SIZE AND INTERPARTICLE INTERACTION EFFECTS ON OPTICAL PROPERTIES OF GOLD NANOPARTICLES SURFACE PLASMON RESONANCE EMISSION BY MNPBEM TOOLBOX

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by

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LIST OF SYMBOLS

A	Vector potential of Maxwell's theory
α	Polarizability
B	Magnetic induction
c	Speed of light, in vacuum
C_{abs}	Absorption cross section
C_{ext}	Extinction cross section
C_{sca}	Scattering cross section
γ	Damping constant
γ_{bulk}	Bulk damping constant
d	Centre-to-centre distance
D	Diameter of a particle
D	Dielectric displacement
δ	Plasmon propagation length
E	Electric field
e	Electron charge
ê	Unit vector
ε	Dielectric function of a material
ε_i	Imaginary part of the dielectric function
ε_m	Dielectric constant of surrounding medium,
ε_o	Electric constant permittivity of vacuum
ε_r	Real part of the dielectric function
ε_∞	High frequency part of the dielectric function

F	Surface derivative of Green function G
G	Green function
G	Cross-sectional area of a particle
$\mathbf{H}$	Magnetic intensity
$\mathbf{h}_j$	Current distribution in medium j
$\mathbf{J}_{\text{ext}}$	Current density
$\boldsymbol{k}$	Wave vector of light
k_j	Wave number in medium j
k	Imaginary part of complex refractive index
k	Wave number in vacuum
l	Order mode
m_e	Mass of the free electron
n	Electron density
n_m	Refractive index of a medium
Λ	Matrix containing the dielectric information for quasistatic
λ	Wavelength of light
λ_0	Resonance wavelength of a single particle
$\Delta\lambda$	Resonance wavelength shift with respect to the single particle
μ	Magnetic permeability
μ_0	Magnetic constant permeability of vacuum
ϱ	Free charge density
σ	Surface charge distribution
Φ	Scalar potential
Φ_{ext}	Potential of an external excitation

$\boldsymbol{P}$	Electric polarization
Q_{abs}	Absorption efficiency
Q_{ext}	Extinction efficiency
Q_{sca}	Scattering efficiency
R	Distance between opposite charges
r	Radius of sphere
$\mathbf{r}$	Spatial position vector
$\boldsymbol{s}'$	Spatial position vector on a surface of nanoparticle
s	Surface-to-surface distance
V	Volume of a nanoparticle.
∂V	Boundary of a region on the surface of a nanoparticle
v_F	Fermi velocity of electron
x	Displacement of electrons
ω	Angular frequency of a photon
ω_p	Bulk plasma frequency of a metal
ω_{sp}	Surface plasmon resonance frequency

LIST OF ABBREVIATIONS

BEM	Boundary Element Method
DDA	Discrete Dipole Approximation
EELS	Electron energy-loss spectroscopy
FDTD	Finite Difference Time Domain
MNPBEM	Metallic Nanoparticles Boundary Element Method
SPR	Surface plasmon resonance

KESAN SAIZ DAN INTERAKSI-INTERPARTIKEL KE ATAS SIFAT OPTIK PANCARAN RESONANS PLASMON PERMUKAAN NANOPARTIKEL EMAS MENGGUNAKAN KOTAK PERALATAN MNPBEM

ABSTRAK

Pada masa kini, nanopartikel emas telah mendapat perhatian yang tinggi dalam kalangan para penyelidik, kerana sifat optiknya yang menarik, yang disebabkan oleh fenomena permukaan resonans plasmon. Kebolehan sifat ini untuk menala menjadikan nanopartikel emas menarik untuk banyak aplikasi. Dengan menggunakan *MNPBEM Toolbox*, sifat-sifat optik nanopartikel emas telah disiasat. Untuk mengesahkan ketepatan pendekatan ini, satu siri spektrum pemupusan untuk nanopartikel emas sfera tunggal yang berlainan saiz telah disimulasikan. Selain itu, kesan saiz telah diambil kira untuk menjadikan simulasi lebih realistik. Seterusnya, kesan jarak antara partikel pada permukaan resonans plasmon telah dijelaskan, dengan mengkategorikannya kepada dua kelas iaitu julat jarak pendek dan julat jarak jauh. Untuk julat pertama, fokus kerja ini adalah untuk meneliti kesahihan persamaan penggaris plasmon yang telah didapati dari kajian sebelum ini apabila struktur nanopartikel berubah dari dimer ke rantaian linear. Pada masa yang sama, tujuan kajian untuk julat jarak jauh adalah untuk menentukan nilai jarak di antara partikel apabila interaksi medan dekat beralih ke interaksi medan jauh. Dari hasil simulasi, diperhatikan bahawa nanopartikel emas tunggal telah mengalami anjakan merah dan perluasan puncak resonans apabila saiz nanopartikel meningkat. Kesepakatan yang baik antara hasil simulasi (yang didapati dari kerja ini) dan hasil eksperimen (yang didapati dari laporan kajian terdahulu) membuktikan kesahihan pendekatan ini. Selain itu, telah didapati bahawa persamaan

penggaris plasmon bergantung kepada saiz. Untuk nanopartikel yang bersaiz kurang daripada 50 nm, ramalan anjakan spektrum mensisih daripada persamaan penggaris plasmon yang telah didapati dari kajian sebelum ini. Dalam kajian julat jarak jauh, telah didapati bahawa anjakan spektrum tidak mengikuti ramalan tingkahlaku apabila jarak di antara partikel melebihi 150 nm, dan nilai jarak ini tidak bersandar pada jenis logam, diameter nanopartikel dan panjang rantaian. Hal ini telah mendedahkan bahawa peralihan daripada interaksi medan dekat ke interaksi medan jauh telah berlaku pada jarak ini. Secara ringkasnya, kajian ini menyumbang kepada pemahaman yang lebih baik tentang ketergantungan jarak pada permukaan resonans plasmon dan mungkin berguna untuk beberapa aplikasi plasmonik contohnya sensor berasaskan himpunan nanopartikel dan penggaris molekul.

SIZE AND INTERPARTICLE INTERACTION EFFECTS ON OPTICAL PROPERTIES OF GOLD NANOPARTICLES SURFACE PLASMON RESONANCE EMISSION BY MNPBEM TOOLBOX

ABSTRACT

Nowadays, gold nanoparticles have gained a great interest among researchers, owing to their fascinating optical properties which arise from the phenomenon of the surface plasmon resonance. The tunability of these properties makes gold nanoparticles attractive for many applications. By employing MNPBEM Toolbox, the optical properties of the gold nanoparticles have been studied. In order to verify the accuracy of this approach, a series of extinction spectra for a single spherical gold nanoparticle of different size had been simulated. Additionally, to make the simulation more realistic, the size effects had been taken into account. Next, the effect of the interparticle distance on the surface plasmon resonance had been elucidated, by categorizing it into two classes namely short-distance range and long-distance range. For the first range, the focus of this work was to scrutinize the validity of the well-known plasmon ruler equation when the nanostructure was transformed from dimer to linear chain. Concurrently, the objective for the long-distance range was to determine the interparticle distance at which the near field interaction of gold linear chains transits to the far field interaction. From the simulation results, it was observed that a single gold nanosphere had experienced the redshift and broadening of the resonance peak when the nanoparticle size was increased. The good agreement between the simulation results (obtained from this work) and the experimental results (obtained from the reported studies) corroborated the validity of this approach. Moreover, it was found that the plasmon ruler equation was size-dependent. For nanoparticles smaller

than 50 nm, the prediction of the spectral shift appeared to deviate from the established plasmon ruler equation. In the study of long-distance range, the spectral shifts were found to disobey the predicted behaviour when the interparticle distance surpassed 150 nm, regardless of the metal type, nanoparticle diameter and chain length. This observation indicated that at this distance, the transition from the near field interaction to far field interaction had occurred. In short, this study contributes to a better understanding of the distance dependence of the surface plasmon resonance and might be useful for several plasmonic devices such as assembly-based sensing and molecular ruler.

CHAPTER 1 INTRODUCTION

1.1 Motivation

The study of nanomaterials has garnered a lot of attention from researchers nowadays, thanks to the uniqueness possessed by the nanomaterial which is absent in the bulk material. A particle can be termed as nanoparticle if its dimension is about 1 nm to 200 nm [1]. Because this size range is in between the size of individual atoms and bulk solid, the properties of the nanomaterials are expected to behave differently from that of the bulk material.

In general, the noble metal nanoparticles show intriguing properties when they interact with light. The Romanian had exploited the distinct optical properties shown by these nanoparticles in their famous Lycurgus cup, in which the color of the cup depends on the light direction [2]. As can be seen in Figure 1.1, the cup appears green in the reflected light but changes to ruby red in the transmitted light. The reason why Lycurgus cup exhibits dichroic characteristic remained mystery until, in 1908, Gustav Mie revealed that the metallic nanoparticles are able to absorb and scatter light at a specific wavelength. Interestingly, this capability originates from the phenomenon of the surface plasmon resonance. This crucial discovery had led to the intense studies in the plasmonic area with an emphasis on the plasmonic properties of gold and silver nanoparticles [3].

Among the noble metal nanoparticles, gold is the most stable one. This stems from the fact that gold nanoparticles offer excellent resistance to oxidation. Because of this inert nature, gold is known to be more biocompatible as compared to the silver nanoparticles [4]. Gold nanoparticles also have unique optical properties that can be easily tuned, which is different from the bulk gold. In particular, at the bulk scale, the

color of the gold is yellow. However, when the gold metals are in the nanometer size regime, they display bright and fascinating colors that are highly sensitive to the surface plasmon resonance [5]. Remarkably, all these captivating properties make the gold nanoparticle as an ideal candidate for the studies of plasmonic applications.

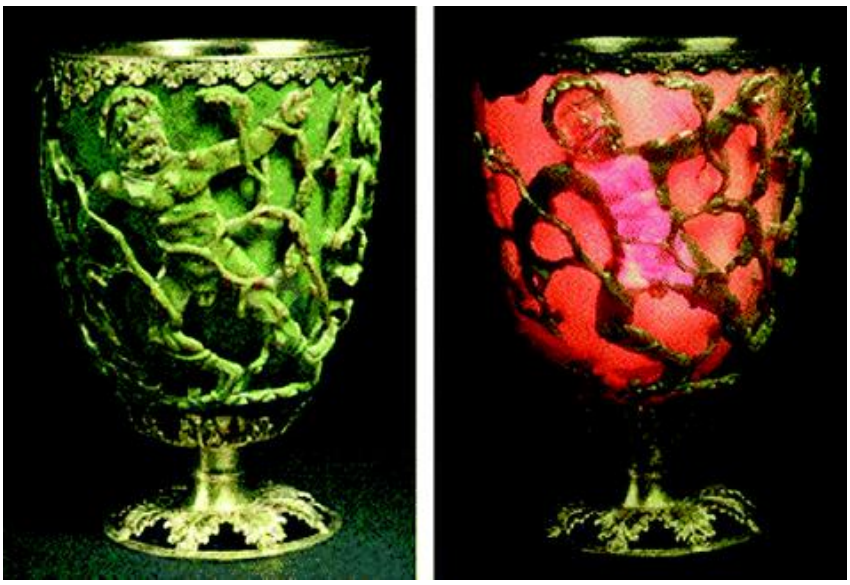

Figure 1.1 Roman Lycurgus Cup appears green when light shines from the front and red when light shines from the back (adapted from [2]).

For a single nanoparticle, the properties of the surface plasmon resonance can be tuned to meet the individual needs by changing the properties of the particle, such as size [6,7], shape [8–12], material properties [13,14], and surrounding medium [15,16]. It is essential to highlight that in this study; the primary interest was focused on the spherical gold nanoparticles due to the highly symmetrical charge distributions on the nanoparticle surface as well as the easy control of the homogenous synthesis [5]. This is because, for the synthesis of anisotropic nanoparticles, the geometrical features such as elongation, curvature or protrusion are often cannot be controlled and deviated from ideal during the fabrication process. Thus, this distortion will generate a significant deviation in the shift of plasmon resonance wavelength [17].

In spite of the advantages offered, it is noted that the tunability of the resonance wavelength with the sphere size is too limited for diverse applications. Therefore, nanoparticle assemblies are currently considered as an alternative route to further enhance the plasmonic response of the nanoparticles or to create a new type of plasmon mode [17–19]. For an assembly of nanoparticles, the plasmon resonance wavelength is strongly influenced by the interparticle coupling effect [21]. One of the properties that affects this plasmonic coupling is the interparticle distance of the nanoparticles. However, depending on the separation distance between the nanoparticles, there are two types of interaction possible: near field coupling and far field interaction. For very short distance (less than a particle diameter), the particles interact through their near fields. If the particles are farther apart, the far field interactions dominate [22]. Simply said, the nature of the plasmonic coupling depends on the interparticle distance.

Though past researches had intensely studied the optical properties of the nanoparticle assembly, there are several topics that are not well addressed. The main purpose of this study is to contribute knowledge in the plasmonic properties of assembled nanostructures, especially on how the interparticle distance tunes the plasmonic resonance properties.

1.2 Problem Statement

Over the past few years, much of the interest has been focused on the optical responses of the assembled nanostructure. This is because, the interaction between the nanoparticles within the assembly often results in new features of the plasmonic properties, which is quite different from the single nanoparticle. In particular, the surface plasmon resonance properties can be easily tuned through the separation distance between the nanoparticles [21–25]. This tunability has received strong attention because it is advantageous in the development of several plasmonic devices such as assembly-based sensing [26,27] and spectrum-based plasmon ruler [28–30]. Note that, the anisotropic particles are less useful in this assembly study since the resonance wavelength of the coupled particles depends not only on the interparticle separation but also on the orientation of the probes which cannot be controlled [17]. This is a disadvantage, especially for in vivo applications.

Before the reader is guided to the discussion on the nanoparticle assemblies, it is best to address all possible sizes effects for a single spherical gold nanoparticle first. The study on this size effect is not something new as it has been scrutinized for decades, originating from the theoretical work done by Gustav Mie [33]. In brief, there are three different effects in the specific size regime namely extrinsic size effect, intrinsic size effects and quantum size effect. Nevertheless, the latter effect is disregarded in this study due to the conflicting results from the previous studies involving quantum-sized plasmonic particles (for diameter less than 10 nm) [5]. While the extrinsic size effects such as retardation effects and the multipolar modes are commonly considered in most studies, the inclusion of the intrinsic size effect in the numerical treatment is somewhat limited [34][35]. It is important to also include this effect because when the size of the nanoparticles becomes smaller than the mean free

path of the conduction electrons (for gold, diameter less than 30 nm), the contribution of the electron surface scattering to the optical properties of the nanoparticles cannot be neglected and its dielectric function appears to be size dependent [5]. Thus, to achieve more accurate results, **i**t is crucial to consider both the extrinsic and intrinsic size effects in the simulation study.

For the case of the assembled nanostructures, despite the intense studies of the distance dependence of the surface plasmon resonance, there has been limited information on the tunability of the resonance wavelength for a wide range of interparticle distance. It is worth to highlight that most of the previous reports focused on the short-distance range. One of the applications that exploits such distance range is spectrum-based plasmon rulers [28–30]. Succinctly, the interparticle distance between the nanoparticles in the biological systems can be measured based on the spectral shift of the coupled system, $\Delta\lambda$ relative to the single nanoparticle, λ_0 or also known as fractional plasmon resonance shift $\Delta\lambda/\lambda_0$. This is because, when the interparticle distance is normalized to the nanoparticle diameter (s/D), the fractional shift in the resonance wavelength is rather general and follows universal scaling behaviour. Hence, a plasmon ruler equation has been formulated in order to evaluate the interparticle distance between the nanoparticles. Prior knowledge about the plasmon ruler equation of two identical nanoparticles has been broadly reported [36–38]. However, the formulation of the plasmon ruler equation for an assembly consists of more than two nanoparticles has not been fully elucidated. Apart from that, it is also found that most of these studies had derived this equation without considering the intrinsic size effect. This subsequently leads to the imprecise interparticle distance estimation as reported by previous works [39][40].

While the distance dependence of the plasmonic properties for the short-distance range has been extensively studied, elucidation on the effect of large interparticle distance has been somewhat limited. Although few studies had shown the behaviour of the far field coupling, incorporating the large separation distance between the nanoparticles [22][31–33], the information on the transition distance at which the coupling behavior changes from the near field to far field is still lacking. Such information is necessary in order to scrutinize the coupling behaviour of the assembled nanostructure. It stems from the fact that this behaviour influences the spectral properties of the surface plasmon resonance namely wavelength, intensity and width of the peak. It should be emphasized that the change in the plasmon resonance wavelength leads to visible changes in the observed nanoparticle colour [44]. Notably, there have been few applications that utilizing this tunability such as assembly-based sensing [26,27] and colorimetric assays [35,36].

To sum up, it is necessary to consider both extrinsic and intrinsic size effects during the calculation process so that accurate predictions of the optical properties of gold nanoparticles can be achieved. Besides, it is known that the plasmonic coupling is highly sensitive to the interparticle distance between the nanoparticles and this tunability can be exploited in myriads applications [47][48]. Thus, the urge to study the distance-dependent optical response of coupled nanoparticles has been raised. It is essential to gain a comprehensive understanding on how the interparticle separation affects the plasmonic properties before the nanoparticles undergo fabrication process for the use in specific applications.

1.3 Research Objectives

The main objectives of this work are:

1. To simulate and analyze the optical properties of gold nanoparticles by using MNPBEM Toolbox.

2. To examine the validity of extending the universal plasmon ruler equation to gold linear chains composed of various nanoparticle size.

3. To determine the interparticle distance at which the near field interaction transits to the far field interaction for gold linear chains.

1.4 Scope of Study

This work focuses on exploring the optical properties of spherical gold nanoparticles in the assembled nanostructure. More precisely, the primary goal in this work is to investigate the distance dependence of the plasmonic coupling interaction in the assemblies. In order to achieve the research objectives, this work first simulates the extinction spectra of the single gold nanoparticle by taking into account the size effect. After confirming the validity of the source code used, this work proceeds to the study of the nanoparticle assembly. In particular, the effect of the interparticle distance on the resonance properties has been studied for two classes: 1) short-range distance and 2) long-range distance. For the first case, this work focuses on the spectral shift of the resonance wavelength for three-particles linear chains. By plotting the fractional plasmon shift against the gap/diameter ratio, the plasmon ruler equation is obtained. For the latter case, the aim of this work is to determine at which separation distance does the plasmonic interaction changes from the near field to far field coupling. This

is done by simulating the extinction spectra of gold linear chains for interparticle distance ranges from 100 to 500 nm with different particle number and diameter.

1.5 Significance of the Study

The significance of the present study leads to the improvement in fundamental understanding regarding the optical response of gold nanoparticles. The inclusion of both extrinsic and intrinsic size effect in the calculation program is probable to provide new information on the parametric features that may be of interest to the researchers working in this field. Furthermore, considering the fact that nanoparticle has entered a commercial exploration period, it is expected that the information concerning the plasmon ruler equation as well as the far field effect would be useful for the rational design of specific applications such as assembly-based sensor and molecular ruler.

1.6 Thesis Outline

After a brief introduction in Chapter 1, the basic idea of the surface plasmon resonance phenomenon and the prerequisite conditions for it to occur will be elaborated in Chapter 2. Then, in the next section of this chapter, the dielectric function, the optical properties and the tunability of the resonance wavelength for the case of a single and aggregated nanoparticle will be deliberated, followed by the discussion on the background and important issues that are related to this present study. In Chapter 3, MNPBEM toolbox is presented as a computational tool to calculate the optical response of the investigated nanostructures in this study, with emphasis on its mathematical formulation, procedures and validity. Chapter 4 discusses the results of this study. In the first section, the optical response of a single gold nanoparticles is scrutinized. After that, the study of the assembled gold nanoparticles becomes the main

scope of this chapter. Briefly, the effect of the interparticle coupling on the plasmonic properties of the gold nanoparticle assembly is analyzed. The first part of this analysis focuses on the short interparticle distance range whereas the second part focuses on the large range of the interparticle distance. Finally, the important findings of the current work along with a few suggestions for future work are provided in Chapter 5.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Upon interaction with light, the gold nanoparticles exhibit fascinating optical properties. The bright intense colours display by these nanoparticles originate from the coherent oscillation of free electrons within the particle. This remarkable characteristic has attracted the interest of researchers due to various potential applications in the field of biomedical [37–39], chemical [40–42] as well as nanophotonic [15][43,44]. However, the tunability of the surface plasmon resonance is required in order to tailor the optical response that fulfils the condition of each application. Thus, the aim of the current chapter is to introduce the basic idea of the surface plasmon resonance and describe how the particle responds when interacting with the incoming light. In addition, the tunability of the surface plasmon resonance properties by a change in several parameters, including nanoparticle size, shape, embedding medium as well as the interparticle interactions is also addressed.

2.2 Basic Idea of the Surface Plasmon Resonance

One of the major attributes offered by the nanoparticles is the unique interaction of light with the free electrons on their surfaces. In general, a phenomenon known as plasmon resonance occurs when the frequency of the incident light is resonant with the collective electron oscillations on the surface of the nanoparticle [57]. The response of the free electrons to an incoming light determines the type of the plasmon resonance namely localized surface plasmon resonance (LSPR) and surface plasmon polariton (SPP). In the latter case, the alternating spatial distribution of the negative and positive charges in a direction parallel to the metal surface creates an electronic density wave that propagates along the interface of the dielectric/metal as shown in Figure 2.1. On

the other hand, localized surface plasmon resonance corresponds to the coherent electron oscillations that are confined within the nanoparticle [19]. Keep in mind, this present work is solely concerned with the localized surface plasmon resonance and the term ‘surface plasmon resonance’ is used throughout this study.

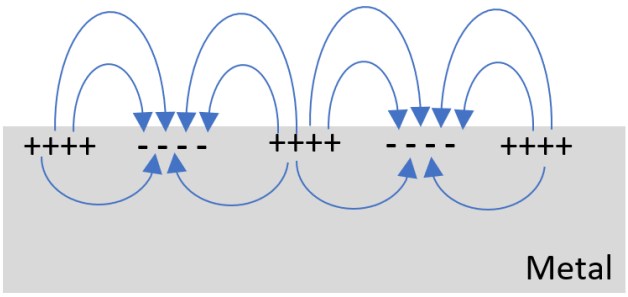

Figure 2.1 Schematic of surface plasmon polariton, the arrows indicate the electric field lines due the distribution of the polarization charge.

Specifically, when the nanoparticles are irradiated by the incident light, the free electrons are displaced relative to the much heavier ionic core of a nanoparticle, leading to the net charge separation. In turn, it gives rise to the Coulombic restoring force, which attempts to pull the polarized electrons back to their equilibrium position. A consequence of this charge separation results in the creation of dipolar oscillation of electron or is also denoted as the surface plasmon oscillation [5]. Figure 2.2 shows the schematic presentation of localized surface plasmon resonance that arises due to the oscillation of free electrons within a nanoparticle.

The exceptional interaction of light with the metal nanoparticle was first explained by Gustav Mie in the nineteenth century. Mie calculated the optical properties of a nanoparticle by solving Maxwell’s equation with appropriate boundary conditions for a small single nanosphere interacting with an electromagnetic field [33]. When the size of the particles is much smaller than the wavelength of light

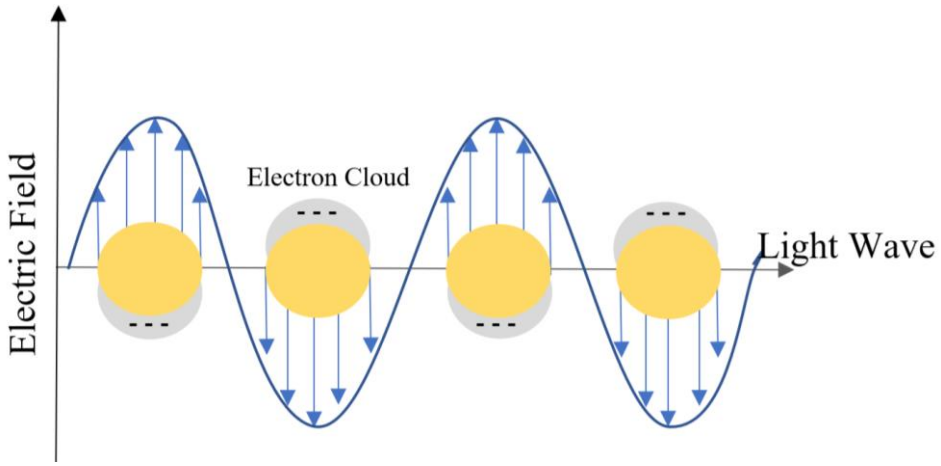

Figure 2.2 Schematic of localized surface plasmon resonance of a spherical metal nanoparticle under incident electric field. The surface charges are locally oscillated around the metal nanoparticles.

(2r << λ), it is sufficient to presume that only the dipole oscillation contributes to the light-nanoparticle interaction (dipole approximation). Thus, it is possible to employ the quasistatic approximation, implying that the electric field of light is assumed to be constant. It is pertinent to know that the quasistatic approximation is the lowest order approach in explaining the behaviour of the nanoparticle upon interaction with the incoming light [34]. Under this circumstance, the polarizability, α of the spherical particle is given by Clausius-Mossotti relation as:

$$\alpha = 3\varepsilon_o V \left(\frac{\varepsilon-\varepsilon_m}{\varepsilon+2\varepsilon_m}\right) \tag{2.1}$$

where ε_o is the permittivity of vacuum, ε_m is the dielectric constant of the surrounding medium, ε is the dielectric function of the metallic nanoparticle and V is the volume of the spherical nanoparticle. The dielectric function of the metal is complex as it takes into account the contribution of its real and imaginary parts and can be expressed as $\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$, wherein ε_r and ε_i denote the real part and the imaginary part of the dielectric function, respectively.

From equation (2.1), the polarizability is maximized when the following relation is satisfied:

$$\varepsilon + 2\varepsilon_m = 0 \tag{2.2}$$

Therefore, when the condition of $\varepsilon_r = -2\varepsilon_m$ is fulfilled by assuming that ε_i is weakly dependent on the frequency and ε_m is a constant and real parameter, the nanoparticle will strongly respond to the light. This situation will lead to the coherent oscillation of free electrons [34].

It is interesting to know that the study of the surface plasmon resonance is commonly carried out with noble metal nanoparticle namely gold, silver and copper because the resonance condition (based on equation 2.2) lies in the range of visible to the near infra-red region of the spectrum, making them promising candidates for various applications. On the contrary, the light-nanoparticle interaction for other metals such as cobalt, chromium, nickel, palladium, platinium, tin and titanium are insignificant. Thus, these kinds of metal nanoparticles do not exhibit unique optical characteristics as compared to noble metals [58].

2.3 Dielectric Function of a Metal

The dielectric function of the bulk metals originates from the intraband and interband electron transitions, hence relates to the free and bound electrons respectively [59]. To account for the contribution of the intraband transition, Drude theory of metals provides the best explanation as it involves the free electron model. According to this theory, in a sinusoidal electric field (**E**(t)) of angular frequency (ω), the equation of free electron motion is given by

$$m_e \frac{\partial^2 \boldsymbol{x}}{\partial t^2} + m\gamma_{bulk} \frac{d\boldsymbol{x}}{dt} = -e\boldsymbol{E}(t) \tag{2.3}$$

where m_e is the mass of electron, e is the charge of electron, γ_{bulk} is the bulk damping constant and x is the displacement of electrons.

Now, the following steps are utilized in order to obtain a mathematical expression of the metal dielectric function, ε(ω):

- By assuming a harmonic time dependence, $\boldsymbol{E}(t) = \boldsymbol{E_0} e^{-i\omega t}$ and $\boldsymbol{x}(t) = x_0 e^{-i\omega t}$ where ω is angular frequency and finding the solution of $\boldsymbol{x}$.
- By defining the macroscopic electric polarization, $\boldsymbol{P}(t) = -ne\boldsymbol{x}(t)$ where n is the electron density.
- By substituting the solution of $\boldsymbol{P}(t)$ into the dielectric displacement, $\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P}$.

By applying all these steps to equation (2.3), the real and imaginary parts of the metal dielectric function can now be described as

$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2+\gamma_{bulk}^2},\ \varepsilon_i = \frac{\omega_p^2\gamma_{bulk}}{\omega(\omega^2+\gamma_{bulk}^2)} \tag{2.4}$$

respectively. Note that a new quantity, $\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0 m}}$ is defined, which is known as the bulk plasma frequency. From this quantity, it is conspicuous that the plasma frequency solely depends on the electronic density. Since the electron densities in both gold and silver are almost similar (for gold, n = 5.90 x 10^{22} /cm^3 and for silver, n = 5.86 x 10^{22} /cm^3), thus, the bulk plasma frequencies for these two metals are comparable [60]. Despite their similar plasma frequencies, the surface plasmon absorption band for an isolated spherical gold and silver nanoparticles is around 520 nm and 390 nm respectively [61]. This deviation arises because the interband transition significantly affects the dielectric function of the metal at high frequency regime (roughly around 1.8 to 2.4 eV) [59]. As mentioned earlier, the interband transition involves the bound electrons which is not considered in the Drude model. Therefore, a high frequency part of the dielectric function ε_∞ is added in order to account for this interband contribution. The expression of ε_r and ε_i in the high frequency regime can be described as

$$\varepsilon_r = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2+\gamma_{bulk}},\ \varepsilon_i = \frac{\omega_p^2\gamma_{bulk}}{\omega(\omega^2+\gamma_{bulk}^2)} \tag{2.5}$$

Now, the surface plasmon resonance frequency, ω_{sp} can be obtained by substituting the expression of ω_p into the real part of the dielectric function in equation (2.5). The resulting expression is then combined with the plasmon resonance condition as shown in equation (2.2), leading to the equation below:

$$\omega_{sp} = \sqrt{\frac{\omega_p^2}{(\varepsilon_\infty + 2\varepsilon_m)} - \gamma_{bulk}^2} \tag{2.6}$$

It is worth noting that the real part of the dielectric function, ε_r incorporates the localized surface plasmon resonance frequency, indirectly delineates the position of the resonance peak. On another note, the imaginary part, ε_i determines the dephasing of the electron oscillations in which can be depicted from the bandwidth of the plasmon resonance peak.

2.4 Absorption, Scattering and Extinction of Light

When light is applied to the nanoparticles, there is an extinction of the light beam. The extinction is attributed to the scattering and absorption of light by the nanoparticle and can be written in terms of cross-sectional area as

$$C_{ext} = C_{sca} + C_{abs} \tag{2.7}$$

These optical properties of light can also be defined in terms of efficiencies as Q_{sca}, Q_{abs} and Q_{ext}; by dividing cross-section of extinction, scattering and absorption with G, where G is the cross-sectional area of particle projected on a plane perpendicular to the incident light (πr^2 for a single sphere).

$$Q_{ext} = \frac{C_{ext}}{G}, \qquad Q_{sca} = \frac{C_{sca}}{G}, \quad Q_{abs} = \frac{C_{abs}}{G} \tag{2.8}$$

Light scattering by the particle is the result of the radiative decay of plasmon oscillation as it emits photon whereas the nonradiative decay gives rise to the light absorption. Both two processes are strongly enhanced when the frequency of the incident light matches with the frequency of the collective electron oscillation. Figure

2.3 depicts the surface plasmon resonance of the nanoparticle, that results in the light scattering and absorption.

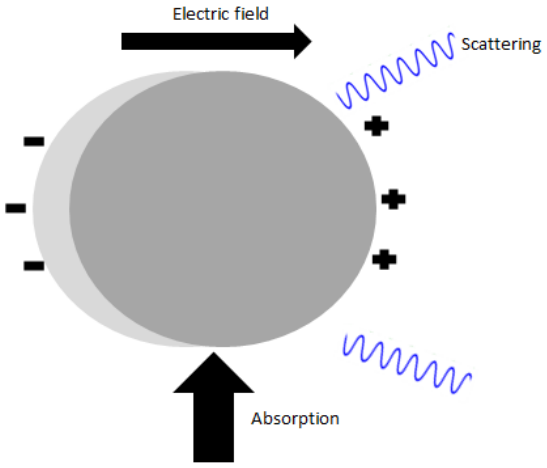

Figure 2.3 Illustration of absorption and scattering when electric field is applied to the nanoparticle.

2.5 Tunability of the Plasmonic Properties of a Single Metallic Nanoparticles

For a single metallic nanoparticle, the coherent oscillation of electrons that contributes to the surface plasmon resonance phenomenon strongly sensitive to the nanoparticle size, shape and its embedding environment [5]. This is because, all these factors can affect the charge distribution on the surface of the nanoparticles and also the separation of the free electron relative to the nuclei of nanoparticle.

2.5.1 Dependence on the Nanoparticle Size

Interestingly, the influence of the particle size on the surface plasmon resonance properties depends on the range of its size. In general, there are three size effects namely extrinsic size effect, intrinsic size effect and quantum size effect. The extrinsic size effect is considered first. In the quasistatic approximation, the surface plasmon resonance is assumed to be solely contributed by the excitation of the dipolar

resonance modes. However, this assumption is no longer valid when the size of the nanoparticle is increased. This is because, the incident light will not homogenously polarize the nanoparticle, leading to the excitation of multipolar (quadrupole, octupole, etc.) resonance modes. Note that, the terms dipolar resonance mode and multipolar resonance modes originate from the difference of the behavior of the surface charge distribution [5]. In this case, the surface plasmon resonance is now contributed by both dipole and multipolar modes. For a mode of order l, the general resonance condition can be expressed as

$$\varepsilon_r = -(\frac{l+1}{l})\varepsilon_m \tag{2.9}$$

where l = 1 for dipole, l = 2 for quadrupole and so on. For l = 1, equation (2.9) is same as equation (2.2). Conspicuously, the emergence of the multipolar mode is always located at a shorter wavelength relative to the dipolar one [62].

The extrinsic size effect, as mentioned above is valid for size range larger than the mean free path of the free electrons. For gold nanoparticles, the mean free path of the electron is roughly 30 nm [19]. Conversely, for gold nanoparticles with diameters smaller than ~30 nm, the intrinsic size effect comes into play. This means that the scattering of the free electrons with the surface of the nanoparticles cannot be neglected. Thus, the additional surface scattering term has to be added to the bulk damping frequency as

$$\gamma = \gamma_{bulk} + \frac{Av_F}{r} \tag{2.10}$$

where v_F is the Fermi velocity of electron (v_F = 1.4 x 10^8 cm/s), A is the dimensionless parameter (A = 1.4) and r is the radius of the nanoparticle. The size-corrected dielectric function for the gold nanoparticle, can then be expressed as

$$\varepsilon(\omega) = \varepsilon(\omega)_{bulk} + \frac{\omega_p^2}{\omega^2 + i\omega\gamma_{bulk}} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \tag{2.11}$$

where $\varepsilon(\omega)_{bulk}$ is the experimental dielectric function of gold from Johnson and Christy [63], ω_p is the plasmon frequency for the bulk gold and γ_{bulk} is the bulk damping constant. In the present work, the values of ω_p and γ_{bulk} were 9.01 eV and 0.072 eV, respectively [59].

From equation (2.10), it can be seen that the rate scattering of the free electrons increases with the decreasing of the particle size. Because of this surface correction, the particles with diameters less than the electron mean free path, have a plasmon bandwidth that broadened inversely proportional to the nanoparticle size [64]. In addition, the increase of the surface scattering rate of electrons also results in the redshift of the plasmon resonance wavelength [65].

Generally, the intrinsic size effect is considered only if the particle size is in the range of 10 to 30 nm [65]. It is prerequisite to know that the above treatment is invalid when the size of the gold nanoparticle is smaller than 10 nm. This is because the quantum size effect starts to become important [66]. The phenomenon that exists within this quantum regime is known as the spill-out effect. In brief, this effect describes the presence of electrons outside the nanoparticle. This, subsequently, leads to the reduction of the electron density, *n* inside the nanoparticle and eventually a decrease of the plasmon resonance frequency, as one can see from the expression of

ω_p. In other words, the plasmon resonance wavelength redshifts as the nanoparticle size decreased, in agreement with the experimental work performed by Doak et al. (2010) [64]. However, Scholl et al. (2012) found that decreasing the nanoparticle size from 20 nm to 2 nm, there was a blueshift of about 0.5 eV in the plasmon resonance wavelength [66]. This blueshift was later experimentally verified by Raza et al. (2015) [67]. Due to this contradiction, it is best to suggest that the investigated nanoparticle cannot be too small (diameter less than 10 nm) in which the quantum size effect becomes an issue.

2.5.2 Dependence on the Nanoparticle Shape

Apart from the nanoparticle size, the properties of the surface plasmon resonance can also be affected by the nanoparticle shape. The spectral position of the plasmon resonance wavelength can be tuned by modifying the shape of the nanoparticles, to shift the resonance peak ranges from around 520 nm into the near-infrared part of the spectrum. Therefore, this intriguing property has prompted many researchers in synthesizing more complex structures [68]. To date, there are abundant reports on the optical properties of the nanoparticles with different shapes such as nanosphere [16][44], nanospheroid [9], nanorods [69], nanocube [70] and nanoshell [61,62], just to mention a few.

Generally, when the shape of the isolated nanoparticle is altered, the nanoparticle geometry becomes asymmetric. This leads to the excitation of the multipolar resonance modes, making the optical properties of the nanoparticle more complex. For example, an elongated nanoparticle shows two distinct plasmon resonance band, which are attributed to the longitudinal and transverse localized surface plasmon mode [69]. In a real experiment, however, it is difficult to achieve the

controlled orientation of the anisotropic nanoparticles [17]. Additionally, previous studies had also revealed how a slight change in the nanoparticle shape can exert a large influence on the surface plasmon resonance properties [1]. By taking these effects into consideration, most of the studies have focused on the spherical geometry because it is easy to homogeneously synthesize the nanosphere and also it shows a non-directional characteristic [73].

2.5.3 Dependence on the Dielectric Function of the Embedding Medium

In addition to the size and shape of the nanoparticles, the nature of the medium surrounding the nanoparticle also has a significant effect on the plasmon resonance frequency. Following equation (2.2), a change in the dielectric constant of a medium, ε_m corresponds to a change in the negative value of the real part of the metal dielectric function, ε_r as they are related to each other by $\varepsilon_r = -2\varepsilon_m$. Thus, it implies that when the medium dielectric constant increases, the plasmon resonance wavelength is redshifted. Donoval et al. (2016) verified this theoretical prediction by using FDTD approach for a monolayer of gold nanoparticles with constant nanoparticle size and separation gap of 7 nm and 3.5 nm respectively. They found that the wavelength increase of about 8 nm per change in the refractive index of 0.1 [16]. It is interesting to know that the nature of the surrounding environment can be changed either due to the change in the medium where the nanoparticle embedded or due to the adsorption of the chemical compounds on the nanoparticle surface. Since the plasmon resonance wavelength is highly sensitive to the environmental dielectric properties, it becomes useful for the sensing application. Nonetheless, the recent development in the sensing field shows that the sensors based on the plasmonic coupling have higher sensitivity than the refractive index nanosensors with the advantage of instrument-free detection, making them suitable for point-of-care testing [73].

2.6 Tunability of the Surface Plasmon Resonance for Metal Nanoparticles Assemblies

For a single particle, the plasmon resonance can be tuned to the most suitable spectral regions by changing the properties of the particle, such as size, shape, and the surrounding medium. It is well known that the change in the shape of the individual nanoparticles offers wider tunability of the resonance frequency compared to the other two properties [5]. Hence, the synthesis and study of the optical response of arbitrary gold nanoparticle structures have been extensively investigated. Due to the certain limitation as had been mentioned in Section 2.5.2, it is important to point out that this present study is concerned with the nanosphere geometry. However, the only variable that can be adjusted in order to tune the plasmon resonance properties is its nanoparticle size, which is rather limited. Thus, apart from manipulating the parameter of the individual particle, nanoparticle cluster can be considered as an alternative route to further enhance these plasmonic properties. The reason of such interest is due to the fact that when nanoparticles come into close proximity to one another, the local field of one particle can interact with the local field from neighbouring particle, leading to a new phenomenon known as plasmon coupling resonance [19]. Usually, the plasmonic properties yielded from this coupling effect is quite different from those of individual nanoparticle. As an example, Reinhard et al. (2005) experimentally observed that the formation of the dimer caused an appreciable change in the colour and intensity of the gold nanoparticles [38].

Thanks to the advanced technology in the nanofabrication technique, the study of the assembled nanostructures has become an active research topic in the plasmonic field. One of the established techniques is electron beam lithography. Interestingly, this technique allows the researchers to fully control the parameters of the fabricated

nanoparticles in order to attain the desired particle cluster. There are numerous studies that successfully used the electron beam lithography in fabricating metal nanoparticles arrays [66–68].

Apart from the lithography-based method, there exists another reliable technique for manufacturing well-defined nanoparticle clusters which known as self-assembly process [77]. In this process, molecular linkers are attached on the surface of the nanoparticles, and by altering the properties of these linkers, one can modify the random nanoparticles into a designated structure. Among cluster geometries that can be constructed from this technique are dimer [78], trimer [78] and linear chain [79]. Moreover, the self-assembly process can even produce three-dimensional aggregate as shown by Luo et al. (2016), who created a flower-like structure by using molecular linkers [80]. Likewise, Barrow et al. demonstrated three-dimensionally nanostructure of tetrahedra, pentamer and hexamer, by modifying the DNA strands that attached on the gold nanoparticle surface [81].

Because of the tremendous development in the fabrication of plasmonic nanostructures, many researchers are interested in understanding how the physical parameters of assembled nanoparticles can manipulate the surface plasmon resonance properties. Hence, in the subsequent sections, the effect of the interparticle distance, the orientation of the nanoparticles with respect to the polarization direction of the incident light as well as the size of the assembly (the number of nanoparticles within the assembly) will be discussed in more detail.

2.6.1 Dependence on the Interparticle Distance

Remarkably, the separation distance between the nanoparticles plays an important role in determining the nature of the plasmonic coupling. The plasmon modes can be coupled via the near- or far-field interaction. The near field interaction is considered when the nanoparticles are placed in close proximity in which they interact through their near field. On the other hand, when the nanoparticles are placed farther apart, the near field of one nanoparticle cannot sense the near field of its neighbouring particles. Thence, the interaction between the nanoparticles is mediated through their radiative field, arising from the plasmonic light scattering.

2.6.1(a) Near Field Coupling

In this section, the near field coupling regime which occurs in a close-packed structure is discussed. According to the earlier studies, the distance between the interacting nanoparticles showed a robust dependence on the plasmonic coupling [74–78]. The initial study of the distance dependence had been reported by Su and co-workers (2003), who studied the interparticle coupling effect for lithographically fabricated pairs of spheroidal gold nanoparticle [86]. They found that the spectral peak shift of the nanoparticles decreased almost exponentially with the increasing of the interparticle separation. In addition, increasing the short axis length of the nanoparticle from 72 to 84 nm, they observed that the exponential decay behaviour was size independent. Subsequently, by using conjugated DNA, Reinhard et al. (2005) utilized this exponential behaviour to measure the distance in biological systems based on the spectral shift upon dimerization (nanoparticle pair formation). In particular, the plasmon resonance spectra of 42- and 87-nm diameter gold nanoparticles were observed by using dark-field scattering spectroscopy for before and after dimerization.