum yield of the molecule.

Figure 5-5: Fluorescence signal ratio of a dye molecule with varying quantum yield placed near a metal NP. The radius of the particle is 20 nm and the molecule is placed at different distance ($x$) from the particle surface.
5.4 Conclusion

In conclusion, we proposed a generalized electrodynamics model to calculate the energy transfer efficiency between a dye molecule and a metal NP. When the particle size is small, the transferred energy from the dye molecule to the metal NP is dominantly absorbed by the metal particle and results in a quenched signal. However, the fluorescence signal will be amplified when a big metal NP is used. The reason of the change is due to the relative ratio variation of the scattering and absorption cross sections of the metal NP. Increasing the electron density or decreasing the damping frequency of the metal NP will also generate the same effect due to the increased ratio between the absorption and scattering cross sections of the metal NP. The quantum yield of the molecule also has significant effect on the enhanced or quenched signal. A molecule with a quantum yield close to one will experience a quenched fluorescence signal when placed near a small metal NP in comparison to an isolated molecule. When the quantum yield of the molecule is extremely small, the signal enhancement will be similar to the surface-enhanced Raman scattering.
CHAPTER 6: SUMMARY

In summary, we investigated the novel optical properties of metal nanostructures based on surface plasmon by theoretical simulation methods. A perforated silver film could provide extremely low scattering efficiency at tunable resonance wavelengths with tunable width. The perforated silver nanofilm was then adopted into a two-layer silver nanofilm which has one more solid silver layer. The two-layer silver nano-film could achieve enhanced absorption efficiency close to 100% at tunable wavelengths. A hollow silver nanorod could be used to propagate light with growing intensities as long as 5 μm. We also investigated the influence of metal nanoparticle on fluorescence. A general electrodynamics model was proposed to simulate the surface enhanced Raman scattering and enhanced/quenched fluorescence. Our simulation shows that a small metal nanoparticle could result in quenched fluorescence due to the relatively large absorption efficiency of the metal particle, and a large metal nanoparticle could enhance the fluorescence signal due to its relatively high scattering efficiency.
12. "Distance-dependent interactions between gold nanoparticles and fluorescent molecules with DNA as tunable spacers" Rahul Chhabra, Jaswinder Sharma, Haining Wang, Shengli Zou, Su Lin, Hao Yan, Stuart Lindsay, and Yan Liu, *Nanotechnology* (2009) 20(48) 485201


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REFERENCES


(99) Nordlander, P. *Nat. Photonics* **2008**, *2*, 387.


