Influenced of electron density on plasmonic behavior of coupled AU nanostructures

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**NANYANG
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UNIVERSITY**

**INFLUENCED OF ELECTRON DENSITY ON
PLASMONIC BEHAVIOR OF COUPLED AU
NANOSTRUCTURES**

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INFLUENCED OF ELECTRON DENSITY ON PLASMONIC BEHAVIOR OF
COUPLED AU NANOSTRUCTURES

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ABSTRACT

Surface plasmon resonance has attracted extensive interest because it allows us to manipulate light in nanoscale which is of paramount importance for optoelectronic switching devices, information processing, biological and chemical sensing, particularly in the field of dynamic controlled device, which can be realized by *in-situ* charging the material via applying electric potential. In this dissertation, we focus on investigating the plasmonic far field (extinction spectra) and near field (field enhancement) properties of coupled nanostructure in response to charging effect.

A Drude-Lorentz model can describes the charging effect on a material. By employing the dielectric constants with different amount of free electron density, we theoretically investigating the charging effects (increase of excess of electrons) on both isolated (monomer) and coupled (dimer) Au nanostructure. The Au dimers are constructed from sphere and ellipsoid monomers building blocks. The increase of charging level induces plasmon peak blue shifting. We find that plasmon shifting depends on the geometries of the nanostructure. Larger the geometrical factors, larger the plasmon shifts. Subsequently, we characterize the sensitivity from the slope of the plasmon shifts. As expected, ellipsoid-ellipsoid dimer exhibits the largest geometrical factor (5.41) among all nanostructures in this study and yields the largest plasmon shifts, thus has the highest far field sensitivity (-2.87) to the charging effect. The results calculate from numerical solution is in agreement with those from analytical solutions.

We also have study the near field response to the charging effect for these coupled nanostructures. The near field can be characterized based on the average electric field enhancement factor of nanostructures. When increasing the excess electrons to the Au nanostructures, the enhancement spectra are blue shifted, the

results are consistent with their far field counterpart. To quantify the sensitivity of the near field response to the charging effect, we calculate the enhancement ratio of each nanostructure as a function of different charging levels. Surprisingly, we find that the ellipsoid-ellipsoid dimer yields the lowest enhancement ratio among all nanostructures despite its largest value of enhancement factor, and shows the lowest sensitivity with the value of 0.48. This phenomenon is because of the strong distorted charges separation in the ellipsoid-ellipsoid dimer, which can be explained by the effective dipole moment model.

To mimic the real system, we conduct a study on the charging effect on sphere-on-substrate. Attributing to the presence of substrate in close proximity, the plasmon band of Au sphere is broaden, which retards the plasmon shifting, hence lower far field sensitivity toward charging effect. Despite the lower value of enhancement factor, we find the sphere-on-substrate shows a comparable value of sensitivity as that of ellipsoid monomer.

Overall, this work provides a guide in designing nanostructure, particularly in the sensing application. In addition, with this knowledge, we can extrapolate to other geometries such as nanoprism, nanobar, and their coupled structures.

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CHAPTER 1 INTRODUCTION

This chapter starts with the overview of surface plasmon resonance that includes the historical developments of surface plasmon resonance, theoretical calculation of the optical properties by solving Maxwell equations, and introduction of two most important ingredients in surface plasmon resonances. Next, we review in details the dynamic manipulation of localized surface plasmon resonance that involves altering the amount of free electron density. Finally, this chapter concludes with the motivations and objectives, hypotheses, and the organization of this dissertation.

1.1 Surface plasmon resonance

1.1.1 Historical developments of surface plasmon resonance

Figure 1. 1 The color of the Lycurgus Cup which depending the direction of the passing light (a) light incident from the front of the cup (b) light incident from inside of the cup. Reprint from reference 9.

When the size of a metallic nanostructure is much smaller than incident light wavelength, the nanostructure exhibits unique optical properties and is significantly different from those observed in their bulk counterpart, which known as surface plasmon resonance.¹⁻⁸ These fascinating phenomena can be traced backed to the Lycurgus cup dated back to 4th century A.D. This cup exhibited green or red color when the light is incident from front or from back of the cup (Figure 1.1).⁹ The mystery was not solved until 1857, when Michael Faraday pointed out that the red color in the cup was actually attributed to the dispersed Au colloidal.¹⁰ Fifty-one years after Michael Faraday's discovery, first mathematical framework was proposed to describe the optical properties of spherical nanoparticle by Gustav Mie. Under this framework, scattering and absorption properties of a spherical particle can be obtained by solving Maxwell equations.¹¹ This work remains a great triumph in the world of physic until today.

Due to the recent revolutionary in science and engineering, different techniques are developed to control over the size, shape, composition, refractive environment, and the amount of free electron density of a noble metal in nanoscale,^{2,12} hence enable us to manipulate the characteristic of the surface plasmon resonance. With the ability to tailor the surface plasmon resonance, it has become one of the hottest topic in science due to its potential applications in various fields, particularly the chemical and biological sensing.¹³

Equivalent to the rapid progress in experimental, theoretical simulation based on advance computational techniques are needed to help us to understand the fundamental physic behind the surface plasmon resonance. Based on the simulation studies, we can characterize the plasmonic behavior in details, as an efficient way to rationalize the experimental finding as well as design of the nanostructure. Several simulation tools that are commonly used in predicting the plasmonic behavior are discrete dipole approximation (DDA),¹⁴⁻¹⁶ finite difference time domain (FDTD),¹⁷ finite element method (FEM).¹⁸ In this work, DDA was used as a tool to numerically solving the Maxwell equations within the classical mechanics framework.

1.1.2 Electrodynamic calculation for optical properties

The frequency dependent optical properties of a material can be expressed by the complex dielectric constants. In general, materials that have negative real and small positive imaginary dielectric constants are known to support surface plasmon resonance.¹⁹ The metal's dielectric constant can be obtained by phenomenological or electroelectrostratical methods.^{20,21} The former can be measured using ellipsometry spectroscopy,²² while the latter can be calculated from Drude model. In Drude model, the kinetic behavior of electrons is treated classically, where the electrons can be pictured as freely moving particles against immobile positive nuclei.²³ This model has been widely used to describe gold (Au),^{7,24-27} silver (Ag),²⁸⁻³⁰ copper (Cu),³¹⁻³³ and aluminum (Al)³⁴⁻³⁶. However, Drude model only account the electrons activity at intraband, depending on the region of electromagnetic region we are interested in, a Lorentz term may need to be included the interband transition of the material such as Au in the range of visible wavelength region (500 nm- 800 nm). Recent discovery

reveals that Drude model also can be used to describe the optical properties of highly doped semiconductor in infrared region.^{37,38} Instead of free electrons, free holes are responsible to couple with the photon to generate surface plasmon resonance, which we will discuss about it in later section.³⁷

Due to the tremendous development in computational tools and hardware's ability for high-speed calculation, it is relatively convenient to calculate the interaction between the electromagnetic wave and the non-spherical metallic nanostructure by numerically solving the Maxwell equations. In Gaussian units, the differential forms of Maxwell equations are expressed as follow:²³

$$\nabla \cdot D = 4\pi\rho \quad (1)$$

$$\nabla \cdot B = 0 \quad (2)$$

$$\nabla \times E + \frac{1}{c} \frac{\delta B}{\delta t} = 0 \quad (3)$$

$$\nabla \times H - \frac{1}{c} \frac{\delta D}{\delta t} = \frac{4\pi}{c} j \quad (4)$$

where E and H denote the electric and magnetic fields. D denotes the electric displacement vector and B denotes the magnetic flux density or magnetic induction. The macroscopic fields (E , H , D , and B) are related through Maxwell equations to external charges (ρ) and current density (j), respectively. It is known that the electric displacement is related to the electric fields via the dielectric constants or permittivity (ε). Therefore, we reach to Equation (5).

$$D = E + 4\pi P = \varepsilon E \quad (5)$$

where P denotes the polarization that describe the electric dipole moment per unit volume in the material, result from the microscopic dipoles alignment with the

electric fields. Meanwhile the magnetic fields are linked to the magnetic induction via the magnetic permeability, μ .

$$B = H + 4\pi M = \mu H \quad (6)$$

where M denotes the magnetization that describes the magnetic moment per unit volume in the material. These equations can be further simplified with $\rho=0$ (which state: no accumulation of charges in the metal) and $M=0$ (which state: the considered medium does not retain magnetization). Another important relation to point out before describing an electromagnetic wave is Ohm's law that relating the electric field (E) to the current density (j).

$$j = \kappa E \quad (7)$$

where κ denotes the conductivity that describe the ability of a noble metal to conduct the electric current. The conductivity and dielectric constants of a material can be connected in a simplified spatially local response via:

$$\varepsilon(\omega) = 1 + \frac{4\pi\kappa(\omega)}{\omega} i \quad (8)$$

$$i = \sqrt{-1} \quad (9)$$

From Equation (8), we show the interchangeable between complex dielectric constants and the complex conductivity, both complex can be in simpler form, that is $\varepsilon(\omega) = \varepsilon'(\omega) + \varepsilon''(\omega)$ and $\kappa(\omega) = \kappa'(\omega) + \kappa''(\omega)$, respectively. Many theoretical approximations to the dielectric constants have been developed.³⁹⁻⁴¹ Among them, Drude model is the simplest function that describes the mechanics of the electrons in

metallic material (Equation (10)). In this model, the electrons are considered free and independent moving particles, while their motion is damped by the collisions, which characterized via collision frequency $\gamma = 1/\tau$, where τ denotes the relaxation time of the free electron cloud.

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (10)$$

where ω_p^2 denotes bulk plasmon frequency and γ denotes damping constant due to electron collisions. The ω_p^2 can be calculated simply based on Equation (11):

$$\omega_p = \sqrt{\frac{Ne^2}{m_e \varepsilon_0}} \quad (11)$$

where N denotes the amount of free electron density, e and m_e are the electron charges and electron mass respectively and ε_0 denote the permittivity of free space. Equation (11) indicated the linear relationship between the bulk plasmon frequency and the free electron density of a material. This simply implies that, the charging effect under influence of applied potential can be mimicked by changing the amount of N in this relation. Moreover, this relationship is the fundamental of dynamical modulation of surface plasmon resonance and will be discuss in details in following section.

1.1.3 Types of surface plasmon resonance

From Mie's theory, surface plasmon resonance is defined as the resonant electromagnetic field of the light that induces a collective coherent oscillation of charges at the metal-dielectric interface. This happened when the incident light's frequency matches the natural frequency of the metal surface electrons oscillations.^{5,42}

Coupling between the light and the free electrons in the metallic nanostructure leads to a charge separation between the free electrons and their positive nuclei. As a result of coulomb repulsion force, the free electrons will be moving in the opposite direction against its positive nuclei, hence generates the collective electrons oscillation.²³

Figure 1.2 There are two types of surface plasmon resonance, propagating surface plasmon resonance (top) and the localized surface plasmon resonance (bottom).

Reprint from reference 19.

There are two forms of surface plasmon resonances, propagating surface polariton (Figure 1.2, top) and localized surface plasmon resonance (LSPR) (Figure 1.2, bottom).^{20,21,43} For propagating surface polariton, the plasmon resonance can

travel in a long distance (hundreds of microns), while evanescently decay in z-direction (Figure 1.2, top), this type of surface plasmon resonance often observed for metallic film with thickness of film that is smaller than the light wavelength. On the other hand, the LSPR happened for isolated nanostructure (Figure 1.2, bottom), where light coupled to the electrons and leads to the local oscillation. This type of resonant has receiving a great attention owing to the ability to concentrate intense field at the surface of the nanostructure and can be tailor by shape, size, composition, refractive index, and free electron density.^{5,44,45}

1.2 LSPR manipulation

Here, we show a comprehensive discussion on the field of LSPR manipulation. In general, surface plasmon can be tuned via static and dynamic approaches. In static tuning, the parameters such as dielectric constant of environment, composition of nanostructure, geometries, and the dimensions of the nanostructure are pre-defined before the measurement, hence tuning the LSPR is not favored during measurement and is irreversible. Nonetheless, due to the advance development of the fabrication and synthesis methods, static controlling of plasmonic properties is a popular strategy and it has high impact in plethora applications.⁴⁶⁻⁴⁹ On the other hand, in dynamic approach, the LSPR is available to be tuned during the measurement and is reversible, under this condition, the dynamic information at the electrode interface down to molecular level can be obtained.⁵⁰ The dynamic tuning is use for *in-situ* tuning in enhanced Raman scattering.^{51,52}

1.2.1 Static tuning of LSPR for single and coupled nanostructures

Over the years, various successful synthesis and fabrication methods have been developed to generate metallic nanostructures with different shapes (sphere, triangle, cube, rod, square, star, pyramid, core-shell, and disk).⁵³⁻⁶⁰ Among all, lithography patterning and colloidal synthesis are the two most common methods used to engineer the metallic nanostructure with unique geometry.^{2,6}

Using lithography patterning, arbitrary shape of two or three dimensional configurations can be created, such as array of disk,⁶¹ dimers of disk,⁶¹ bowtie,⁶² and metamaterials^{53,63}. Electron-beam-lithography (EBL) and focused-ion-beam (FIB) are the examples of the lithography methods creating nanoscale patterns. Despite the advance and flexibility of the lithography techniques, this technique is relatively difficult in fabricating the high-quality features such as sharp corner and coupled nanostructure with gap distance below 10 nm.

Figure 1.3 Reaction pathways to produce metallic nanostructure with different shapes.

Reprint from references 6 and 65.

On the other hand, colloidal synthesis is another practical technique used to control the shapes of metallic nanostructure at the atomic scale. Schematic illustration in Figure 1.3 shows the metallic nanostructure synthesis pathway that lead to major different geometries under different experimental conditions. Here, a metal precursor is reduced to form the nuclei. Once the nuclei have grown past a certain size, they will form relatively stable seeds with well-defined crystallographic facets on their surface, which determined by the minimization of surface energy.⁶⁴ Depending on the ratio of growth rate along [111] and [100] direction, the seeds can evolve into different polyhedron geometries. For a longer growing time, anisotropy nanocrystal such as octagonal rod, rectangular bars, will be formed.⁶⁵

Figure 1.4 Nanostructures with different shapes and sizes, (a) Au sphere, (b) Au rod, (c) Au cage, (d) Ag sphere, (e) Ag rod, (f) Ag cube. Each extinction spectra is accompanied with electron micrographs. Reprint from references 7 and 65 to 69.

Using methods mentioned above, in principle, the optical properties of the metallic nanostructure can be fine-tuned,⁵ and is illustrated in Figure 1.4.⁶ For a given shape, the LSPR features are strongly depending on the nanoparticle's size. These features include ratio of absorption to scattering, number of plasmon modes, as well as its resonance position, and the bandwidth.⁶⁶⁻⁶⁸ Clearly, as the size of the nanostructure is increased, the LSPR will red shifted due to retardation of the collective oscillation of electrons. Similar results can be observed as the refractive index of the nanoparticle's surrounding increased.^{69,70} Significant electric field density change as shape of the nanostructure changed, thus, results in the change of oscillation frequency of the electrons.^{71,72}

Through the proper design and engineering of the assembly process, a dimer can be arranged in a close distance.^{61,73} In close proximity, interparticle electromagnetic interaction can generate a strong electric field around the gap region between two nanoparticles. This strategy is to achieve strong field enhancement because it allow the detection of single molecule.⁷⁴ As any other parameters mentioned in previous paragraph, changing the distance between two nanostructures also can alter the optical properties of the nanostructure. For example, the LSPR of sphere dimer will shifts to lower energy in relative to their isolated structure, because of the electromagnetic interaction in coupled nanostructure.⁷⁵

Figure 1.5 Nanorod dimer assemble (a) in side-by-side configuration, (b) in end-to-end configuration, in longitudinal polarization direction (c) Plasmon hybridization model of molecular orbital. Where π and σ are bonding modes, while π^* and σ^* are antibonding modes. Reprint from references 75 and 76.

Coupled nanorod has been theoretically studied by Jain and co-workers Figure 1.5.⁷⁶ In this study, the nanorod dimer arranged in side-by-side and end-to-end was calculated using DDA method. The plasmon shifts as a function of interparticle distance between two nanorods is showed in Figure 1.5a and Figure 1.5b. As the distance between two particles in side-by-side configuration decreased, the plasmon peak is blue shifted, which is contrast to that of end-to-end configuration, where the plasmon peak is red shifted, as the distance between two particles decreased. The LSPR shifting manner can be intuitively explained by plasmon hybridization model in Figure 1.5c. When two metallic nanostructures are bringing in close proximity distance, the plasmon modes are hybridized, which analogy to the hybridization of atomic orbital in molecules.⁷⁵ In bonding mode (σ), the energy will go lower than their individual particle, while in antibonding (π^*) mode the energy will go higher than their individual particle. Based on the dimer configuration, the coupling modes can be intuitively understood from Figure 1.5c, hence we can predict the shifting pattern of that particular system.⁷⁵

Understanding the nature of the bonding and antibonding plasmon modes in simple coupled nanostructure is very useful as it help us to predict the plasmonic behavior of complex nanostructure such as nanodisk,⁷⁷ nanoshells,⁷⁸ hexagonal prisms,⁷⁹ metamaterials.^{53,80}

We believe that the LSPR of the any geometries fabricated either by lithography or wet chemistry methods, they can be *in-situ* tuned by charging or discharging that leads to the changing of the amount of free electrons density of their nanostructure.

1.2.2 *In-situ* altering the free electron density in metallic nanostructures

Figure 1.6 LSPR shifting corresponding to injection or withdrawing of charges carries in various materials. Reprint from reference 81.

Electrochemical reaction is one of the prominent techniques for *in-situ* induced plasmon shifts. Depend on the applied potential, the electrons can either injected into or withdraw from a metallic nanostructure, hence changing the bulk plasmon frequency (Figure 1.6),⁸¹ which indicated in Equation (11). The correlation between the applied electrical potential and the change in plasmonic behavior can be

monitored via surface-enhanced Raman spectroscopic or ultraviolet-visible measurement.^{50,82} Generally, increasing the amount of free electron density into the metallic nanostructure will results in LSPR shifts to the higher frequency and producing larger electric field confinement, in relative to their neutral state, vice versa.⁸³⁻⁸⁵

Choosing a suitable metal for electrochemical tuning is crucial so that it can sustains a repeating voltage potential over the measurement. For silver (Ag) nanostructure, because of its interband transition is within ultraviolet region, hence Ag shows an ideal Drude-like behavior in visible region.⁸⁶ Unfortunately, because of its low susceptibility to oxidation, Ag has great limitation in electrochemical application, nonetheless, some studies still carefully carried out using Ag.^{82,87-90} Copper (Cu) on the other hand has a high electrical conductivity and support LSPR in visible range, but it also suffer from the oxidation issue similar as Ag, which make it less popular in electrochemical process. Meanwhile, platinum has high oxidative stability but barely supports the surface plasmon resonance in visible region. Last but not least, Au has interband transition around 500 nm,⁹¹ but due to its high chemical stability and strong plasmonic resonance within visible spectrum,^{26,92} Au is a popular plasmonic material used for electrochemical process.

Figure 1.7 LSPR position of Ag nanosphere in response to the electrode potential.

Reprint from reference 82.

Using the electrochemical method, Mulvaney and co-workers has first to correlation between the electrons transfer and the LSPR peak position shifts.^{82,90} In their study, the mobility of electrons was controlled via spectroelectrochemical cell, which designed to monitor the change of LSPR position as a function of the amount of the Ag's electron density via the UV-vis. This approach is important because it offers a good way of determining the number of electrons transferred in and out of the particle. Based on Figure 1.7, as many as 1600 ± 300 electrons transfer into the Ag nanosphere at -0.4 V versus Ag/AgCl were measured. Simultaneously, the plasmon peak was blue shifted from 404 nm to 380 nm. Given the initial and the final LSPR position we can calculate the percentage of electrons have transferred into the Ag nanoparticles using following relation:

$$\lambda_f = \lambda_i \sqrt{\frac{N_i}{N_f}} \quad (12)$$

Where λ_f and λ_i denote the final and initial LSPR peak position, and N_i and N_f denote the free electron density at initial and final state. Given the initial N_i equal to 5.9×10^{28} electrons/m³.⁹³ They concluded that a net change of free electrons densities of ~6%/V/particle based on this study.

By exploiting the ability to control the dimensions of a nanorod, the same group also conducted a study on the far field sensitivity of different aspect ratio to the charging effect.¹² By giving the same amount of charges to the nanorod, the plasmon-shift varies linearly with the geometry factor of the nanorod, which shown in Figure 1.8,⁹⁴ the inset shows the Au nanorod with scale bar of 2.5 nm.

Figure 1.8 LSPR shift as a function of Au nanorod aspect ratio, at 11.4% of charging level. Inset shows the nanorod micrograph from scanning electron micrograph with scale bar of 2.5 nm. Reprint from reference 94.

To explain this result, a relationship between plasmon shifts, $\Delta\lambda$ as a function of a single nanorod's geometrical factor was derived analytically from Drude model, which showed in equation (13).

$$\Delta\lambda = -\frac{\Delta N}{2N}\lambda_p \sqrt{\varepsilon_\infty + \left(\frac{1}{L} - 1\right)\varepsilon_m} \quad (13)$$

Where $\Delta N/N$, λ_p , L , and ε_m denote the excess of electrons due to charging, Au plasma wavelength (130 nm), shape dependent constant, and environment dielectric constant. The L can be calculated using Equation (14):

$$L = \frac{1 - e^2}{e^2} \left(-1 + \frac{1}{2e} \ln \frac{1 + e}{1 - e} \right) \quad (14)$$

$$e^2 = 1 - \frac{b^2}{a^2} \quad (15)$$

Where a and b are the major and minor axis of the ellipsoid. Clearly, higher the aspect ratio, larger the plasmon shifts.

Experimentally, charging of a plasmonic material can be achieved via physical or chemical method.^{12,52,88,89,95-98} From Equation (11), increasing of the amount of free electron density will directly increase the bulk plasma frequency of a plasmonic material, hence the blue shifting of LSPR peak position, and vice versa. Based on this notion, charging effect can be implementing into Drude model by manipulating of the bulk plasmon frequency. The analytical expression for the real and imaginary part of charged Drude model can be written as:⁹¹

$$\varepsilon'(\omega) = \varepsilon_\infty - \frac{\omega_p^2 \left(1 + \frac{\Delta N}{N}\right)}{\omega^2 + \gamma^2} \quad (16)$$

$$\varepsilon''(\omega) = \frac{\gamma \omega_p^2 (1 + \frac{\Delta N}{N})}{\omega^3 + \gamma^2 \omega} \quad (17)$$

Where γ is the damping constant, and can be calculated by $Ne^2/\sigma m_e$. σ is the conductivity. Note that the damping constant also consists of the free electron density term, however, this effect is cancelled out by the conductivity term which also depends on the free electron density parameter.²³ At neutral state, Equation (16 and 17) above will be reduced into their normal Drude model form. From the dielectric constant calculated with this model, the charging effect can be simulated theoretically. Juluri and co-workers applied this model in Mie's theory to study the volume fraction of core-shell nanostructure in response to the charging effect.⁹¹

(a)

(b)

Figure 1.9 (a) Extinction spectra of silica-Au core-shell. The solid lines are at neutral state, while the dot lines are at 14% charging. (b) Increasing the volume of core at 14% charging. The solid lines are fitted with quasistatic theory. The hollow circles are nanoshell with hollow core; The solid circles are nanoshell with solid silica core. All the radius of nanoshell radius is fixed at 10 nm. (note: R_c is the core radius, while the R_m is the total radius of the nanoshell). Reprint from reference 91.

Figure 1.9 shows the response of the different core volume fraction of the nanoshell in response to the charging effect.⁹¹ In Figure 1.9a, the peak position is blue shifted upon charging, a similar behavior as Au nanorod mentioned in previous paragraph. The response towards charging effect is depending on the composition and the volume fraction of the core. To evaluate the charging effect on the volume fraction of the core, a series of electrodynamic calculations were done and summarized in Figure 1.9b. As expected, the blue shifting is increased with increasing R_c/R_m ratio. Clearly, the response was slow at R_c/R_m ratio smaller than 0.7, and exponentially increased with ratio larger than 0.7. Both hollow and solid nanoshell are exhibiting the same behavior in response to the charging effect. It is observed that the shell with solid core has higher sensitivity than that of hollow shell, this pattern is contributed by the higher refractive index experience by the solid core-shell system.

Figure 1.10 Study of charges effect on single monolayer gold disk (diameter equal 8 nm) using quantum model (left column) and classical model (right column). (a, d) Extinction spectra position of single monolayer gold disk in response to the charges effect. (b, e) Summary of plasmon peak position of Au disk. (c, f) Optical extinction cross-section and the FWHM as a function of charging effect. Reprint from reference 101.

In large particle (diameter around 20 nm for sphere), classical model can accurately predict the charges effect to the LSPR properties, however, for a nanostructure in few atomic layers such as graphene, calculation under quantum mechanics is needed.⁹⁹ Recently, a study on charges effect to the single monolayer Au disk was done using quantum model (random-phase approximation) and classical model (boundary-element method).^{100,101} Both methods have result same LSPR shifting trends that is blue shifting as increased and red shifting as the electron density

decreased, both shifting pattern are with respect to their neutral state (Figure 1.10a and Figure 1.10d). Figure 1.10b and Figure 1.10e show the linear plasmon shifts with increasing charging effect predicted using classical model. In contrast, nonlinear LSPR shifts were observed under the quantum model calculations. Interestingly, when examining the maximum extinction cross-section intensity and its full width half maximum (FWHM), the quantum model shows an oscillatory manner (Figure 1.10c). While this behavior is not observed under the classical mechanics calculation, where the maximum extinction cross-section intensity appeared linearly increasing and the FWHM remain unchanged over the different charging effect (Figure 1.10f). Disagreement between these two methods conclude that the classical model fail to predict the plasmon feature in a single layer of Au metallic layer, because of the splitting of the orbital energy level.

Thus far, we show the influence of the charging effect to the LSPR shifting pattern. However, when applying electrochemical potential to the metal particle, is the electron transfer the only process that occurred? Here, we will discuss several effects at applied electrochemical potential to the metallic nanostructure that might contribute to the LSPR interpretation.

1.2.3 Effects under the influence of electrochemical potential

Figure 1.11 LSPR peak shift at 250 mV as a function of different salt concentration.

Reprint from reference 102.

Dahlin's group studied the influences of electrochemical reaction and the electric double layer to the LSPR spectral shifting.^{102,103} In their experiment, 50 nm Au particles were immobilized on an indium tin oxide glass substrate; the system was conducted in a stagnant solution with different concentration of salt (NaCl). The result is showed in Figure 1.11. At constant giving potential at +250 mV, they found that the LSPR peak shifts to the lower energy as the NaCl concentration increased from 0.001 mM to 1000 mM. Two possibilities may lead to the shifting trend. First, is the electron diffuse out from the Au, this argument is proven to influence the red shifting for metal particle that has size smaller than 10 nm.^{104,105} Nonetheless, the effect of diffusion layer is quite small, hence we can rule out this possibility that responsible for the plasmon shifts.¹⁰³ Another possibility that affecting the plasmon shifts is owing to the formation of higher refractive index double layer between the metal surface and the solution. In aqueous solution, chloride ion has higher polarizability

compared to water molecule. Therefore, when applying positive potential, water molecule can be easily displaced by the chloride ion that attracted to the surface of Au surface. With increasing the salt concentration, more water molecule is being displaced. Based on their simulation result, at high salt concentration, hexagonal packing of chloride ion monolayer with the thickness of 0.362 nm can be formed. This layer has the refractive index of 3.0, hence the formation of higher refractive index environment as the salt concentration increased, is the major contributor to the observed red shifting. The similar explanation also can hold true with negative potential, as the double layer is speculated to build up based on sodium ion, instead of chloride ion.^{52,106,107} Under this aqueous solution, the magnitude of the shifting is less than 1 nm at 1000 mM, which imply that formation of double layer based on chloride or sodium ion has slight influenced the overall result interpretation under the apply electrochemical potential.

Figure 1.12 Longitudinal plasmon band shifting trends at 1 mM of ascorbic acid to the solution containing Au nanorod with aspect ratio of 4. Reprint from reference 95.

Besides increasing the refractive index of the local environment experienced at the surface of the metal structure, injecting electrons also can induce the mechanical instability of the metal nanostructure. A research was done by Mulvaney's group demonstrated that the end caps of nanorod will be flattened, with increasing the amount of electrons transfer to the Au nanorod.⁹⁵ The shape changing process happened within few minutes. At the beginning, the LSPR is blue shifting with increasing of the amount of free electron density, an overturn of LSPR position to the lower energy is observed after 1 minute, however, LSPR shifting is reaching a plateau after 8 minutes, this trend is illustrated in Figure 1.12.

Figure 1.13 High resolution transmission electron microscope image of Au nanorod at aspect ratio of 4, (a) before addition of 1 mM of ascorbic acid (b) after addition of 1 mM of ascorbic acid. Reprint from reference 95.

To explain this shifting overturn trend, an image of nanorod is taken under high resolution transmission electron microscope in Figure 1.13. The image proved the shape has changed when the amount of electrons transferred from the acid to the nanorods was increased. Based on the our analysis to the plasmon shifting relation

and the percentage of charging level from Mulvaney,¹² an addition of 1mM of ascorbic acid, nanorod LSPR has showed blue shifting from 850 nm to 770 nm. This mean that Au nanorod gained extra ~23% of extra free electrons from ascorbic acid, therefore, high electrons loading might induced the Rayleigh instability and etch the tip of the nanorod. The flatten nanorod has induced the LSPR to shift about 10 nm to the lower energy and remain unchange for 95 minutes. Similar etching process also observed in nanoprism when applying potential via electrochemical method.⁸⁸ Unless purposely doing so, the electron injection or withdrawing process will etch the nanostructure to some degree and is irreversible, which yielding undesired rounding/flatten feature on nanostructure morphology.

Due to the flexibility of the electrochemical method, it has been a popular method to control the electron density in metal and often integrated into enhanced Raman spectroscopy for *in-situ* controlling the plasmonic properties. There are few other ways to altering the amount of free electron density in metal, which we will discuss further in next section.

1.2.4 Other electrons density controlling methods

Figure 1.14 (a) Schematic of experimental setup of argon plasma (b) Charging of nanodisk (c) micrograph from scanning electron microscope. Reprint from reference

93.

A rapid LSPR shifts by changing the amount of free electrons can be induced by low-temperature argon plasma (Figure 1.14a).⁹³ In this method, Au nanodisk can be directly charged with negative ion from ionic argon gas (Figure 1.14b and c). The experiment was done in vacuum environment, in another word, there is no dielectric double layer between the nanostructure and the vacuum, and hence the electrons can be directly injected into the nanodisk without any obstacle, which give rise to its high efficiency to control the plasmon properties. When discharged, the LSPR peak position of the Au nanodisk can returns to its original position. This method indicates a more efficient way of tuning the metal LSPR. Beside physical method to injecting electrons into the nanoparticles, it also can be done chemically.

Figure 1.15 Schematic of chemically adding the excess electrons to the silver nanoprism. Reprint from reference 108.

A chemical charging of a metallic nanostructure can be done by putting an electron donor species near to it. In Figure 1.15, when poly(3-hexylthiophene) is photoexcited, it will generate free electrons which later transfer to the phenyl-C61-butyric acid methyl ester, and lastly to the embedded Ag nanoprism.¹⁰⁸ Electron transfer was proved by the observed blue shifts of the Ag nanoprism LSPR. This step is commonly found in photovoltaic device and photocatalysis process.^{109,110} Understanding this process is crucial to increase the photocurrent and power conversion efficiency of the device.

1.2.5 Altering free carriers density in non-metallic nanostructures

Figure 1.16 Oxidation and reduction process of copper selenide nanocrystal. Reprint from reference 111.

LSPR is recently found not only limited to metallic nanostructure, but highly doped semiconductor with appreciable free hole concentration also can support LSPR like noble metal.³⁷ The dynamic tuning of plasmonic response in the near-infrared for colloidal Cu_{2-x}Se nanostructure (p-type semiconductor) can be summarized in Figure 1.16.¹¹¹ Using sonoelectrochemical, hydrothermal, and solventless thermolysis, free holes can be created in the valance band of the semiconductor and tuning LSPR properties.¹¹² Take copper selenide (Cu_{2-x}Se) as an example, Dorfs and co-workers had demonstrated by gradual oxidation of Cu_{2-x}Se nanostructure under ambient condition (oxygen) or adding the Ce(IV) complex will change the Cu:Se stoichiometry from close to 2:1 down to lower limit of 1.6:1; which mean that the subscript “x” could be varied from 0 to 0.4.¹¹¹ The LSPR of Cu_{2-x}Se is tuned on the basis of the copper deficiency. Increasing the value of x by oxidation, the optical response in the near infrared regime will shifted from 1700 nm at (x equal to 0) to 1100 nm (x equal to 0.4).¹¹¹ Reduction of Cu_{2-x}Se nanostructure will decrease the value of x and the position of LSPR will red shifted in relative to their original position.^{37,113}

Similar to the metal nanostructure, the free hole's motion in the semiconductor can be described using Drude model.³⁷ Here, the bulk plasmon frequency is slightly different to the one that describe metallic nanostructure, that is N and m_e in Equation (11) are replaced by N_h and m_h to signify the hole's concentration and the hole effective mass.^{37,38}

$$\omega_p = \sqrt{\frac{N_h e^2}{\epsilon_o m_h}} \quad (18)$$

Where the m_h is approximately $0.8m_o$ (m_o is electron mass). Charging effect can be included with simply adding the varied the N_h .

Figure 1.17 (a) Schematic and optical image of graphene field-effect transistor device.

Blue dots indicate the methylene blue. Dash red lines show the scanning direction, with the scanned voltage from 50V to -50V (b) Raman signal of methylene blue on the hole-doped, normal, and electron-doped graphene with 647 nm laser excitation. Note: the spectra are normalized to 520 cm^{-1} Si Raman peak (labeled by †). Reprint

from reference 51.

Other than metal-sulfide semiconductor, graphene also found to support LSPR.³⁷ Hao and co-workers has studied effect of changing the electrons and holes in graphene to the Raman intensity of methylene blue.⁵¹ Figure 1.17a shows schematic of experimental setup of electrical contacts with graphene. In this case, altering the electrons and holes in graphene was done using chemical doping. By exposing to the hydroxyl group (-OH) molecule or exposing to the amine group (-NH₂) molecule, graphene monolayer can be either hole-doped or electron-doped. As showed in Figure 1.17b, electron or hole doping to graphene result in plasmonic position shifting, consequently fields enhancement can be altered, which enable us to manipulate the enhanced Raman intensity.

1.2.6 Near field properties of metal nanostructures

Figure 1.18 Schematic illustration near field interacting with a molecule with the strong field enhancement confined in the gap between two Au nanoparticles. The red dots indicate the vector of the field. Reprint from reference 114.

Another interesting aspect of LSPR is the strong electric field confinement at small volume known as “hot spot” at the metallic surface that allows us to go beyond the diffraction limit.^{24,44} The hot spot normally found stronger at the edge of sharp protrusion surface and gap between two or more nanoparticles (Figure 1.18).¹¹⁴ With such a strong field enhancements (enhancement factor of 10^4 - 10^6), it allows us to probe to a single molecule detection.^{2,115-117} This finding was important for practical application such as surface-enhanced Raman scattering (SERS). The accepted mechanism for the field enhancement are chemical and physical enhancements,⁵² the latter is responsible for the major contribution to the SERS signal enhancements.¹¹⁸

Figure 1.19 Electric field distribution of different nanoparticle shapes and dimers at respective resonance wavelength (a) prism (b) prism dimer (c) sphere dimer (d) hollow pyramid dimer. Reprint from reference 119.

Similar to the far field, tuning of near field also can be statically and dynamically tuned. Figure 1.19 shows the electric field distribution of different

geometries.¹¹⁹ Clearly, most of the electromagnetic fields are concentrated at the asperities of the shapes, particularly at the apex, in Figure 1.19a. When two nanoparticles are brought proximity together, intense ‘hot spot’ will be formed at the junctions between the nanoparticles, which is depicted in Figure 1.19b to d, as a result, SERS signal of molecules in this region will greatly increase.

Figure 1.20 Experimental set up of *in-situ* modulation via electrochemical-surface-enhanced Raman scattering. Raman spectrometer is shown in blue box. Potential is applied via potentiostat, the result is recorded in computer. WE, CE, and RE, are working electrode, counter electrode, and reference electrode. Reprint from reference

52.

For static tuning, the distribution of the hot spot varies significantly subjected to the different shapes and sizes. For dynamic tuning, it yields insignificant hot spot

variations, since shape and size are fixed, and only the amount of free electron density is varied. Nonetheless, increasing the amount of free electrons density of the nanoparticle will result in increasing the field enhancement, because increasing of the amount of electrons in the conduction band of the nanostructure will lead to larger polarizability, this phenomenon resemble the lightning rod effect, hence it yield larger field enhancement in relative to their neutral counterpart. Figure 1.20 shows the experimental set up of electrochemical integrated surface-enhanced Raman spectroscopy. The amount of free electron density of the plasmonic material is externally controlled by a potentialstat that connected to the sample cell via working electrode. Measurement is then record in the computer. This technique has been widely used in trace specific molecules in live cells or animals and detecting the dynamic of electron transfer during the redox process in cytochrome complex.¹²⁰

1.3 Research Motivation and Objectives

State-of-the-art fabrication techniques have enabled us to fine-tune the surface plasmon resonance by changing the size and shape based on different materials. However, in some application such as active photonic waveguide,¹²¹ optoelectronic switches,¹²² and surface-enhanced Raman scattering,⁵² where the ability to *in-situ* modulation to obtain the real time measurement is desirable. In addition, detecting the change of the amount of free electron density of the nanostructure is also showed the potential to use in detecting the redox activity in the vicinity of nanostructure, and might be able to use for sensing.

Increasing attention has been directed to the assembly building blocks, as it shows a higher tunability and strong electric field concentrated at the gap region, which can benefit multidiscipline applications. However, the charges effect to the LSPR behavior on the coupled metallic nanostructures has not been study. In order to achieving this task, several objectives are summarized as below:

1. To calculate the plasmon shifts due to the charging effect in individual and coupled metallic nanostructures.
2. To calculated the response of electric field enhancement to the charging effect on the same geometries
3. To evaluate the sensitivity of both far field and near field of different geometries to the charging effect.

1.4 Hypothesis

Based on previous studies, the far field is linearly in response to the charging effect, and the response is greater for a nanostructure with larger geometrical factor. Based on this knowledge, we assumed that coupled nanostructure would have larger plasmon shifts as well as higher sensitivity compared to their individual nanostructure. Moreover, we also assumed that the coupled nanostructures with larger geometrical factor also yield larger plasmon shifts and sensitivity in response to charging effect compared to the coupled nanostructures with lower geometrical factor.

Other the other hand, based on hybridization model, bonding mode usually excited in coupled nanostructure with perpendicular polarization along to their gap, hence larger the geometry factor will result in stronger coupling and larger electric

field confinement. Therefore, we assume that, structure with large geometry factor will also result in high field enhancement and sensitivity towards the charging effect.

1.5 Organization of the thesis

This thesis has five chapters. Chapter 1 provides the overview of the surface plasmon resonance, which started with historical developments of surface plasmon resonance, theoretical calculations of the surface plasmon resonance by solving Maxwell equations, and discussed the two most important ingredients of fundamental plasmonic modes. Subsequently, we reviewed the surface plasmon tuning via static and dynamic methods. Details of static tuning via different advance methods were discussed, followed by a dynamic tuning which focus on *in-situ* changing the free electron density of a nanostructure. Next, we also discussed the effect under the influence of charging effect using electrochemical potential, and other type of free electron density tuning methods for metallic nanostructure and non-metallic nanostructure. Finally, we address some update of charging effect on the field enhancement of single nanostructure. We conclude this chapter with a research motivation and hypotheses.

In chapter 2, we showed in details how a charging effect could be calculated theoretically using Drude-Lorentz model, and introduction of discrete dipole approximation (DDA) that we used in this research.

In Chapter 3, numerically calculated far field in response to the charging effect were studied and discussed. Together with an analytical solution, we provide an

intuitive understanding of the charging effect to the plasmon behavior can be used to support numerically calculated (using DDA method) results.

In Chapter 4, details of the near field in response to the charging effect were carried out. In this chapter, analytical solutions were also used to support the numerical calculations. The near field sensitivity toward the charging effects was interpreted via the field enhancement ratio and we further explained the results by adapting an effective dipole moment model.

Last but not least, in Chapter 5, we concluded this work and proposed some future perspectives based on this project.

CHAPTER 2 METHODOLOGY

Practically, charging of a metallic nanostructure can be done by externally applying electrical potential to the system. As discussed in previous chapter, charging can lead to changing the amount of free electron density of a metallic nanostructure. This effect can be captured by the dielectric constant, and can be described using Drude-Lorentz model. For simplicity, here onward, we use charging only refer to indicate negative potential, meaning increasing the amount of free electron density of a metallic nanostructure. The reason we choose negative bias because it can avoid the oxidation of Au. In this chapter, several assumptions were made to establish our study. Then we discuss the detail of numerical method used in our simulations.

2.1 Assumptions in the calculations

When applying electrical potential to the nanostructure, this process will attract ion or molecules from the surrounding. As a result, the local refractive index surrounding the metallic nanostructure surface will be slightly increased.^{106,107} However, since this effect contributed small impact on the LSPR properties, we assume that the change of local refractive index near the metallic particle's surface is the same as the refractive index of the surrounding environment. In addition, we also do not consider the chemical bond between stabilizing or capping molecules on the metallic nanoparticle which might restricting the motion of electrons at the surface, and this effect is obvious for small nanoparticle (below 10 nm).^{104,123} As the size increased, the ratio between the bound electrons to the free electron will become insignificant.

The charging effect may be inhomogenous in experiment due to the uneven distribution of electric potential and attached molecules to the nanoparticle, however, this effect may played an important role in small gap coupled nanostructure (below 1 nm). Under this condition nonlinearity non-local correction or quantum mechanics calculation may needed.^{124,125} Since the gap distance we considered in this work is still significantly large, therefore, we can assume that the electrons are evenly distributed on the surface of the nanostructure with no electrons spill out.

2.2 Theoretical charged Au nanostructure

In this study, we investigated a wider range (0 to 16%) of excess electrons $\Delta N/N$ based on two reasons. First, we considering the variation of the amount of charges injected into the nanostructure may varies with the applied electrochemical potential and the double layer capacitance.⁹¹ In our second consideration, ions may presence at the surface of metal, which may screen the injected electrons to the nanostructures, hence, larger potential may needed to compensate these variation.

In the noble metal family, Au is a suitable candidate to be utilized in dynamic tuning, attributing to its high electrical conductivity, chemical and thermal stability. In visible region, free electron motion in Au can be described using Drude-Lorentz model.

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + \omega\gamma i} - \frac{\Delta\epsilon\Omega_L^2}{\omega^2 - \Omega_L^2 + \omega\Gamma_L i} \quad (19)$$

where, ϵ_{∞} , ω_p , and γ denote frequency independent dielectric constant, plasma frequency, and damping constant, respectively. In the Lorentz term, $\Delta\epsilon$, Ω_L , and Γ_L are

the Lorentz weighting factor, the Lorentz oscillator strength, and the damping constant of the Lorentz oscillator, respectively. In Equation (19), γ and Γ_L are independent of the free electron density of materials.⁹¹ ω_p^2 is proportional to the free electron density N by $\omega_p^2 = Ne^2/m_e\epsilon_0$, where e , m_e , and ϵ_0 denote electron charge, effective mass of electrons, and vacuum permittivity, respectively. The term of Ω_L^2 is linearly dependent to plasma frequency by $\Omega_L^2 = f_o\omega_p^2$, where f_o is a constant.¹²⁶ The charging effect can be taken care of by adding excess electron ($\Delta N/N$) to ω_p^2 term and Ω_L^2 term, which is Equation (11).

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2(1 + \Delta N/N)}{\omega^2 + \omega\gamma i} - \frac{\Delta\varepsilon\Omega_L^2(1 + \Delta N/N)}{\omega^2 - \Omega_L^2(1 + \Delta N/N) + \omega\Gamma_L i} \quad (20)$$

Or

$$\varepsilon'(\omega) = \varepsilon_\infty - \frac{\omega_p^2(1 + \frac{\Delta N}{N})}{\omega^2 + \gamma^2} - \frac{(\omega^2 - \Omega_L^2(1 + \frac{\Delta N}{N}))\Delta\varepsilon\Omega_L^2(1 + \frac{\Delta N}{N})}{(\omega^2 - (\Omega_L^2(1 + \frac{\Delta N}{N})))^2 + \omega^2\Gamma_L^2} \quad (21)$$

$$\varepsilon''(\omega) = \frac{\gamma\omega_p^2(1 + \frac{\Delta N}{N})}{\omega^3 + \gamma^2\omega} + \frac{\omega\Gamma_L\Delta\varepsilon\Omega_L^2(1 + \frac{\Delta N}{N})}{(\omega^2 - (\Omega_L^2(1 + \frac{\Delta N}{N})))^2 + \omega^2\Gamma_L^2} \quad (22)$$

where $\varepsilon_\infty = 5.9673$, $\omega_p = 8.7411$ eV, $\gamma = 0.0658$ eV, $\Delta\varepsilon = 1.090$, $\Gamma_L = 0.4337$ eV, and $\Omega_L = 2.6885$ eV.¹²⁷

When $\Delta N/N = 0$, Equation 20 is reduced into Equation 19, where the material is at neutral state.

2.3 Numerical method using discrete dipole approximation (DDA)

In this study, electrodynamics calculations were done using DDA method. DDA is a numerical method to solve Maxwell's equations for low symmetry particles. It was originally proposed by Purcell and Pennypacker in 1973¹²⁸, to study the light scattering of interstellar dust grain. Subsequently, this technique was employed by Draine and Flatau¹⁵ into DDSCAT program to calculate the scattering and absorption electromagnetic wave of an arbitrary geometry target.

Figure 2.1 Discretizing of sphere into N_{dipole} polarizable points with d lattice spacing between two neighbor dipoles.

In this approximation, the anisotropy shape of particle is represented by N_{dipole} polarizable point on a cubic lattice located at position $\mathbf{r}_i$ ($i=1,2,3,\dots,N_{\text{dipole}}$). Each dipole at $\mathbf{r}_i$ has polarization $\mathbf{P}_i = \alpha_i \mathbf{E}_i$,¹⁵ where α_i , the polarizabilities, which is determined from the particle's dielectric constants. α_i can be computed analytically via lattice dispersion relation (Equation 23). In DDA, an object is discretized into lattice spacing, d between two neighboring dipole, which is much smaller than the incident light wavelength (Figure 2.1).

$$\alpha_i = \frac{\alpha_i^{\text{cm}}}{1 + \left(\frac{\alpha_i^{\text{cm}}}{d^3}\right) [b_1 + m^2 b_2 + m^2 b_3 S] (kd)^2 - \left(\frac{2}{3}\right) i (kd)^3} \quad (23)$$

Where $b_1 = -1.891531$; $b_2 = 0.1648469$; $b_3 = -1.7700004$; $S = \sum_{j=1}^3 (\mathbf{a}_j \mathbf{e}_j)^2$; α_i^{cm} is the Classius-Mossotti polarizabilities¹²⁸:

$$\alpha_i^{\text{cm}} = \left(\frac{3d}{4\pi}\right)^3 \frac{\varepsilon_i - 1}{\varepsilon_i + 2} \quad (24)$$

Where ε_i = dielectric function of target material at position r_i .

When the system is excited by an electromagnetic wave, the response of a particle is determined by self-consistent solution. The local field of each dipole, $E_{\text{loc},i}$ is contributed from both a) incident radiation field, $E_{\text{inc},i}$ b) radiation field from neighboring induced dipole, $E_{\text{neigh},i}$ and is given by Equation (25):

$$E_{\text{loc},i} = E_{\text{inc},i} + E_{\text{neigh},i} = E_o e^{ik \cdot r_j} - \sum_{i \neq j} A_{ij} \cdot P_j \quad (25)$$

Where P_i is the dipole moment at location r_i , retardation effects is included. Each A_{ij} element with $i \neq j$ ($j=1,2,3 \dots N_{\text{dipole}}$) is a 3x3 matrix interaction, such that:

$$A_{ij} \cdot P_j = \frac{e^{ikr_{ij}}}{r_{ij}^3} \left\{ k^2 r_{ij} \times (r_{ij} \times P_j) + \frac{1 - ikr_j}{r_{ij}^2} \times (r_{ij}^2 P_j - 3r_{ij}(r_{ij} \cdot P_j)) \right\} \quad (26)$$

Where $k = \omega/c = 2\pi/\lambda$ (ω =angular frequency and c = speed of light); r_{ij} = magnitude of vector dipole i to dipole j .

Substitute Equation (25) into (26) and defining $A_{ij} = \alpha_i^{-1}$; Equation (27) is generated, which allows us to find unknown polarization, P_i that satisfies the 3N complex linear equation:

$$\sum_{i=1}^N A_{ij} \cdot P_i = E_{inc,i} \quad (27)$$

After determined P_j , extinction cross-section (C_{ext}) and absorption cross-section (C_{abs}) can be evaluated from:

$$C_{ext} = \frac{4\pi k}{|E_o|^2} \sum_{j=1}^{N_{dipole}} \text{Im}(E_{inc,i}^* \cdot P_i) \quad (28)$$

$$C_{abs} = \frac{4\pi k}{|E_o|^2} \sum_{j=1}^{N_{dipole}} \{ \text{Im}[P_i \cdot (\alpha_i^{-1})^* P_i] - \frac{2}{3} k^3 |P_i|^2 \} \quad (29)$$

Where the asterisk (*) signifies the complex conjugate. The scattering cross section, C_{scat} can be calculated via Equation (30):

$$C_{ext} = C_{abs} + C_{scat} \quad (30)$$

For this approximation, the efficiency of extinction (Q_{ext}), absorption (Q_{abs}) and scattering (Q_{scat}) of target particle can be calculated via:

$$Q_{ext} = \frac{C_{ext}}{\pi a_{eff}^2} \quad (31)$$

$$Q_{abs} = \frac{C_{abs}}{\pi a_{eff}^2} \quad (32)$$

$$Q_{scat} = \frac{C_{scat}}{\pi a_{eff}^2} \quad (33)$$

Where α_{eff} = effective radius of target particle.

Unfortunately, no clear guide to determine how many dipoles is best for any arbitrary target, though, it is suggested by the author of DDSCAT that $N_{dipole} \sim 10^4$ is consider

reasonable enough to represent a particle. Of course, the higher N_{dipole} the better the DDA representation the actual object, but it also could increase the computational burden.

Appropriate N_{dipole} can be determined with lattice spacing, d . With the list of occupied sites created by i ($i=1,2,3\ldots N_{\text{dipole}}$), one can assume that each occupied sites is correspond to cubic subvolume, d^3 . Therefore, the entire system of arbitrary with a defined actual volume, V can be restated as Equation (34):

$$d = \left(\frac{V}{N_{\text{dipole}}} \right)^{1/3} \quad (34)$$

Following from calculated d one can determine the effective radius of a nanoparticle, r_{eff} by:

$$r_{\text{eff}} = \left(\frac{3V}{4\pi} \right)^{1/3} \quad (35)$$

The electromagnetic enhancement is represented by the average enhancement factor (EF) over the whole nanostructure surface and is described in Equation (36).¹²⁹

$$\text{EF} = \left\langle \frac{|E_{\text{loc}}|^2}{|E_{\text{inc}}|^2} \right\rangle \quad (36)$$

The behavior of EF increment in response to the charging effect is characterized by the enhancement ratio, given by Equation (37).

$$\text{Enhancement ratio} = \frac{\text{EF}(\Delta N/N)}{\text{EF}(\Delta N/N = 0)} \quad (37)$$

With the same amount of excess electron, larger enhancement ratio means the near fields of a nanostructure has higher sensitivity to the charging, and vice versa.

CHAPTER 3 FAR FIELD PROPERTIES OF Au

NANOSTRUCTURES

3.1 Introduction

From previous studies, the LSPR position is demonstrated to be blue shifted with excess of electrons,^{82,89,130} while it will red shifted with lack of electrons; both conditions are in compared to their LSPR position at their neutral state. Some past studies have been devoted to the charging effect on isolated metallic nanostructure based on experimental works.^{89,91,94} Nonetheless, an intuitive understanding of the charged isolated nanostructure's behavior also been revealed using quasistatic limit theory. Turns out, the geometry of a nanostructure has a very high impact to the plasmon shifting as a function of charging effect.⁹¹ To our knowledge, limited study has been focus on the charging effect on the coupled nanostructures. In this chapter, we will present the far field position shifts in response to the charging effect on both isolated Au nanostructure (ellipsoid and sphere monomer) and coupled Au nanostructure (ellipsoid-ellipsoid dimer, ellipsoid-sphere dimer, and sphere dimer). For this sake, we numerically calculated the extinction spectra and compared the results with the analytically calculated one. In addition, to interpret the behavior of the plasmon shifts, we also step-by-step show the derivation of an analytical solution to describe the dependency of a coupled geometry in response to the charging effects.

3.2 Analytical solution under quasistatic limit

Analytical solution is crucial for intuitive understanding the physical insight of the plasmon position shifts than numerical solution, however, the validity of the quasistatic theory falls into small particles that only exhibit dipolar surface plasmon modes in response to the incident electromagnetic wave.¹³¹ Since the charging effect is more pronounce for shape with a protrusion surface, therefore, we begin this study using an ellipsoid monomer. The other reason we choose ellipsoid is because so far only sphere, oblate spheroid, and prolate spheroid can fulfil the condition of analytical solution.²³ Nevertheless, using ellipsoid as a fundamental study, we can speculated that these results also can help us to interpret other protrusion shapes such as: triangular prism, star-shape, core-shell and cubical nanostructures, as well as their coupled configurations. In this section, analytical solution for ellipsoid monomer is showed, subsequently, we step-by-step derive the plasmon shift, $\Delta\lambda$ for the coupled nanostructure using the average polarizability.

3.2.1 Calculations of extinction spectra

The extinction spectrum of an ellipsoid monomer can be calculated using Equation (38):¹³²

$$C_{ext} = \frac{2\pi V \varepsilon_e^{3/2}}{\lambda L^2} \frac{\varepsilon''(\lambda)}{(\varepsilon' + \kappa \varepsilon_e)^2 + \varepsilon''^2} \quad (38)$$

where, V , ε_e , L , ε' , and ε'' are the volume of particle, the dielectric constant of environment, the shape dependent constant, the real part, and the imaginary part of Au dielectric constants, while the geometrical depolarization factor, κ , is defined:

$$\kappa = \frac{1}{L} - 1 \quad (39)$$

3.2.2 LSPR shifts, $\Delta\lambda$ of monomers and dimers

The $\Delta\lambda$ of ellipsoid monomer and sphere monomer from its neutral state to a charged state can be determined analytically under quasistatic limit using Equation (13) in Chapter 1.^{94,95}

Step-by-step derivations of charging effect on the coupled Au nanostructure are shown in below, starting with a polarizability, α of a single nanostructure.

$$\alpha = \frac{4\pi\epsilon_0 ab^2}{3L_x} \frac{\epsilon - \epsilon_e}{\epsilon + \kappa\epsilon_e} \quad (40)$$

Where, ϵ_0 is the permittivity of vacuum, a and b are the short and long semi-axes of the spheroid, L_x is the depolarization factor of the shape, ϵ and ϵ_e are the dielectric constant of material and dielectric constant of surrounding.

L_x can be obtained from:

$$L_x = \frac{1 - e^2}{e^2} \left(\frac{1}{2e} \ln \left(\frac{1 + e}{1 - e} \right) - 1 \right) \quad (41)$$

Where the conical section of an object is determined from the e is the eccentricity.

$$e^2 = 1 - \frac{a^2}{b^2} \quad (42)$$

In this thesis, a and b represent the minor and major axis of the ellipsoid, respectively.

When two nanoparticles are far apart and non-interacting, they only experience local field, E . But, when they bring in close proximity, electric field experienced by one nanoparticle is influenced by the incident electromagnetic wave

and the field component arising from its neighbor nanoparticle within the dimer.^{133,134}

Therefore, the dipolar interaction between two close proximity nanostructures of same material (dielectric constants) can be constructed via the electric dipole moment.

$$\mu_1 = \varepsilon \alpha_1 E_1 \quad (43a)$$

$$\mu_2 = \varepsilon \alpha_2 E_2 \quad (43b)$$

Where μ_1 and μ_2 are the electric dipole moment of first and second particle. α_1 and α_2 are the polarizabilities of first and second particle.

It is assume that the fields of each particle to be the sum of the applied field E to the material and from the neighboring nanostructure.

$$E_1 = E + g \frac{\mu_2}{\varepsilon \varepsilon_o d^3} \quad (44a)$$

$$E_2 = E + g \frac{\mu_1}{\varepsilon \varepsilon_o d^3} \quad (44b)$$

g is the geometry constants that depend on the orientation of the dimer with respect to the applied field, and equal to $1/2\pi$.¹³⁵ In this case, we only consider the dimer are in end-to-end orientation, because of its huge field enhancement generation,¹³⁶ d is center to center distance of two nanoparticles.

To calculated the field at each nanostructure in dimer, we can substitute the electric dipole moment in Equation (43) into Equation (44),

$$E_1 = E + g \frac{\varepsilon \alpha_2 E_2}{\varepsilon \varepsilon_o d^3} \quad (45a)$$

$$E_2 = E + g \frac{\varepsilon \alpha_1 E_1}{\varepsilon \varepsilon_o d^3} \quad (45b)$$

(45a) Substituted into (45b), we get:

$$E_1 = E + g \frac{\alpha_2(E + g \frac{\alpha_1 E_1}{\epsilon_o d^3})}{\epsilon_o d^3} = E + g \frac{\alpha_2 E}{\epsilon_o d^3} + g^2 \frac{\alpha_1 \alpha_2 E_1}{\epsilon_o^2 d^6} \quad (46a)$$

Same procedure is used to calculated E_2 .

$$E_2 = E + g \frac{\alpha_1(E + g \frac{\alpha_2 E_2}{\epsilon_o d^3})}{\epsilon_o d^3} = E + g \frac{\alpha_1 E}{\epsilon_o d^3} + g^2 \frac{\alpha_1 \alpha_2}{\epsilon_o d^6} \quad (46b)$$

Rearrange (46a) and (46b), then:

$$E_1 \left(1 - g^2 \frac{\alpha_1 \alpha_2}{\epsilon_o^2 d^6}\right) = E \left(1 + g \frac{\alpha_2}{\epsilon_o d^3}\right) \quad (47a)$$

$$E_2 \left(1 - g^2 \frac{\alpha_1 \alpha_2}{\epsilon_o^2 d^6}\right) = E \left(1 + g \frac{\alpha_1}{\epsilon_o d^3}\right) \quad (48)$$

The average polarizability, $\langle \alpha \rangle$ of a dimer system can be defined as:

$$\frac{1}{2}(\mu_1 + \mu_2) = \epsilon \frac{1}{2}(\alpha_1 E_1 + \alpha_2 E_2) = \epsilon \langle \alpha \rangle E \quad (49)$$

From Equation (47) insert into Equation (49), the electric field of each particle is:

$$E_1 = \frac{E(1 + g \frac{\alpha_2}{\epsilon_o d^3})}{1 - g^2 \frac{\alpha_1 \alpha_2}{\epsilon_o^2 d^6}} \quad (50)$$

$$E_2 = \frac{E \left(1 + g \frac{\alpha_1}{\epsilon_o d^3}\right)}{1 - g^2 \frac{\alpha_1 \alpha_2}{\epsilon_o^2 d^6}} \quad (51)$$

The new average polarizability $\langle \alpha \rangle$ can be formed by combination the Equation (49), Equation (50), and Equation (51).

$$\langle \alpha \rangle = \frac{1}{2} \left\{ \frac{E \left(1 + g \frac{\alpha_2}{\varepsilon_o d^3} \right) \alpha_1 + E \left(1 + g \frac{\alpha_1}{\varepsilon_o d^3} \right) \alpha_2}{1 - g^2 \frac{\alpha_1 \alpha_2}{\varepsilon_o^2 d^6}} \right\} \quad (52)$$

Rearrange Equation (52), $\langle \alpha \rangle$ in Equation (53) can be achieved.

$$\langle \alpha \rangle = \frac{1}{2} \left\{ \frac{\alpha_1 \left(1 + g \frac{\alpha_2}{\varepsilon_o d^3} \right) + \alpha_2 \left(1 + g \frac{\alpha_1}{\varepsilon_o d^3} \right)}{1 - g^2 \frac{\alpha_1 \alpha_2}{\varepsilon_o^2 d^6}} \right\} \quad (53)$$

Before we begin the formalism of $\Delta\lambda$ in dimer nanostructure, we assumed that the nanostructures are sparsely distributed; therefore, the electromagnetic interaction from the other pair of nanostructure is very small and negligible. The average polarizability in Equation (53) accounts the polarizability contribution from each nanoparticle with a defined distance, d .

After obtain the $\langle \alpha \rangle$, the influence of the charges to the plasmon shift of a dimer system can be further formulated.^{133,134,137,138} At LSPR, the real part (Re) of denominator =0, therefore,

$$Re \left[1 - g^2 \frac{\alpha_1 \alpha_2}{\varepsilon_o^2 d^6} \right] = 0 \quad (54)$$

Equation (54) is valid provided the imaginary part of dielectric constants is weakly or small depend on frequency.¹³⁹

Substitute the polarizability of first and second particle in the dimer from Equation (40) into Equation (54), and rearrange, we can get the following form:

$$d^6 \varepsilon_o^2 - g^2 \varepsilon_o^2 \left(\frac{4\pi a b^2}{3} \right) \frac{1}{L_{x1} L_{x2}} \left(\frac{\varepsilon - \varepsilon_e}{\varepsilon + \kappa_1 \varepsilon_e} \right) \left(\frac{\varepsilon - \varepsilon_e}{\varepsilon + \kappa_2 \varepsilon_e} \right) = 0 \quad (55)$$

Eliminating ε_o and rearrange again:

$$(\varepsilon - \varepsilon_e)^2 = \frac{d^6}{g^2 C_1 C_2} (\varepsilon + \kappa_1 \varepsilon_e)(\varepsilon + \kappa_2 \varepsilon_e) \quad (56)$$

To simplify, we denote C_1 and C_2 to represent $4\pi ab^2/3L_1$ and $4\pi ab^2/3L_2$, and Z to represent $d^6/g^2 c_1 c_2$

Expand (56)

$$\varepsilon - 2\varepsilon\varepsilon_e + \varepsilon_e^2 = Z(\varepsilon^2 + \varepsilon\kappa_2\varepsilon_e + \varepsilon\kappa_1\varepsilon_e + \kappa_1\kappa_2\varepsilon_e^2) \quad (57)$$

$$\varepsilon^2 - Z\varepsilon^2 - 2\varepsilon\varepsilon_e - Z\varepsilon\kappa_2\varepsilon_e - Z\varepsilon\kappa_1\varepsilon_e + \varepsilon_e^2 - Z\kappa_1\kappa_2\varepsilon_e^2 = 0 \quad (58)$$

$$(1 - Z)\varepsilon^2 - (2\varepsilon_e + Z\kappa_2\varepsilon_e + Z\kappa_1\varepsilon_e)\varepsilon + (1 - Z\kappa_1\kappa_2)\varepsilon_e^2 = 0 \quad (59)$$

Note: $\varepsilon = \varepsilon' + \varepsilon''i$ and $\varepsilon^2 = \varepsilon'^2 - \varepsilon''^2 + 2\varepsilon'\varepsilon''i$

Because the LSPR is weakly depend on ε'' , therefore,

$$(1 - Z)\varepsilon'^2 - (2 + Z\kappa_1 + Z\kappa_2)\varepsilon_e\varepsilon' + (1 - Z\kappa_1\kappa_2)\varepsilon_e^2 = 0 \quad (60)$$

Factoring Equation (60) into below form:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (61)$$

Thus, Equation (60) becomes:

$$\varepsilon' = \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)} \right) \varepsilon_e \quad (62)$$

Because the $\Delta\lambda$ is strongly depend on the geometry of the nanostructure, hence to include the charging effect theoretically, we can substitute the real part from Equation (62) with the real part of Drude model, as following:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma\omega i} \quad (63)$$

Real part of Equation (63), and in perfect free electron condition; $\omega \gg \gamma$, thus

$$\varepsilon'(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2} \sim \varepsilon_\infty - \frac{\omega_p^2}{\omega^2} \quad (64)$$

Altering the free electrons density only will affecting the bulk plasmon frequency in Drude model. To account the charges effect, simply add $(\Delta\omega_p)^2$.

$$\varepsilon'(\omega) = \varepsilon_\infty - \frac{\omega_p^2 + (\Delta\omega_p)^2}{\omega^2} \quad (65)$$

At resonance, Equation (62) is equal to Equation (65), we have

$$\begin{aligned} & \varepsilon_\infty - \frac{\omega_p^2 + (\Delta\omega_p)^2}{\omega^2} \\ &= \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)} \right) \varepsilon_e \end{aligned} \quad (66)$$

Equation (66) can be rewrite into Equation (67)

$$\begin{aligned} & \varepsilon_\infty - \frac{\lambda^2}{\lambda_p^2} \left(1 + \frac{\Delta N}{N} \right) \\ &= \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)} \right) \varepsilon_e \end{aligned} \quad (67)$$

Rearrange again,

$$\frac{\lambda^2}{\lambda_p^2} \left(1 + \frac{\Delta N}{N}\right) \quad (68)$$

$$= \varepsilon_\infty$$

$$- \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)} \right) \varepsilon_e$$

$$\lambda = \lambda_p \sqrt{\varepsilon_\infty - \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)} \right) \varepsilon_e \left(\frac{1}{\left(1 + \frac{\Delta N}{N}\right)} \right)} \quad (69)$$

with Taylor expansion method, provided that $\frac{\Delta N}{N} \ll 1$, we can achieve Equation (70).

$$\lambda = \lambda_p \left(1 - \frac{\Delta N}{2N}\right) \sqrt{\varepsilon_\infty - \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)} \right) \varepsilon_e} \quad (70)$$

$$\lambda = \lambda_o \left(1 - \frac{\Delta N}{2N}\right) \quad (71)$$

Substituted Equation (70) into Equation (71), to get the initial LSPR position, we get Equation (72).

$$\lambda_o = \lambda_p \sqrt{\varepsilon_\infty - \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)} \right) \varepsilon_e} \quad (72)$$

$\Delta\lambda$ between of neutral state and charged state can be calculated by subtracting Equation (70) to Equation (72)

$$\Delta\lambda = \lambda - \lambda_o = \lambda_p \left(1 - \frac{\Delta N}{2N}\right) \sqrt{\varepsilon_\infty - \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)}\right) \varepsilon_e} \quad (73)$$

$$- \lambda_p \sqrt{\varepsilon_\infty - \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)}\right) \varepsilon_e} \quad (74)$$

$$= \left\{1 - \frac{\Delta N}{2N} - 1\right\} \lambda_p \sqrt{\varepsilon_\infty - \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)}\right) \varepsilon_e}$$

Finally, the plasmon shift for dimer system is applicable in Equation (75).

$$\Delta\lambda = -\frac{\Delta N}{2N} \lambda_p \sqrt{\varepsilon_\infty - \left(\frac{(2 + Z\kappa_2 + Z\kappa_1) \pm \sqrt{(2 + Z(\kappa_1 + \kappa_2))^2 - 4(1 - Z)(1 - Z\kappa_1\kappa_2)}}{2(1 - Z)}\right) \varepsilon_e} \quad (75)$$

The analytical calculation of plasmon shifts for monomer (Equation (13)) and dimer (Equation (75)) predicted that, at the same charging level, the plasmon shifts will be larger for the system that has high geometrical factor that defined within the parenthesis of these equations.

3.3 Results and discussion

3.3.1 Verification of calculated charged Au dielectric constants

Here, we first compare the calculated Au dielectric constant with the one obtained from experimental measurement, to validate the parameters used in Drude-Lorentz model for Au. In order to theoretically study the charging effect and for consistency, we only use the fitted Au dielectric constants (both neutral and charged states) on nanostructure with different geometries.

Figure 3.1 Comparison of the (a) real part and (b) imaginary part of Au dielectric constants. Note: Experimental data are obtained from Johnson and Christy (J&C, symbols) and the calculated data are obtained from Drude-Lorentz model at neutral (0, red lines) and 16% charged state (16, blue lines).

The comparison of Au dielectric constants in charged and neutral states are shown in Figure 3.1. The square symbols (hollow and solid) indicating neutral real and imaginary part of Au dielectric constants obtained experimentally (Johnson and Christy).⁸⁶ Meanwhile, the solid lines and dash lines indicate real and imaginary part of calculated Au dielectric constants using Drude-Lorentz model in Equation (19) and (20). At their neutral state ($\Delta N/N=0$), it is clear that the dielectric constants calculated by Drude-Lorentz model are in excellent agreement with the experimental measured data in the range of wavelength from 500 nm to 800 nm. As the charging level increased, the amount of electrons also increased, creating an excess of electrons compared to their neutral counterpart. At $\Delta N/N= 16\%$, the value of real part becomes smaller than its neutral state, while the imaginary part only show the decrease of value from 450 nm to 650 nm, and no significant change from 650 nm to 800 nm.

To capture the general trend of the role of excess electrons to the Au dielectric constants, we gradually increasing the excess electrons at 4% interval to the Au dielectric constants, and the results are plotted in Figure 3.2. It is clear that increasing the amount of electrons will drives the overall dielectric constants to blue shifting. Since the amount of free electrons is linearly related to the bulk plasmon resonance. Increasing the amount of free electrons, the energy of bulk plasmon resonance also increased, as predicted by Drude-Lorentz model. This behavior also reported elsewhere in previous study based on Drude model.⁹¹

Figure 3.2 Neutral and charged Au dielectric constants calculated using Drude-Lorentz model.

Figure 3.3 DDA calculated extinction spectra for ellipsoid monomer using Drude-Lorentz calculated dielectric constants and experimentally obtained dielectric constants.

Furthermore, after the validation of the calculated Au dielectric constants, we numerically calculated ellipsoid monomer's extinction spectra at neutral state based on the Drude-Lorentz model and experimental dielectric constants⁸⁶ and plotted in Figure 3.3. Obviously, the extinction spectra based on two sets of dielectric constants showed plasmon resonance at 600 nm. This is another proof that the chosen parameters in Drude-Lorentz model are excellently describe Au optical properties. From here onward, only the calculated Au dielectric constants were used to study both charged and neutral state of various geometries.

Figure 3.4 (a) Ellipsoid monomer with $a = 17.5$ nm and its aspect ratio $a/b = 2$ (b) Sphere monomer with radius, $r = 11$ nm. Note that the ellipsoid monomer and the sphere monomer have equal volumes.

Figure 3.4 shows the isolated geometries of Au monomer nanostructures. In order to induce the plasmon frequency at the biological optical window (~ 600 nm to 1300 nm), major axis a was chosen to be 17.5 nm and the aspect ratio a/b is maintain to 2 . For fair comparison between ellipsoid monomer and sphere monomer, an equal volume of sphere was constructed with radius r equal to 11 nm. These monomers are the fundamental building block for the dimers, namely ellipsoid-ellipsoid dimer, ellipsoid-sphere dimer, and sphere dimer. The gap distance in dimer between two nanostructures is fixed at 2 nm. The electric field was polarized along the major axis of the nanostructures. The environment dielectric constant used in simulation was 1.77 , which was water. All nanostructures (monomers and dimers) were discretized by 0.5 nm grid size.

3.3.2 Extinction spectra of charged Au monomer

Figure 3.5 (a) Extinction spectra of ellipsoid monomer calculated by DDA method. (b) Comparison of extinction spectra from DDA method (Solid lines) and analytical solutions under quasistatic limit (dash lines).

Figure 3.5 shows the extinction spectra of the ellipsoid monomers at their charged and neutral states. From the numerical calculated results in Figure 3.5a, increasing of the amount of free electrons to the ellipsoid monomer resulting the LSPR positions blue shifted from 594 nm for $\Delta N/N=0$ to 553 nm for $\Delta N/N= 16\%$. Extinction spectra of ellipsoid monomer calculated using analytical method in Equation (38) also showed the same LSPR shifting. Direct comparison between extinction spectra calculated numerically (solid lines) and analytically (dash lines) is shows in Figure 3.5b. The LSPR peak positions obtained from two methods are quantitatively different. The numerically calculated results showed slightly red-shifted compared to the results calculated analytically. The reason for the disagreement of LSPR peak position between both numerical and analytical method is that, the phase retardation is omitted in analytical solution.^{136,140} Nevertheless, the deviation between the extinction spectra from two methods are less than 1%, which defined from $(|\lambda_{DDA} - \lambda_{quasistatic}|) / |\lambda_{DDA} +$

$\lambda_{quasistatic})$,⁵³ this proves an excellent agreement between two independent calculation methods. Nevertheless, it is worth noting that, the analytical model is under the assumption of quasistatic limit, which is more suitable for small particle where particle's radius is substantially smaller than the vacuum wavelength of light. As the particle size increased, the retardation effect become significant.^{7,141} Thus, the deviation between extinction spectra calculated from this model and DDA method should be larger than 1%.

Figure 3.6 Extinction spectra of sphere monomer calculated by DDA method.

Since the LSPR is strongly depend on the geometry of a nanostructure. Here, we also performed the numerical calculation for spherical nanostructure. The charging effect on sphere monomer is shows in Figure 3.6. When increasing the amount of

electrons from $\Delta N/N = 0$ to $\Delta N/N = 16\%$ into the sphere monomer, the LSPR blue shifted from 526 nm to 489 nm, with the plasmon shifts, $\Delta\lambda$ equals to 37 nm, which is 4 nm shorter than ellipsoid monomer ($\Delta\lambda$ equals to 41 nm). Based on Equation (13), the $\Delta\lambda$ is linearly related to the geometrical factor of a nanostructure, since ellipsoid monomer has a higher geometrical factor comparing to the sphere monomer, it exhibiting larger $\Delta\lambda$. The result we obtained is consistent with Mulvaney's finding.¹² Using this knowledge as a fundamental platform, we predicted that coupled nanostructures at close proximity gap distance would result a much more significant $\Delta\lambda$ in relative to their monomer counterpart, because of their larger geometrical factor.

3.3.3 Extinction spectra of charged Au dimer

Figure 3.7 Extinction spectra of Au dimer calculated by DDA method, with gap, g equals to 2 nm, (a) sphere dimer (b) ellipsoid-sphere dimer (c) ellipsoid-ellipsoid dimer.

In coupled nanostructures, the dimension of each nanostructure is the same as their corresponding monomers. The gap distance we select is the smallest where the classical mechanics still valid. At this distance, we perceive strong plasmon hybridization played an important role in determining the LSPR peak position of each pair of nanostructure.

The extinction spectra of the coupled Au nanostructure are showed in Figure 3.7, with the inset illustrating the corresponding geometry configurations. As expected, the simulation results indicate that the resonance energy of two coupled nanostructure in close proximity are shifted to lower energy compared to their monomer counterparts, this results agreed with previous studies.^{142,143} The sphere dimer has LSPR at 560 nm while the sphere monomer has LSPR at 526 nm. Meanwhile, the ellipsoid-sphere and ellipsoid-ellipsoid dimers have LSPR resonance at 630 nm and 657 nm, respectively, while the ellipsoid monomer has LSPR at 594 nm. The red shifting is due to the attraction coupling between two close proximity nanostructures that retarding the Coulombic restoring force on the displaced electron cloud.^{23,144,145} The attraction coupling is increased for higher aspect ratio nanostructure, hence ellipsoid-ellipsoid dimer exhibit the highest red shifting compare to the rest of the dimers. Although we did not investigate the effect of distance between two nanoparticles, but based on hybridization model, we can predict that as the distance between two nanoparticles increased, the plasmon hybridization will gradually become weaker.¹⁴⁶ Eventually the pair will behave as a single nanoparticle

if the distance is larger than the diameter of a nanoparticle,^{61,73} hence for dimer that has large gap distance, their far field response toward charging effect would be equal to that of their monomer counterpart.

Figure 3.8 Response of plasmon peak position to varied charged state of different nanostructure geometries simulated using DDA method. Nanostructure geometries include ellipsoid-ellipsoid dimer (squares), ellipsoid-sphere dimer (circles), ellipsoid monomer (triangles), sphere dimer (inverted triangles), and sphere monomer (diamonds). Note: the gap in dimers is 2 nm. The solid lines are representing best fit.

Figure 3.8 summarizes the extinction spectra of all geometries as a function of increasing charging level. Due to the strong plasmon hybridization, LSPR peak position of ellipsoid-ellipsoid dimer shows the lowest resonance energy. Notwithstanding the coupling effects for the dimers, all nanostructures show an

apparent linear relationship between the LSPR position and the variation amount of free electron density. We further evaluate the charging effect to these nanostructures by calculating the $\Delta\lambda$ for all the nanostructures.

Figure 3.9 Magnitude of plasmon position shift in response to charging effects for ellipsoid-ellipsoid dimer (squares), ellipsoid-sphere dimer (circles), ellipsoid monomer (triangles), sphere dimer (inverted triangles), and sphere monomer

(diamonds). (a) Calculated from extinction spectra simulated by DDA method. (b) Calculated from analytical method. The solid lines are representing best fit.

Figure 3.9 illustrates the magnitude of $\Delta\lambda$ of different Au nanostructures with respect to the increasing free electron density. In numerical method (Figure 3.9a), the $\Delta\lambda$ can be calculated by finding the difference between the charged state and neutral state, $(\lambda_{\Delta N/N}) - (\lambda_{\Delta N/N=0})$ at respective maximum intensity of LSPR peak of each nanostructure. In analytical method (Figure 3.9b), the response of $\Delta\lambda$ of monomer is calculated using Equation (13), and $\Delta\lambda$ of dimer is calculated using Equation (75). The values of $\Delta\lambda$ obtained from numerical method are qualitatively agreed with the analytical methods. In this work the analytical method derivation is based on Drude model for both Equation (13) and Equation (75) instead of Drude-Lorentz model, the reason is because $\Delta\lambda$ is shape dependent, under this condition, interband transition can be neglected for simplicity. From numerical calculation, the results showed that ellipsoid-ellipsoid dimer (squares) exhibited the largest $\Delta\lambda$, -45 nm (negative sign means blue shifting from neutral state) from $\Delta N/N = 0$ to $\Delta N/N = 16\%$ compared to the rest of the geometries, while the sphere monomer (diamonds) exhibited smallest $\Delta\lambda$, -37 nm (Figure 3.9a). These results agreed well with the plasmon shifts calculated from analytical method for both ellipsoid-ellipsoid dimer (-45 nm) and sphere monomer (-35 nm) (Figure 3.9b). Excellent agreement between two independent calculation methods again confirms the validity of the results. Up until now, we have discussed the plasmon shifts in response to the charging effect. Another important criterion in sensing application is the sensitivity. Here, we defined the sensitivity from the slope in Figure 3.9.

Table 3.1 Sensitivity of the LSPR position shift in response to the charging effect.

Geometries	Geometry factor	Numerical method	Analytical method
Ellipsoid-ellipsoid dimer	5.41	-2.87	-2.80
Ellipsoid-sphere dimer	4.97	-2.78	-2.72
Ellipsoid monomer	4.76	-2.61	-2.69
Sphere dimer	3.79	-2.46	-2.33
Sphere monomer	2.00	-2.36	-2.19

With respect to various geometries nanostructures (monomer and dimer) used in this study. The geometry factor is calculated from the analytical expression in Equation (13) and Equation (75), while the sensitivity of a nanostructure is determined from the slope of the fitted $\Delta\lambda$ from Figure 3.9. As expected, the sensitivity toward charging effect of a nanostructure is linearly correlated to the shape of the nanostructure. Generally, dimers have higher geometrical factor and sensitivity compared to their monomer counterparts. Higher geometrical factor results in higher sensitivity, that is -2.87 (numerical method) for ellipsoid-ellipsoid dimer, while lower geometrical factor results in lower sensitivity, that is -2.36 (numerical method) for sphere monomer. Slope calculated from the $\Delta\lambda$ based on Equation (13) and Equation (75) also show a similar trend as that obtained in the numerical method, which is -2.80 (analytical method) for ellipsoid-ellipsoid dimer and -2.19 (analytical method) for sphere monomer. The negative sign is due to the direction of the plasmon shifting,

in this study; it means the shifting to the higher energy is in relative to the LSPR in neutral state. Because of neglecting the restoring force in quasistatic limit, generally, it shows lower sensitivity value compared to the slope calculated from DDA.

Figure 3.10 Geometry of sphere-on-substrate. With Au sphere monomer at 2 nm (g =gap) above the Au substrate, r is defined as radius with 11 nm.

We have demonstrated the charging response in LSPR for monomer and dimer nanostructures. In most of the experimental cases, the nanostructures are immobilized on a supporting substrate, for this reason, a sphere-on-substrate system is also investigated here in order to study the optical properties of a charged nanostructure in the presence of a substrate. In this system, the sphere monomer with a radius of r was used; the gap between sphere and substrate is restricted to 2 nm. In this simulation, a finite Au cylinder with diameter of $3r$ and height of $2r$ was used to represent the substrate.^{62,147} The electric field polarization is perpendicular to the gap between sphere and substrate. We used 0.5 nm grid size to discretize the sphere-on-substrate nanostructure and embedded it in water environment.

Figure 3.11 Far field properties of a sphere-on-substrate nanostructure at various charged states. (a) Extinction spectra and (b) The plasmon peak positions (black stars) and the plasmon shift (red stars) in response to varies charged states. The solid lines are representing best fit for plasmon peak position and plasmon shift, respectively.

The metallic substrate is acts as a conductor that bridge between the sphere monomer and the applied electrical potential; therefore, we can assume that the Au

sphere and Au substrate having the equal percentage of excess electrons. Figure 3.10a shows the extinction spectra of Au sphere-on-substrate at varied $\Delta N/N$. In the presence of substrate, the LSPR peak showed slightly red shifted comparing to sphere monomer, which is 7 nm from 527 nm (sphere monomer) to 534 nm (sphere-on-substrate) at $\Delta N/N=0$. Similar to the monomer and dimer systems, charging results in extinction spectra to blue shifts (Figure 3.11a) where the SPR position is 534 nm for $\Delta N/N=0$ and 508.5 nm for $\Delta N/N=16\%$. The dependence of LSPR wavelength and the plasmon shifts on charging effect are plotted in Figure 3.11b. Because of intrinsic damping in the present of substrate, it induces LSPR band broadening, hence the sensitivity of the sphere-on-substrate plasmon shifts on charging effect is reduced, which gives the slope of -1.46 that is even lower than sphere monomer in Table 3.1.

3.4 Conclusion

To sum up, we theoretically studied the far field response of various Au nanostructures to the charging effect. Monomers and dimers were built from sphere and ellipsoid shapes. By fixing the size, gap, and dielectric environment, we correlated the influence of charging effect to the geometry factor of each monomer and dimer via numerical and analytical methods. We also showed the details of derivation in quasistatic limit under analytical solution to describe the plasmon shifting for the dimer nanostructures. Together with the plasmon shifting equation under quasistatic for monomer derived by Mulvaney,⁹⁴ we found that dimers have generally larger geometry factor, which result in highest plasmon shifting among the nanostructures in this thesis, that is -45 nm for ellipsoid-ellipsoid dimer. Other than that, higher geometry factor also yield a higher sensitivity that is -2.87 (from

numerical method) or -2.80 (from analytical method). To mimic a real system, the far field properties of a sphere-on-substrate also studied in response charging effect. LSPR blue shifting attributing to excess free electrons was observed and because of the band broadening effect in the presence of substrate, this system yields a low sensitivity (1.46) to charging effect. These results might be able to help to understand of design experiment particularly in sensing application.

In a nutshell, we have achieved the first objective in this thesis that is quantitatively correlating the influence of charges to the geometry factor that characterized by plasmon shifts and sensitivity; furthermore, we proved the validity of the first hypothesis. In next chapter, we will explore the second objective that is how the charging effect influencing the sensitivity in the near field properties.

CHAPTER 4 NEAR FIELD PROPERTIES OF Au NANOSTRUCTURES

In the preceding chapter, we have quantitatively highlighted the relationship between the far field response to the charging effect in different isolated and coupled nanostructures. In this chapter, using the same nanostructures, we carefully investigate the field enhancement properties upon the charging effect. Furthermore, we proposed an effective dipole moment model to explain the sensitivity of the near field behavior with respect to the charging effect, and offer the understanding of how charges distortion would affecting the near field sensitivity in response to excess electrons.

4.1 Introduction

Two undisputed mechanisms that enhance the Surface-enhanced Raman scattering (SERS) signal are electromagnetic and chemical enhancements. Electromagnetic enhancement is due to the oscillation of free electrons at the surface of metallic nanoparticle. By confining the electric field, this process alone allows the single molecule signal to be enhanced several orders of magnitude upon the right condition.^{1,21,148} Due to this advantage, SERS remains one of the most active studied topics from the date of its discovery four decades ago.¹⁴⁹⁻¹⁵¹

In this chapter, we also focus on the charging effect on the near field properties using the shapes described in previous chapter. Earliest theoretical accounts

of the LSPR mechanism has been limited to the classical electrodynamic formulation on neutral metallic substrate, and characterized by the bulk complex dielectric constants, subsequently, more sophisticated quantum theory also been employed based on density functional theory. Since the size of the nanostructure we considered is valid under classical mechanics, we can use it to characterize the near field properties by calculating the enhancement factor of each system. While from the electric field distribution of nanostructures, the hot spot volume can be estimated. Thus far, coupled nanostructure with protrusion surface has the highest hot spot volume compared to mere sphere nanostructure with rounding edge.¹⁵² However, question arises as to what will happen to the enhancement factor of coupled nanostructures, if it were to be tuned dynamically (inclusion of excess of electrons)? Note that the charging effect in this study is different from that of charges transfer between admolecule and the metal surface, where the neutrality of the whole molecule-substrate system is maintained.⁸³

Previous studies have demonstrated that applying different potential dynamic information of molecules can be monitor via SERS.^{50,103,153,154} Theoretically, relationship between the changing of SERS intensity on an isolated spherical nanostructure and charging effect can be established by Gersten-Nitzan model.^{83,155-157} From their studies, charging (increasing the amount of electrons) will results in larger polarizability of the metallic nanostructure, which is analogy to the “lightning rod effect” of a sharp edge,⁵⁰ hence higher field enhancement than its neutral counterpart.¹⁵⁸ To the best of our knowledge, dynamic tuning of the electric field enhancement was not reported elsewhere for coupled nanostructures.

4.2 Analytical calculation for ellipsoid monomer's near field

The average electromagnetic enhancement factor, EF of an ellipsoid monomer can be determined analytically using Equation (76).¹⁵⁹

$$\text{EF} = \left[|1 - \xi|^2 + \frac{2\text{Re}(1 - \xi)\xi^*}{Q_1(\xi_o)} + \frac{|\xi|^2}{Q_1(\xi_o)(\xi_o^2 - 1)} \right] \left[\frac{-\sqrt{(\xi_o^2 - 1)} + \xi_o^2 \sin^{-1}(1/\xi_o)}{\sqrt{(\xi_o^2 - 1)} + \xi_o^2 \sin^{-1}(1/\xi_o)} \right] \quad (76)$$

Where $\xi = (\varepsilon - \varepsilon_o)/(\varepsilon + \kappa\varepsilon_o)$; $\xi_o = 1/\left(1 - \frac{a^2}{b^2}\right)^{\frac{1}{2}}$; $Q_1(\xi_o) = \frac{1}{2}\xi_o \ln\left(\frac{\xi_o+1}{\xi_o-1}\right) - 1$; and ε is the dielectric constant of material. a and b are the major axis and minor axis of a ellipsoid.

In contrast to the analytical solution, the enhancement factor calculated numerically is showed in Equation (36) in Chapter 2. In equivalent to the analytical method, field enhancement calculated numerically is obtained at the position half the grid size above the surface of the nanostructures.¹⁶⁰ Furthermore, due to the limitation of analytical solution, the electric field distribution is only mapping using DDA method.

4.3 Results and discussion

4.3.1 Field enhancement of monomers and dimers

Figure 4. 1Near field properties of ellipsoid monomer calculated by DDA method. (a) Enhancement factors spectra. (b) Comparison of the enhancement factors spectra calculated analytically (dash lines) and numerically (solid lines) (c) Electric field distribution at its resonance when $\Delta N/N=0$, the scale bar is 15 nm.

The near field properties of the ellipsoid monomer under the influence of charging effect are investigated systematically. Figure 4.1a shows the numerically calculated average EF of an ellipsoid monomer over visible frequency region at different value of $\Delta N/N$. With increasing $\Delta N/N$, the EF spectra show blue shifts from its neutral state that consistent with their far field properties discussed in Chapter 3. The results from DDA method are quantitatively agreed with the results from analytical solution shows in Figure 4.1b. Although the EF values are agreed between analytical method and numerical method, but because of neglecting the phase retardation consideration in analytical method, the results always shows slightly blue shifted than numerical method, which also has discussed in the preceding chapter. From Figure 4.1c, the electromagnetic fields distribution is strongly confined at the end of the nanostructure, which is along the polarization direction.

Figure 4.2 Enhancement factor spectra (left column) accompanied by the electric field distribution (right column) of various geometries. (a and e) sphere monomer. (b and f) sphere dimer. (c and g) ellipsoid-ellipsoid dimer. (d and h) ellipsoid-sphere dimer, the scale bar is 15 nm.

A series of numerical calculation of EF and electric field distribution is plotted in Figure 4.2. From the EF spectra, ellipsoid-ellipsoid dimers show the largest red shifted compared to the others nanostructures. Based on the electric field distribution on the right column, dimers exhibited larger electric field confinement than the monomer nanostructures as expected. Besides, nanostructures with sharper protrusion surface is exhibiting larger field enhancement, which can be seen in ellipsoid nanostructures, and sphere nanostructures on the other hand show less field enhancement at the rounding edge.

Figure 4.3 (a) Maximum average enhancement factor from DDA calculations for various Au nanostructures. (b) The enhancement ratio of charged nanostructures in relative to their respective neutral counterpart. The geometries includes ellipsoid-ellipsoid dimer (squares), ellipsoid-sphere dimer (circles), ellipsoid monomer (triangles), sphere dimer (inverted triangles), and sphere monomer (diamonds) with varied charging states. The solid lines are representing best fit.

The EF value at their resonance peak from Figure 4.1 and 4.2 for different geometries is summarized in Figure 4.3a. In general, the EF increases monotonically with excess electrons for different geometries. Among all the systems in this studied, the ellipsoid-ellipsoid dimer shows the highest EF in the range of 485 to 521, which is 7.4% increase from its neutral state to 16% of excess electrons state. On the other end, the sphere monomer has the lowest EF (in the range of 13.04 to 14.15, from $\Delta N/N = 0$ to $\Delta N/N = 16\%$, with 7.7% EF increment). Surprisingly, despite the absolute magnitude of EF exhibited by every nanostructure, ellipsoid-ellipsoid dimer exhibits the lowest relative EF increment comparing to the other geometries.

To quantify the charging effects to the field enhancement with respect to their neutral state, an enhancement ratio is calculated and plotted in Figure 4.3b. The descending order of highest to lowest enhancement ratio at $\Delta N/N = 16\%$ is ellipsoid monomer (1.13), sphere dimer (1.10), ellipsoid-sphere dimer (1.10), sphere monomer (1.09), and ellipsoid-ellipsoid dimer (1.08).

Figure 4.4 Summary of slope of enhancement ratio calculated from Figure 4.3b.

The sensitivity of the near field response toward the charging effect can be interpreted from the slope calculated from Figure 4.3b. Ellipsoid monomer shows the highest sensitivity compared to the rest of the geometries. Next, sphere dimer and ellipsoid-sphere dimer exhibiting second highest sensitivity to charges effect, followed by sphere and ellipsoid-ellipsoid dimer. In order to interpret these phenomena, we proposed a scheme based on effective dipole moment model.

	$\Delta N/N = 0$	$\Delta N/N = 16\%$
Ellipsoid monomer
Ellipsoid-sphere dimer
Ellipsoid-ellipsoid dimer

Figure 4. 5 Effective dipole moment Models for ellipsoid monomer, ellipsoid-sphere, and ellipsoid-ellipsoid dimer. Note: $L_x N$ is the charge separation distance for an ellipsoid, with subscript x corresponding the shape (e= ellipsoid monomer, es= ellipsoid-sphere dimer, and ee= ellipsoid-ellipsoid dimer) and N corresponding the percentage of excess electrons. While g is the gap between two nanostructures.

Estimated charge separation distance in descending order: $L_e 0 \sim L_e 16 > L_{es} 0 > L_{es} 16 > L_{ee} 0 > L_{ee} 16$. We speculate the charges distribution of sphere experience insignificant distortion.

The near field response on charging effect is explained by an effective dipole moment model sketched in Figure 4.5. Upon LSPR excitation, the distribution of charges on the nanostructure will be rearranged in bonding mode based on hybridization model (Figure 1.5). Under this condition, the charges that carried the same amount of opposite sign will be localized at the both end of ellipsoid or sphere along the

polarization direction, and forming a dipole moment, $L_x N$, where L represent the charges separation distance, N represents the percentage of excess electrons, and subscript x corresponding to the shape.

Charging of nanostructure can directly increase the polarizability, hence the lightning rod effect to each respective nanostructure, consequently, increasing the field enhancement for all geometries. Because of this effect is more pronounce for nanostructure with the protrusion surface, ellipsoid monomer (first row in Figure 4.5) exhibiting higher enhancement ratio than sphere monomer.

For dimer, taking neutral state as an example, when two ellipsoids are put in close proximity, the charges tend to localized close to the gap region. As a result of the distortion, the opposite charges at the other end of the ellipsoid will be tend to be drawn close to the gap region, and reduce the charges separation distance $L_x N$ (Figure 4.5 first column in second and third row).

The effective dipole moment is determined by two competing factor that is total amount of charges, N and charges separation distance, L . Effectiveness of each factor in determining the effective dipole moment is strongly influenced by the shape of the nanostructure. Due to larger polarizability, the charges separation distance of ellipsoid nanostructure is relatively easier to be distorted than the spherical shape one. For ellipsoid-ellipsoid dimer, shortening of the charges separation distance is playing more major role than increasing the amount of electron density. As a result, the effective dipole moment is strongly reduced (last row in Figure 4.5), hence retarding the near field sensitivity in response to the charging effect.

On the other hand, spherical nanostructure has lower polarizability compared to protrusion nanostructure, therefore, it shows rather consistent charges separation distance in response to the charging effect. In this case, charging effect is playing more major role in determine the effective dipole moment. This can be seen in sphere dimer and ellipsoid-sphere dimer (Second row in Figure 4.5). Based on this model, we speculate the sequence of charges separation distance in descending order: $L_{e0} \sim L_{e16} > L_{es0} > L_{es16} > L_{ee0} > L_{ee16}$ (e = ellipsoid monomer, es = ellipsoid-sphere dimer, and ee = ellipsoid-ellipsoid dimer).

4.3.2 Near field of sphere-on-substrate system

Here, we also adapted the same sphere-on-substrate system mentioned in preceding chapter. In general, with increasing the charging level, the enhancement factors spectra also showed blue shifted (Figure 4.6a). The maximum average EF values increased with respect to the charges increment (black stars symbols depicted in Figure 4.6b). Judging from the value of enhancement ratio (red stars symbols depicted in Figure 4.6b), the sphere-on-substrate nanostructure showed an effective response toward the charging effect and reaching enhancement ratio of 1.13 at $\Delta N/N = 16\%$, where the near field response has higher sensitivity than both the sphere monomer and sphere dimer. Adapting the image charges theory to the proposed model in Figure 4.5, at small gap, a dipole from a sphere would be screened by the opposite-polarized image dipole in the metal substrate. Taking account of the sphere's dipole and the image dipole in sphere-on-substrate, the average polarizability is larger than that of isolated sphere and their dimer; hence, more effective in near field response to the charging effect. Electric field distribution in Figure 4.7 shows the evidence of strong

coupling between sphere monomer with the substrate, which leads to a strong electric field concentrated in the gap region.

Figure 4. 6 Near field properties of a sphere-on-substrate at various charged states. (a) The spectra of enhancement factors. (b) The maximum average enhancement factor (black stars) and the enhancement ration (red stars). The solid and dash lines are representing the best fit for enhancement peak positions and the peak shift.

Figure 4. 7 Electric field distribution of sphere-on-substrate at $\Delta N/N=0$, the scale bar is 15 nm

4.4 Conclusion

In this chapter, we have studied the near field properties of various geometries. Near fields calculations between analytical solution and numerical solution subjected to ellipsoid monomer are agreed quantitatively with each other. Furthermore, among all geometries in this study, ellipsoid-ellipsoid dimer exhibits the highest field enhancement, that is 458 at $\Delta N/N= 0$. Nonetheless, based on enhancement ratio at $\Delta N/N= 16\%$, the ellipsoid-ellipsoid dimer has lowest enhancement ratio at (1.08), meanwhile the ellipsoid monomer exhibit the highest enhancement ratio (1.13) upon charging effect. To explain this phenomenon, we proposed an effective dipole moment model. Based on this model, the ellipsoid-ellipsoid dimer shows large amount of charges localized close to the gap region, the opposite charges at the end will draw toward the gap, resulting in shorter charges separation distance compared to

the rest of the nanostructures. Charging effect on sphere-on-substrate system is also studied. Notwithstanding the enhancement factor of this system, it has a comparable enhancement ratio as the ellipsoid monomer (1.13) at $\Delta N/N = 16\%$.

In the nutshell, we have successfully achieved the second objective of this thesis. However, what we found in this chapter is contrast to that of our second hypothesis, which in turn, the near field sensitivity is more bound to the charges separation distance rather than their coupling strength between two nanoparticles.

CHAPTER 5 CONCLUSIONS AND FUTURE OUTLINE

5.1 Conclusions

The body of this work describes the dynamic tuning based on altering free electron density of the plasmonic material on isolated and coupled metallic nanostructures. Various coupled Au metallic nanostructure were constructed from Au ellipsoid and Au sphere monomer building blocks. Using numerical solution (DDA) and analytical solution (quasistatic limit), plasmon shifts and field enhancement of various nanostructures in response to charging effect were successfully calculated.

Charging effect was known to alter the amount free electrons density of a material, hence the dielectric constant. Using this notion, we were able to mimic the charging effect by increasing the free electron density in Drude-Lorentz model for Au in the visible frequency region. Due to the presence of the double layer between the water and the Au nanostructure, we considered a wide range of charging level from 0 to 16%.

In general, all the LSPR positions were shifted to higher energy with increasing of the charging effect from 0 to 16%. The magnitude of plasmon shifts, $\Delta\lambda$ varies corresponding to different geometries. Because of its highest geometrical factor compared to other geometries considered in this study, we found the ellipsoid-ellipsoid dimer has the largest $\Delta\lambda$, that is -45 nm at $\Delta N/N = 16\%$ from its neutral condition. The far field response to the charging effect (from $\Delta N/N = 0$ to $\Delta N/N = 16\%$)

in descending order is as follow: ellipsoid-ellipsoid dimer> ellipsoid-sphere dimer> ellipsoid monomer> sphere dimer> sphere monomer. The far field sensitivity to the charging effect can be estimated based on the slope of $\Delta\lambda$ as a function of different magnitude of $\Delta N/N$. Ellipsoid-ellipsoid dimer shows the highest far field sensitivity as expected with the value of -2.87 based on DDA calculation, this result is supported by the analytical solution with the slope of -2.80. The descending order of sensitivity is same as the plasmon shifts, that is ellipsoid-ellipsoid dimer> ellipsoid-sphere dimer> ellipsoid monomer> sphere dimer> sphere monomer.

On the other hand, due to the largest geometric factor of ellipsoid-ellipsoid dimer, it also shows the largest value of field enhancement, which characterized by average enhancement factor (EF). Second highest EF is ellipsoid-sphere dimer, followed by ellipsoid monomer, sphere dimer, and sphere monomer. Despite the largest EF value exhibited by the ellipsoid-ellipsoid dimer, it shows the lowest enhancement ratio. We characterized the sensitivity based on the slope of the enhancement ratio; we found that the ellipsoid-ellipsoid dimer has the lowest sensitivity with the slope of 0.48, while the ellipsoid monomer shows the highest near field sensitivity with the slope of 0.8. An effective dipole moment model was proposed to explain the low enhancement ratio of ellipsoid-ellipsoid dimer. For dimer in close proximity, large amount of charges will pile up near the gap region; consequently, the opposite charge from the other end of the ellipsoid will be drawn to the center in order to reach equilibrium of charges distribution, and leads to the short charges separation distance. This effect is strongly affecting the lightning rod effect of the ellipsoid-ellipsoid dimer, and results in retarded near field response to the charging effect.

Last but not least, Au sphere-on-substrate nanostructure was proposed based on experimental work. From the far field response to the charging effect, the Au sphere-on-substrate is much less sensitive than those Au monomers and dimers nanostructures, the main reason for the low sensitivity of this system is due to the peak broadening in the presence of substrate. Moreover, the near field response of this system also being carefully studied, although it has low EF value but it does shows comparable enhancement ratio as that of ellipsoid monomer that is 1.13 at $\Delta N/N=16\%$.

Overall, this study provides a new guideline and physical insight for manipulating the far field and near field of coupled plasmonic nanostructures in response to the charging effect. Using the analytical solution derived plasmon shifts and the effective dipole moment model, the performance of plasmonic coupled nanostructure to the charging effect can be predicted.

5.2 Future outline

Based on the understanding in this thesis, future efforts can be directed to study nanostructure, with high sensitivity and at the same time provide a large enhancement factor. A structure with protrusion edge has relatively higher enhancement compared to round edge. However, round edge structure has less distorted charges separation distance than that sharp edge structure, and that might improve the sensitivity of the near field in response to the charging effect. Combining advantages of both geometries, we propose that the future study should be focused on rounding edge nanostructure with a sharp protrusion surface such as spiky nanosphere. One of the

most important parameter is the ratio between the length of the sharp protrusion surface and their radius of the rounding edge. Because, changing the ratio, the behavior of the system might can be tuned to prone either ellipsoid-like or spherical-like to balance between their strength and their weakness. It is also suggested to perform this study in experiments. By using lithography method, different geometry and size of nanostructure can be fabricated with precise edge-to-edge configuration, and charges effect can be included by connected to the electrochemical electrodes.

Other than that, new class of plasmonic has emerged based on semiconductor particularly copper sulfide and copper selenide. Due to abundancy of these materials, this material has high potential in replacing noble metal in near infrared region to support surface plasmon resonance, which is very useful due to it match the biological optical window. However, the research on this material still at an infancy stage, many potential applications is not been explored. Especially on the charging effect which can be of potential in sensing the redox reaction.

So far, we are using the local dielectric constant to describe the charging effect. This study also can be further by including the non-local effect, which allows the study to be carried at gap distance smaller than 2 nm, where the electron tunneling could occur. Charging effect on the close proximity is worth of investigate because it has great impact on the performance of a capacitor as well as the SERS signal.

LIST OF PUBLICATIONS

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