Sudan University of Science and Technology

College of Graduate Studies

Optical Properties of Gold and Silver Nanoparticles

الخصائص الضوئية لجسيمات النانوية للذهب والفضة

A dissertation Submitted in Partial Fulfilment for the Requirement of a Master Degree (M. Sc) in Physics

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Abstract

Nobel metals nanoparticles particularly silver (Ag) and gold (Au) exhibit unique and tuneable optical properties owing to localized surface plasmon resonance. This phenomenon occurs when noble metals have size in nanoscale interact with electromagnetic radiation. As the result, strong electric field is created near nanoparticle surface and being maximized at resonance frequency. The resonance frequency is actually depends on the type of metal nanoparticles and their size, shape as well as the dielectric function of the environment around nanoparticles.

This work is focus on the investigation of the effect of particle sizes on the dielectric function and quality factor of silver and gold. The dielectric function of bulk silver and gold was taken from experimental data reported by Johnson and Christy. The theoretical model used to calculate size dependent dielectric function was based on Drude-Summerfeld model for free electrons. In addition, the obtained results were used to calculate size dependent quality factor.

The obtained results showed significant effect of particle sizes between 5-100 nm on the dielectric function of both silver and gold while for sizes larger than 100 nm, the dielectric function almost matches the bulk values in agreement with definition of nanoparticles reported in literature. Moreover, this effect is found to be more pronouncing in silver compared to the gold. The quality factor results (for silver and gold) also showed significant variation when the particle size become smaller than 100 nm. In addition, silver showed higher quality factor for all sizes compared to the gold. Moreover, the maximum quality factor is found to be in visible and infrared regions for silver and gold, respectively.

المستخلص

أظهرت الجسيمات النانوية للمعادن النبيلة تحديدا الذهب والفضه خصائص ضوئية فريده من نوعها ويمكن توليفها وذلك بسبب الرنين البلازموني السطحي الموضعي. تحدث هذه الظواهر عندما يتفاعل المعدن النبيل ذو المقياس النانوي مع الاشعاع الكهرومغنطيسي، ونتيجة لذلك ينشأ مجال كهربي حول سطح الجسيم النانوي ويبلغ أقصي قيمة له عند التردد الرنيني. يعتمد هذا التردد في الواقع علي نوع الفلزات النانوية وحجمها وشكلها وكذلك دالة العزل الكهربي للبئية المحيطة بالجسيمات النانوية.

هذا البحث يركز علي التحقق من أثر حجم الجسيمات علي دالة العزل الكهربي ومعامل الجودة لكل من الذهب والفضة. تم أخذ دالة العزل الكهربي لكل من الذهب والفضة في المقياس الطبيعي(غير النانوي) من البيانات التجريبية لتجربة جونسون وكريستي. أعتمد النموذج النظري المستخدم لحساب دالة العزل المعتمدة علي أبعاد الجسيم علي نموذج درود - سمرفيلد للإلكترونات الحرة، بالاضافة الي ذلك تم أستخدام النتائج التي حصل عليها لحساب معامل الجودة المعتمد علي أبعاد الجسيم.

أظهرت النتائج التي تم الحصول عليها تاثيرا ملحوظا للاجسام التي أبعادها بين 5 الي 100 نانوميتر علي دالة العزل الكهربي لكل من الفضة والذهب. وعندما كانت أبعاد الجسيمات اكبر من 100 نانوميتر فان دالة العزل الكهربي تتوافق تقريبا مع المقياس الجاهري (غير النانوي) وهو ما يتطابق مع تعريف الجسيمات النانوية الذي ذكر في الدراسات السابقه، علاوة علي ذلك، فان هذا التاثير يكون أكثر وضوحا في الفضة مقارنة مع الذهب، كما أظهرت نتائج معامل الجودة للفضة والذهب تباينا ملحوظا عندما يكون بعد الجسيم أصغر من 100 نانوميتر. و أظهرت الفضة معامل جودة أعلي لجميع الأبعاد مقارنة بالذهب. ووجد أن أقصي قيمة لمعامل الجودة تقع في المنطقة المرئية وتحت الحمراء للفضة والذهب علي التوالي.

Keywords and acronyms

Keywords

Dielectric function - Localized surface Plasmon resonance (LSPR) - Drude model - Mie theory - Quality factor.

Acronyms

FDTD: Finite difference time domains.

EMR: Electromagnetic radiation.

LSPs: Localized surface Plasmon.

SPP: Surface Plasmon Polariton.

LSPR: Localized surface Plasmon resonance.

DDA: Discrete dipole approximation.

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Chapter 1

Introduction

1.1 Overview

The word "Nano" has attracted much attention in the last century. Now, it has been included in several research fields such as chemistry, physics, medicine and biology (Korbekandi, 2012, Ning, 2012). Nanoscale refers to the length scale from 1-100 nm and sometimes several hundreds of nanometer are considered (Ning, 2012). Nano-materials are defined as materials that have dimensions in nanoscale. The most important characteristics of nano-material are their high surface area to volume ratio. As the results, nano-materials exhibits specific physical and chemical properties which entirely different from their bulk form (Derkachova et al., 2016).

Metal nanoparticles (NPs) have been extensively studied in the past decades due to their promising physical properties which made them as the base of the next nano-science and nanotechnology. Recently, metal NPs utilized in a wide range of applications such as surface-enhanced Raman spectroscopy, catalysts, photo-electronic, photovoltaic cells and cancer treatment (Charbgoo, 2016, Amendola et al., 2017, Korbekandi, 2012, Trügler, 2011). The most attractive property of metals NPs is electromagnetic resonances due to collective oscillation of free electrons (conduction electrons) which is termed localized surface Plasmon (LSP) (Rycenga et al., 2011). This phenomenon occurs in various metals NPs, most importantly in noble metal such as gold and silver. Therefore, the optical properties of metals NPs can be determined by their Plasmon energies which are strongly depends on the size and shape of NPs as well as the dielectric of the environment (Kelly, 2003, Noguez, 2006, Zeena, 2003).

It is well known that in order to determine the optical properties of metal, the complex dielectric function $\varepsilon(\omega)$ is considered as the important parameter which describes the interaction between a medium (metal) and incident electromagnetic wave of frequency ω. In addition, the frequency dependence of dielectric constant is also considered as basic importance in shaping the optical properties of metals (Derkachova et al., 2016). Therefore,

this work is to study the effect of particle sizes on the dielectric function and the quality factor of silver and gold to highlight their optical properties at particular sizes.

1.2 Literature review

Optical properties of noble metals nanoparticles have gained considerable interest in the last decades due to their wide range of applications in almost all branches of science (Gorup et al., 2011). Successful theoretical and experimental studies have been achieved to obtain the optical properties of metal NPs by determining their plasmon energies or dielectric function (Hao and Nordlander, 2007). For examples, F. Hao & P. Nordlander (Hao and Nordlander, 2007) have used finite difference time domain (FDTD) simulation to determine the optical properties of silver and gold NPs, by comparing different analytical model with experimental data and they found that the four Lorentz model (L4) for the dielectric function of Ag and Au provides an excellent fit of the experimental data over frequency ranging from 0.6 to 6.6 eV. Furthermore, Z. maminskiene, et al. (Willets and Van Duyne, 2007) evaluated the optical properties of Ag, Cu, and CO NPs with different sizes synthesized in organic medium by obtaining the Plasmon resonance for each metal NPs ((Ag,430nm), (Cu, 570nm) and (CO, 350nm and 430nm)).

The most important challenging problems in studying optical properties of metal nano particles are the definition of nanoparticles according to their size range and the dependency of quality factor on the particle sizes. VJ Mohanraj and Y Chen (Mohanraj, 2006) defined nanoparticle as particle having sizes in the range of 10-1000 nm while Par Ning SUI (Ning, 2012) defined nanoparticle as a particle with length scale from 1-100 nm and may be extended to several hundreds of nanometers.

On the other hand, there are lot of reports studied the quality factors of metals in literature. For examples Matthew Rycenga (Rycenga et al., 2011) studied the quality factor for different metals and concluded that, larger the quality factor, the stronger localized surface Plasmon resonance and vice versa. More overe, R. Carmina Monreal, et al. (Monreal, 2014) examined the quality factor of localized surface Plasmon in silver NPs for different sizes and they found that the maximum width of Plasmon peak resulted in minimum quality factor.

Despite intensive studies on metals nanoparticles properties, several problems remain challenging such as the size range of noble metal nanoparticles and the dependency of quality factor on the particle sizes.

This work will be focused on these two problems to give precise definition of noble metal nanoparticles and to study the effect of particle sizes on the quality factor using an experimental data of dielectric constant of bulk metals obtained by Johnson and Christy.

1.3 Problem statement

The dielectric function of noble metals nanoparticles particularly silver and gold has played an important role in understanding of the electronic structure of these metal nanostructures. Most applications of noble nanoparticles depend on the enhanced field (near or far field) produced at the resonance frequency (Plasmonic effect). The challenging questions are which metal and what the suitable particle sizes will be used to give maximum field enhancement. This work will expect to highlights these questions and therefore guided experimental researchers for good choice.

1.4 Research objectives

1.4.1 General objectives

To investigate the effect of particle sizes on the dielectric function and quality factor of silver and gold.

1.4.2 Specific objectives

- To use experimental data of dielectric constant of silver and gold obtained by Johnson and Christy to calculate the dielectric constant for different particle sizes in the range between 5-150 nm.
- To plot the bulk dielectric constant together with dielectric constant at different particle sizes to examine the effect of particle sizes on the dielectric constant.
- To use the obtained data for dielectric constant in the objective No. 2 to calculate the quality factor for different particle sizes.
- To plot the bulk quality factor together with quality factor at different particle sizes to examine the effect of particle sizes on the quality factor.

1.5 dissertation layout

This dissertation consists four chapters as follow: chapter one provides general information and aim of this work. Chapter two focuses on the physical concept of plasmons and theoretical background of dielectric models of metals. The results and discussions were presented in chapter three while conclusion and the future work were given in chapter four.

Chapter 2

Theoretical background

2.1 Synthesis of metals nanoparticles

Synthesis of nanoparticles undergoes to two kinds general approaches namely top-down and bottom-up (Ning, 2012). In the top-down approach, the bulk material is brought into smaller dimension using various techniques, such as mechanical milling, spark explosion and photolithographic process while in the bottom up approach, one can use the chemical characteristics of single components such as atoms and molecules to produce self-organized or self-assembled required nano-metals. Examples of bottom up approach are hydrothermal, sol-gel and micro-emulsion methods.

Experimentally, there are two methods used to synthesis metal nanoparticles namely physical and chemical methods (Kaminskiene, 2012, B.Prasad, 2013). The most common physical methods are exploding wire technique, plasma, chemical vapour deposition, microwave irradiation, supercritical fluids, sonochemical reduction, Gamma radiation and pulsed laser ablation (B.Prasad, 2013). Shape consistency and lack of contamination are the advantages of physical methods while consuming a great amount of energy and raising environmental temperature are their disadvantages.

The most used chemical methods include chemical reduction of metal salts, microemulsions, thermal decomposition of metal salts and electrochemical synthesis.

2.2 Interaction of bulk material with electromagnetic radiation

The interaction of bulk materials with electromagnetic radiation has been subjected to number of models such as Lorentz model, Drude model and Drude-Summerfeld model (Sonnichsen, 2001, Fox, 2001, Trügler, 2011). It is important to note that the Lorentz model is used for dielectric materials while the other two models are used for metals only. Moreover, Summerfeld modified Drude model by adding the interaction between the electrons with its environment and therefore he used Boltzman statistic instead of Fermi Dirac statistic used by Drude. The both model deals with the metals as a free electron gas

and considered that the dielectric function of metals is produced due to the contribution of conduction band electrons only.

2.2.1 Lorentz model

This model considered the electrons in the atom is bound to the nucleus as the same way that a small mass bound to large mass by spring.

The motion of an electron bound to the nucleus due to applied electromagnetic radiation with electric field $E = E_0 e^{-i\omega t}$ where E is electric field of incident radiation, $E_0$is the amplitude of electric field and ω is the frequency of incident radiation, is described by damped oscillator as follow (Fox, 2001, wooten, 2002):

$$m_e \frac{\partial^2 r}{\partial t^2} + m_e \Gamma \frac{\partial \mathrm{r}}{\partial \mathrm{t}} + m_e {\omega_o}^2 r = -eE_0 e^{-i\omega t} \qquad (2.1)$$

Where m_e is electron mass, r is displacement, ω is angular frequency of oscillation and Γ is damped constant of oscillation.

The first term represents the acceleration of the electron. The second term is the frictional damping force of the medium. The thread term is Hooke's force while the right-hand side term is the driving force due to the electric field E.

This work will be focused only on the metals. Therefore, the theoretical explanation of Durde model will be discussed in the following section. Details about Lorentz model can be found elsewhere (Fox, 2001).

2.2.2 Drude-Summerfeld model

In this model, Drude treated the metal as a free-electron gas around the nucleus and neglected the positive ion core. When the electromagnetic radiation applied to the metals, the free electrons exhibits collisions with an average damping constant Γ. These collisions result in decreasing the velocity of electrons.

In the presence of an external electric field the electron will be distorted producing a dipole moment P which is directly proportional to the strength of the electric field, $P \propto E$ then $P = \alpha n E$ where α termed as polarization, n is the conduction electron density in the metal. The dielectric function of the metal $\varepsilon(\omega)$ gives the polarization of the metal due to applied electric field with a frequency ω. So one can use the following expression to obtain the dielectric function (Kreibig, 1993):

$$\varepsilon = 1 + \frac{n\alpha}{\varepsilon_0} \qquad (2.2)$$

where ε_0 is the permittivity of free space, n is conduction electron density. Using the equation of motion (2.1) given in Lorentz model after placing $\omega_o = 0$ (because there is no spring to connect free electrons to ions), one can get the dielectric function in term of plasma frequency and damping constant as follows (Kreibig, 1993, wooten, 2002, Arboleda et al., 2016):

$$\varepsilon(\omega) = 1 - \left[\frac{\omega_p^2}{\omega^2 + \Gamma_{\text{bulk}}^2} + i\,\frac{\omega_p^2 \Gamma_{\text{bulk}}}{\omega\left(\omega^2 + \Gamma_{\text{bulk}}^2\right)}\right] \qquad (2.3)$$

where $\omega_p = \left(\frac{ne^2}{\varepsilon_0 m_e}\right)^{\frac{1}{2}}$ is the Drude plasma frequency and Γ_{bulk} is the bulk damping constant. Since the dielectric function is complex then equation (2.3) can be separated into real and imaginary part:

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma_{\text{bulk}}^2} \qquad (2.4)$$

And

$$\varepsilon_i(\omega) = \frac{\omega_p^2 \Gamma_{\text{bulk}}}{\omega(\omega^2 + \Gamma_{\text{bulk}}^2)} \qquad (2.5)$$

Where $\varepsilon_r(\omega)$ and $\varepsilon_i(\omega)$ are the real and imaginary part of dielectric function respectively. The complex refractive index of the metals can be calculated from the following equations (Kaminskiene, 2012):

$$\varepsilon_r(\omega) = n^2(\omega) - k^2\,(\omega) \qquad (2.6)$$

$$\varepsilon_i(\omega) = 2n(\omega)k(\omega) \qquad (2.7)$$

Then:

$$n(\omega) = \frac{1}{\sqrt{2}}\left(\varepsilon_r(\omega) + \left(\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)\right)^{\frac{1}{2}}\right)^{\frac{1}{2}} \qquad (2.8)$$

$$k(\omega) = \frac{1}{\sqrt{2}}\left(-\varepsilon_i(\omega) + \left(\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)\right)^{\frac{1}{2}}\right)^{\frac{1}{2}} \qquad (2.9)$$

where $n(\omega)$ and $k(\omega)$ are the real and imaginary parts of complex refractive index respectively.

For simplicity one can place the following equation $|\varepsilon(\omega)| = \sqrt{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)}$ into equation (8.2) and (9.2) to get:

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + \varepsilon_r(\omega)}{2}} \qquad (2.10)$$

$$k(\omega) = \sqrt{\frac{|\varepsilon(\omega)| - \varepsilon_i(\omega)}{2}} \qquad (2.11)$$

2.3 Effect of the particle size on the dielectric function of metals

When the size of metal particles reduced below the electron mean free path l_∞ the collision of the conduction band electrons with the surface of metal become more significant and the damping constant in term of size can be written as (H. Hovel, 1993, Kolwas and Derkachova, 2013):

$$\Gamma_{\mathrm{R}} = \Gamma_{\mathrm{bulk}} + \frac{AV_F}{R} \qquad (2.12)$$

where Γ_{R} is damping constant size dependent, V_F is the Fermi velocity equal $1.4 \times 10^6 \mathrm{ms}^{-1}$ (Cai, 2009) R is the metal particle radius and A is empirical parameter to match the calculated damping with the experimental value, for simplicity $A = 1$. The last term in equation (2.12) accounts for the effect of scattering of free electrons by the surface. Now, the dielectric function in term of particle size becomes (Amendola, 2010, Derkachova et al., 2016).

$$\varepsilon(\omega, R) = \varepsilon_{bulk}(\omega) + \left[\omega_p^2 \left(\frac{1}{\omega^2 + \Gamma_{\mathrm{bulk}}^2} - \frac{1}{\omega^2 + \Gamma_{\mathrm{R}}^2}\right)\right] + i\left[\frac{\omega_p^2}{\omega}\left(\frac{\Gamma_{\mathrm{R}}}{\omega^2 + \Gamma_{\mathrm{R}}^2} - \frac{\Gamma_{\mathrm{bulk}}}{\omega^2 + \Gamma_{\mathrm{bulk}}^2}\right)\right] \qquad (2.13)$$

The complex refractive index also can be modified using the above relation (2.13).

$$n(\omega, R) = \sqrt{\frac{|\varepsilon(\omega, R)| + \varepsilon_r(\omega, R)}{2}} \qquad (2.14)$$

$$k(\omega, R) = \sqrt{\frac{|\varepsilon(\omega, R)| - \varepsilon_i(\omega, R)}{2}} \qquad (2.15)$$

2.4 Interaction of metals nanoparticles with electromagnetic radiation

When the electromagnetic radiation exposed to the metal nanoparticles, the electrons in these NPs make an oscillation converting the energy of the incident electromagnetic radiation into

thermal energy in absorption process or these electrons can be accelerated and then they can radiate energy in a scattering process.

One of the important theory that govern the interaction of metal nanoparticle with electromagnetic radiation is suggested by Gustav Mie in 1908.

2.4.1 Mie theory

Drude-Summerfeld model assume that the dielectric function of metal is caused only by excitations of the free electrons in the conduction band, while Mie proved that the inter-band transitions from lower lying valence band can also contribute to the dielectric function (Borys, 2011). Mie also proved that the sum of absorption cross section C_{abs} and scattering cross section C_{sc} (which is the effective area over which the nanoparticles absorb or scatter light) is give the loss of incident energy and it called extinction cross section C_{ext} (Khlebtsov, 2010, Rivera et al., 2012):

$$C_{ext} = C_{abs} + C_{sc} \quad (2.16)$$

According to Mie theory one can classify metal nanoparticles size regimes into: small size nanoparticles where ($R \ll \lambda$) and this governs by what is called Quasi-static approximation theory attributed to Lord Rayleigh. In this size regime, single dipole produced and therefore the absorption dominates over scattering.

For small and spherical nanoparticle Mie derives quasi-static expression of the extinction cross section as given below (Amendola et al., 2017):

$$C_{ext} = \frac{18\pi\,[\varepsilon_m(\lambda)]^{\frac{3}{2}}}{\lambda}\, V_{NPs}\, \frac{Im[\varepsilon(\lambda)]}{[Re(\varepsilon) + 2\varepsilon_m(\lambda)]^2 + Im[\varepsilon(\lambda)]^2} \quad (2.17)$$

Where V_{NPs} is volume of nanoparticle, ε_m is dielectric function of surrounding medium, $Re(\varepsilon)$ and $Im(\varepsilon)$ are the real and imaginary part of dielectric function, respectively. The maximum absorption occurs at the frequency where

$$Re\ \varepsilon(\omega) \approx -2\ \varepsilon_m(\omega)$$

Where $Re\ \varepsilon(\omega)$ is real part of dielectric function. This is called Frohich condition of LSPR.
On the other hand, in large sizes of metal nanoparticles where ($R \approx \lambda$), the quasi-static is no longer valid because higher order modes of dipole are produced and therefore electrodynamics approach are required. Mie used this electrodynamics approach to solve Maxwell's equations. For more details about full Mie theory, reader is advice to read the following references (Rivera et al., Murry, 2005).

2.5 Plasmons

Plasmon is defined as the collective oscillations of the free electrons in the conduction band of metals due to existence of an external electric field. According to the dimensions of metal there are two main types of Plasmon namely bulk Plasmon (3D) and surface Plasmon (2D or 1D). Details about the types of Plasmon will be discussed in the following section.

2.5.1 Bulk Plasmon

In equilibrium state, the charge of positive ions and electrons inside the bulk metal are cancel each other and metal will be neutral, and when there is an external field applied to the metal the free electrons will make a longitudinal oscillations through the metal. These oscillations occur at certain frequency called plasma frequency ω_p and is given by (Borys, 2011):

$$\omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m}} \qquad (2.18)$$

where n is the electrons density, e and m are charge and mass of electron respectively and ϵ_0 is the permittivity of free space.

Bulk Plasmon cannot be excited by photon due to miss matching between longitudinal oscillation of free electrons in metals and transverse oscillation of light. Instead, one can use a beam of electrons to excite bulk Plasmon (see figure (2.1)) (Amendola et al., 2017).

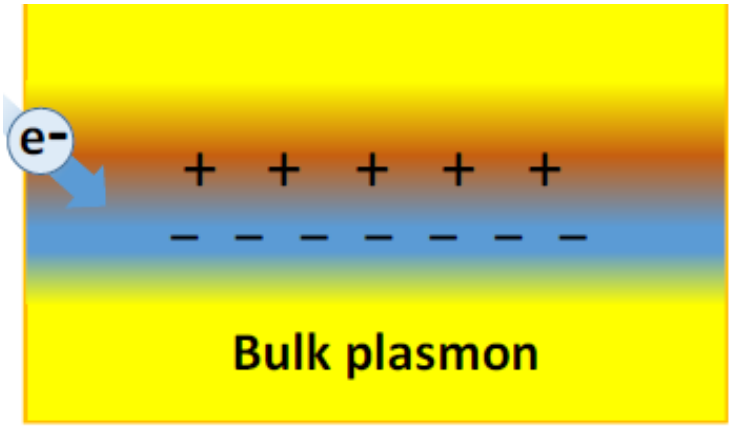


Figure 2.1. Schematic diagram illustrating bulk Plasmon (Amendola et al., 2017).

2.5.2 Surface Plasmon

There are two modes of surface Plasmon that metal can support, one is localized at the metal nanoparticle called localized surface Plasmon (LSP) and another is propagating at the interface between metal and dielectric called surface Plasmon polaritons (SPP).

2.5.2.1 Localized surface Plasmon

Localized surface Plasmon occurs in metals nanoparticles having dimensions much smaller than the wavelength of incident light($R \ll \lambda$), and when the oscillation frequency of electrons match the frequency of incident light, resonance is set up resulted in absorption band in the visible region of electromagnetic spectrum (Tabor, 2009, Rycenga et al., 2011). This phenomenon is the so called Localized Surface Plasmon Resonance (LSPR) (Willets and Van Duyne, 2007). LSPR occurs in silver and gold NPs in 5- 100 nm size range and can amplify the electric field of incident electromagnetic radiation near the NPs surfaces by two orders of magnitude (J.Haes, 2005).

The electric field associated with incident light interacts with the metal nanoparticle and produce an electric dipole where surface electrons move to one side of nanoparticles leaving the positive charge on the other side as shown in figure (2.2).

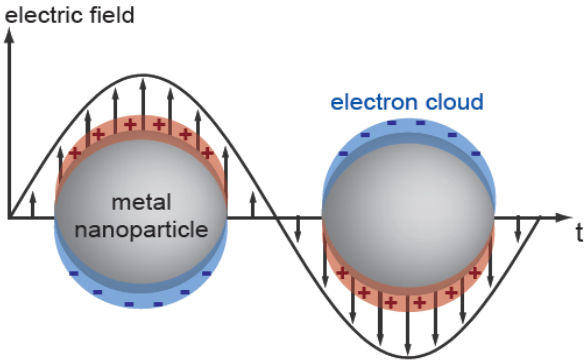


Figure 2.2. Schematic diagram illustrating localized surface Plasmon (Borys, 2011).

The resonance frequency (position of absorption band of LSPR) depends on different factors namely type of metal, sizes of nanoparticles, shape of nanoparticles and the dielectric of surrounding media. Details about these factors will be given in section 2.6.

2.5.2.2 Surface Plasmon polariton

This mode of surface Plasmon is occurring only when a thin metal and dielectric material come into contact such as thin films.

In contrary to localized surface Plasmon, propagating surface Plasmon (Surface Plasmon Polariton**)** does not produced unless the momentum of electric field associated to incident light is matches to the surface plasmon of metal (coupling between Plasmon and photon)

(Ning, 2012). To achieve this, some optical apparatus such as glass prism are used to manipulate the momentum of photons.

As the above condition is satisfied the coupling between Plasmon and light wave will be achieved and therefore evanescent wave propagates at the interface between metal and dielectric material and this what is called surface Plasmon polariton.

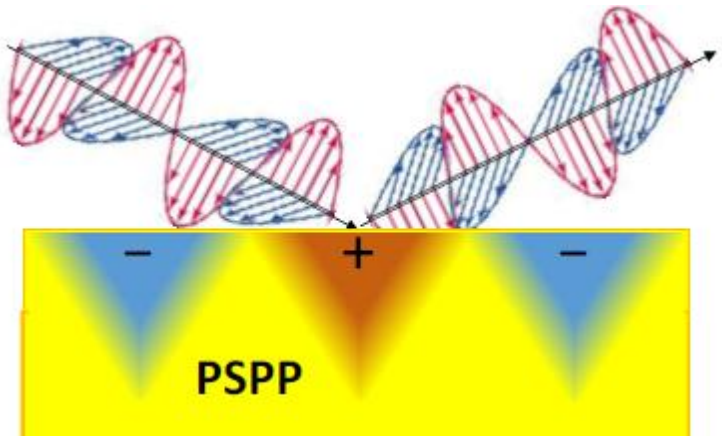


Figure 2.3. Show the propagating surface Plasmon polariton (Amendola et al., 2017).

2.6 Tuning of the localized surface Plasmon resonance

The position of the absorption band (resonance wave length) of the LSPR is playing an important role in its applications. In fact, the resonance wave length is depending on three different parameters, namely size and shape of nanoparticles and the dielectric constant of the environment. Details about these parameters will be discussed in sections 2.6.1, 2.6.2 and 2.6.3.

2.6.1 Effect of nanoparticles size

Particles having sizes between 1-100 nm are defined as nanoparticles (Rivera et al., 2012). It is important to note that there are two different size effects in this particular size regime, namely intrinsic and extrinsic (Kreibig, 1993). Intrinsic size effect which also called quantum size effect is occurred in very small size less than 5 nm (often called cluster) where the energy level become discrete and therefore, electrons will have high possibility to transfers between these levels. Due to this effect (electrons transfer between energy levels), classical theory cannot be applied and quantum theory is required (Kreibig, 1993, Rivera et al., 2012). As a particle size increases the spacing between energy level decreases and continuous band is formed. This is called extrinsic size effect. The extrinsic size effect also is divided into two size regime when interact with electromagnetic radiation.

For nanoparticle with size much less than the incident radiation ($R \ll \lambda$) the absorption dominates over scattering (Fig. 2.4a) resulting in near field enhancement. In this size regime, the light can homogenously polarize the particle resulting in dipole absorption (Fig. 2.4a). In contrast, for large nanoparticle ($R > 40nm$) (Rycenga et al., 2011) the scattering dominates over absorption (Fig. 2-4b) leading to far field enhancement. It is interesting to note that as the size of nanoparticle increases the frequency of collective oscillation of electrons decreases because the separation of charge on NPs increases resulting in the red shift of LSPR peak. In addition, increasing the size of nanoparticles above 40 nm leads to additional LSPR peaks located on the high energy side (Fig. 2.4b) attributed to high order modes (ex, quadrupole).

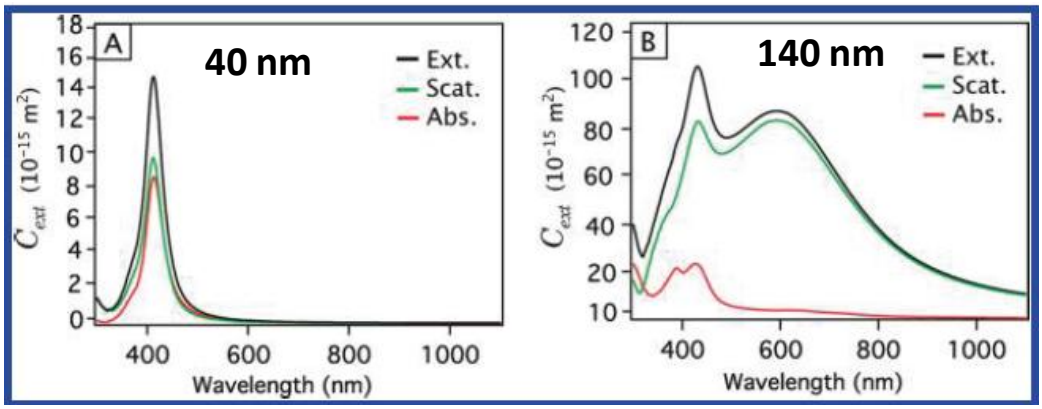


Figure 2.4. The absorption, scattering, and extinction spectra of silver Nano sphere with (A) 40 nm and (B) 140 nm in diameter (Rycenga et al., 2011).

2.6.2 Effect of nanoparticles shape

Mie theory deals with study of the interaction between electromagnetic radiation and spherical nanoparticles (Rivera et al., 2012). Later on, further approximation of Mie equations has been developed to cover wide range of arbitrary shapes, resulting in different numerical method such as discrete dipole approximation (DDA), the T-matrix method, the multiple multipole method (Hu et al., 2006, Noguez, 2006). For example, M. Rycenga *et al.* calculated the extinction spectra for silver nanoparticles with different shapes using Mie theory for spherical shape and DDA method for other geometries (Fig.2.5). As can be seen from figure 2.5, non-spherical shapes display red-shifted resonance peaks, which are assigned to the accumulation of surface charges on the particle corners. The distribution of charges on these corners leads to increase the surface polarization and therefore reduces the restoring force for the dipole oscillation, resulting in the red shift of the plasmon resonance peak and the appearance of higher modes (Rycenga et al., 2011).

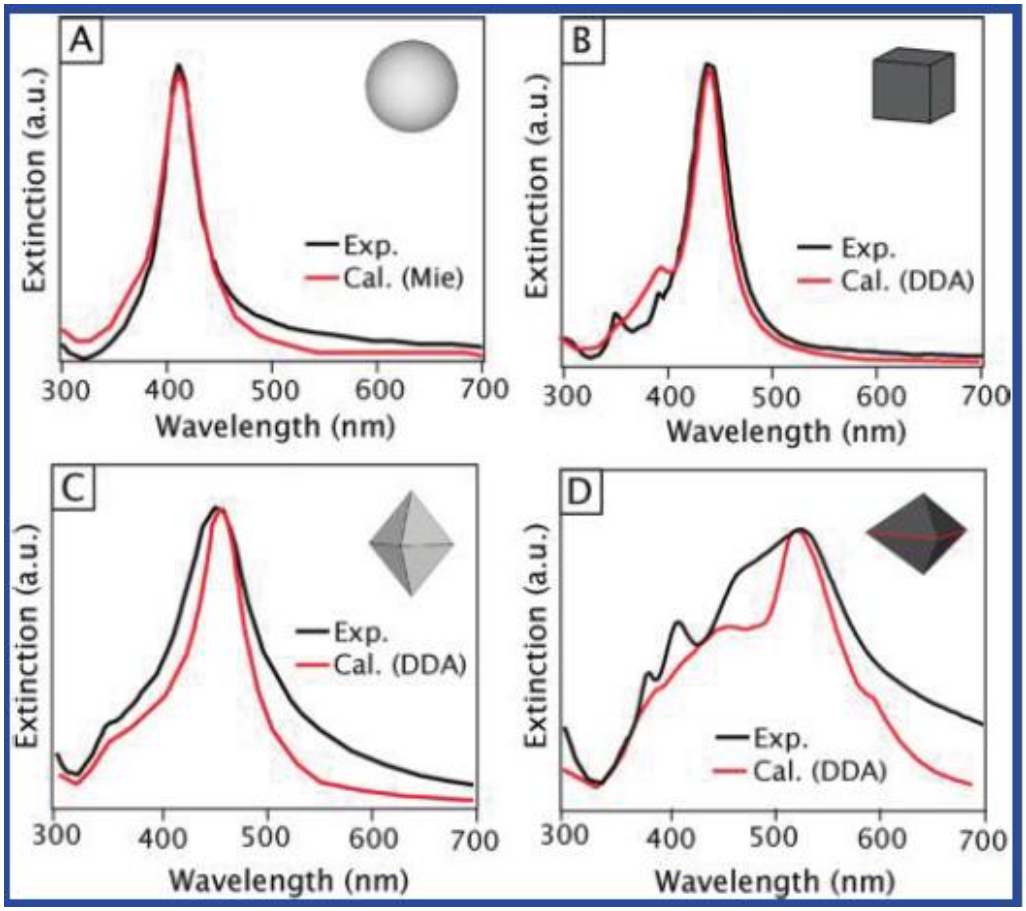


Figure 2.5. Extinction spectra for Ag with different shapes (Rycenga et al., 2011)

2.6.3 Effect of dielectric of the environment

The dielectric environment of nanoparticle has a good impact in the LSPR. Equation 2.17 obviously showed the relation between the dielectric environments $\boldsymbol{\varepsilon}_m$ with the extinction cross-section C_{ext} . It is clear that the dielectric constant of the environment has significant effect on the LSPR wavelength of nanoparticles. An increase in the relative permittivity of the dielectric medium results in a decrease in the restoring force of electron oscillation and therefore shifts the plasmon resonance towards longer wavelength.

2.7 Noble metals as good Plasmonic materials

Noble metals are considered as the most important metals that intensively used in plasmonic applications due to their relatively low loss in the visible and near-infrared (NIR) ranges. Other metals than Ag and Au have limited use in experimental work due to their low quality factor resulting from either the interaction between them and the environment (e.g. form metal oxides) or the overlap between their interband excitation and Plasmon excitation

(Rycenga et al., 2011). The quality factor (Q) is defined as measure of field enhancement around nanoparticles (Sonnichsen, 2001). For Bulk metal, the quality factor (Q) is given by (Rycenga et al., 2011).

$$Q = \frac{\omega(d\varepsilon_r/d\omega)}{2(\varepsilon_i)^2} \qquad (2.19)$$

where ε_r and ε_i are the real and imaginary parts of the metal dielectric function respectively, while ω is the frequency of the light. In most plasmonic applications the quality factor Q should be more than 10 (Rycenga et al., 2011). Figure 3.3 shows the quality factors of different Bulk metals (Ag, Au, Al, Cu, Li, Pd and Pt) plotted using equation 2.19. As can be seen, Ag has a high quality factor in the spectral range from 300-1200 nm. Al shows high quality factor only in the UV region while Au and Cu exhibit high quality factor in the NIR. Other metal (Li, Pd and Pt) showed very low quality factor less than ten.

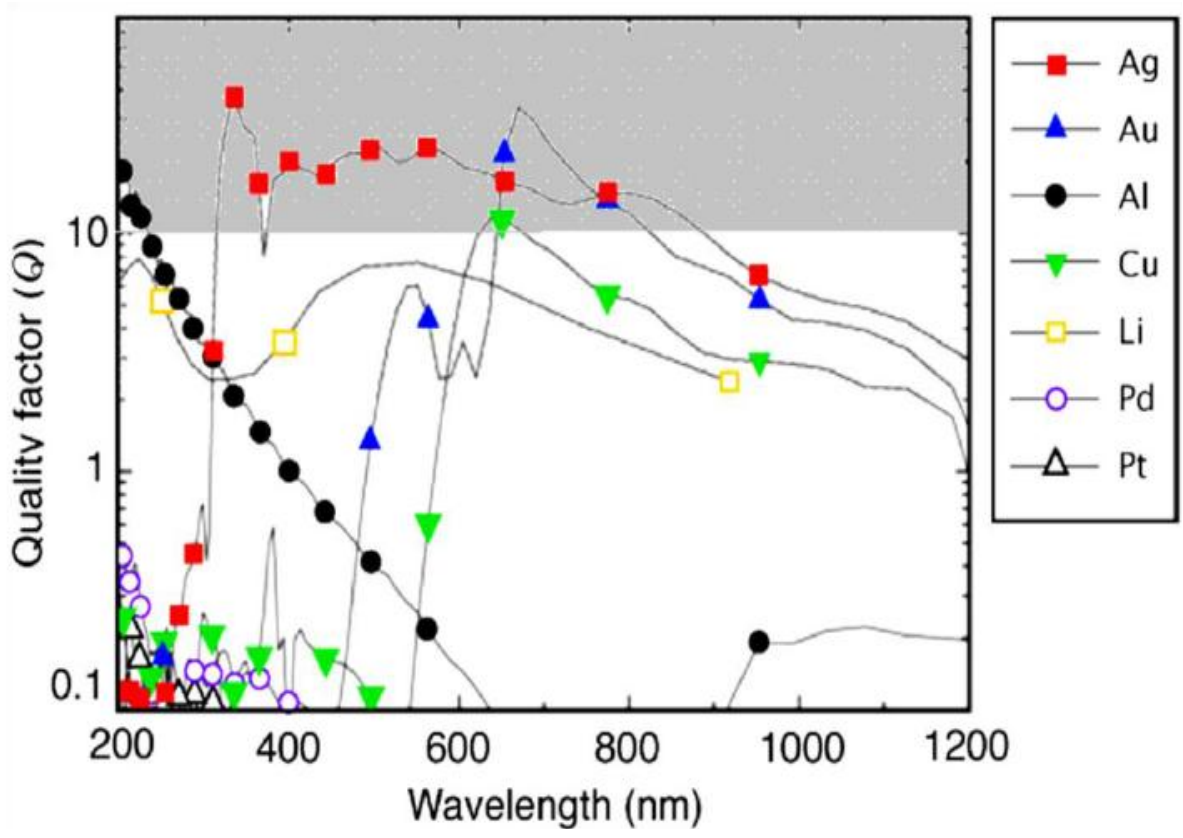


Figure 2.6. The quality factor (Q) of the LSPR for a metal/air interface (Rycenga et al., 2011).

It is well known that the higher Q denotes less damping and therefore a stronger plasmon resonance. The shaded area represents the desired quality factor for plasmonic applications (Rycenga et al., 2011).

To study the effect of particle sizes on the quality factor of Ag and gold, the ε_r and ε_i in equation 2.19 will be replaced by the size dependent dielectric function calculated using equation 2.13.

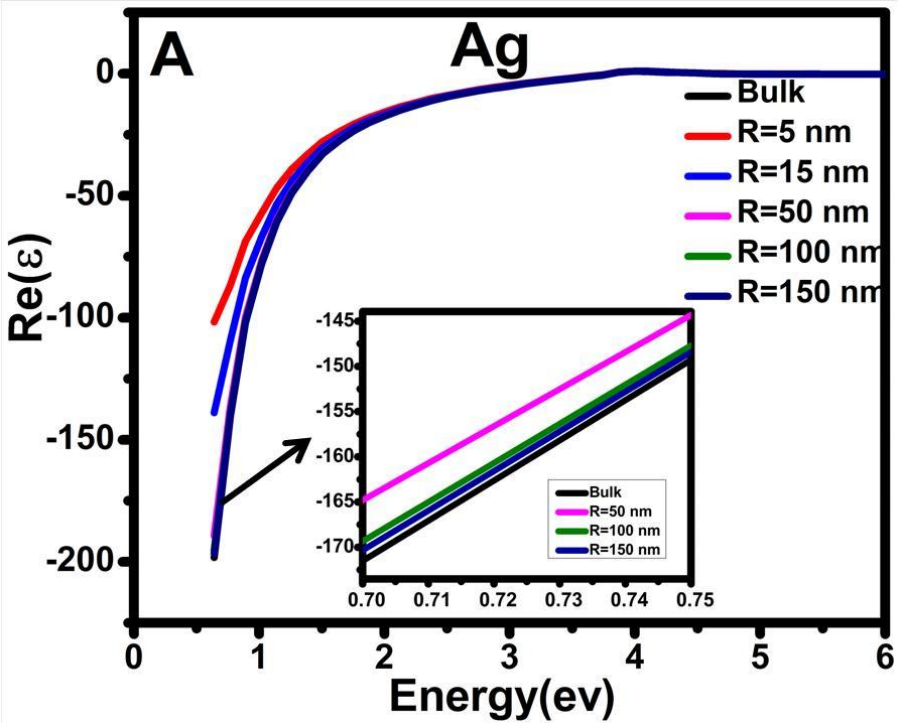
Chapter 3

Results and Discussion

3.1 Effect of particle sizes on the dielectric constant and quality factor of gold and silver:

3.1.1 Silver

Figure 3.1 shows the dielectric function (A) real and (B) imaginary part of silver metal as the function of photon energy for bulk and nanoparticles with different sizes. These results were calculated using Drude-Summerfeld model for free electrons (equation (2.13)). The inset in figure 3.1 shows the deviation of real dielectric function for sizes 50, 100 and 150. For more accuracy, experimental data of dielectric function for bulk silver (with the thickness in the range between 185 – 500Å) were used (Johnson, 1972). The reason of using particle sizes above 5 nm in our calculations is due the fact that for small particles (R less than about 5 nm) the energy levels become discrete and therefore, the classical theory is no longer valid so the quantum theory is required (Balamurugan and Maruyama, 2005).



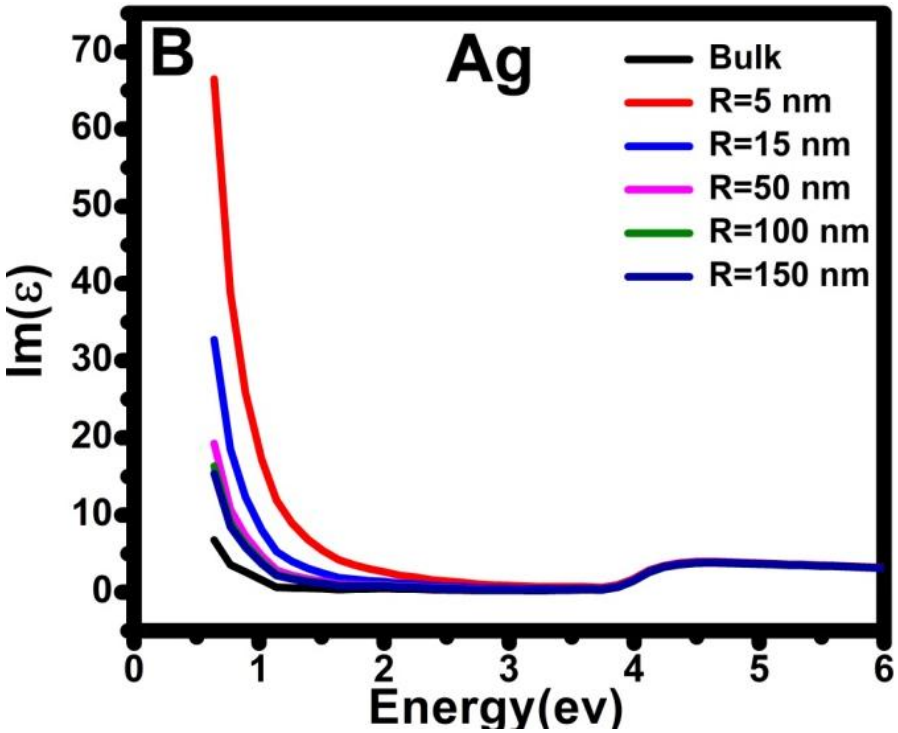


Figure. 3.1. Shows the (A) real and (B) imaginary part of dielectric function of silver metal as the function of photon energy for bulk and nanoparticles with different sizes. The inset in Fig.3.1A shows the deviation in real dielectric of Ag NPs having sizes of 50,100 and 150 nm from bulk.

As can be seen from figure 3.1 A (real part), for R> 50 nm, the real dielectric coincides with the experimental bulk values and almost matches the experimental bulk values when the particle sizes get large than 100 nm. As the size of nanoparticles get smaller than 50 nm, the real dielectric function departs from bulk values for the photon energy larger than 1.5 eV (800 nm). This behavior is due to the fact that when the particle size becomes comparable with mean free path of silver (e.g. 52 nm for Ag), then the collision of the conduction electrons with the NP surface becomes important (Amendola, 2010), reducing the mean free path and therefore increasing the collision frequency (see equation (2-12)). Moreover, after 1.5 eV the real dielectric for all sizes increases simultaneously. At 4 eV the real dielectric function reaches positive values due to the inter band transition from 4*d* to 5*s* band. This leads to decrease the Plasmon energies in this region.

Figure 3.1 b shows the imaginary part of dielectric function. It is important to note that the imaginary part of dielectric function describes the dissipation or losses of electromagnetic radiation when interacting with metals. This is due to several processes, but the most

important one is the inter band transition. As can be seen from figure 3.2b, decreasing the size of NPs resulted in more losses particularly in visible region (due to Plasmonic effect). In addition, in this case the absorption dominates over scattering when the particle size is decreasing. At the region of inter band transition (4 eV) the losses increase again and stay constant for all sizes. It is worth noting that the imaginary part, instead start to deviate from 2.2 eV (564 nm). Furthermore, it can be clearly seen that whatever increases the size after 100 nm the dielectric does not change, indicating that above this size regime (> 100 nm) the Ag metal considered as bulk in all properties.

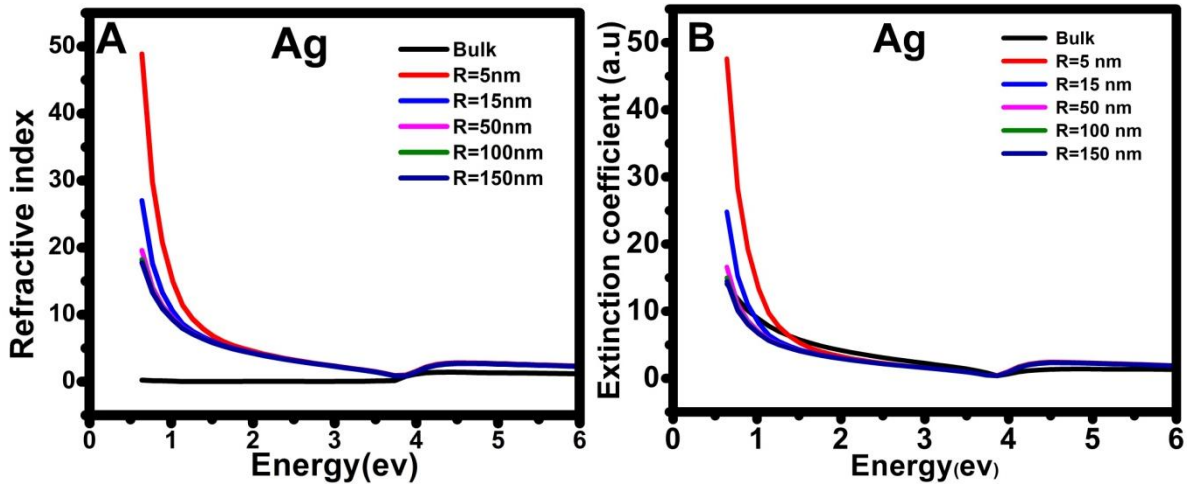


Figure. 3.2. Shows the (A) real and (B) imaginary part of the refractive index of silver metal as the function of photon energy for bulk and nanoparticles with different sizes.

Figure 3.2A shows the real part of the refractive index of silver metal as the function of photon energy for bulk and nanoparticles with different sizes. The real and the imaginary part of refractive index can be described by a quantity called complex refractive index, $n_{complex} = n + ik$ where n is the normal refractive index which describes the phase velocity of the wave in the metal and k is the called extinction coefficient and it describes the decay of the wave in the metals. The above results (real and imaginary part of refractive index) are plotted using equation (2-14) and equation (2-15) respectively. As can be seen from Fig. 3.2, there is a significant change in both the real and imaginary of refractive index. The interpretation of this result is similar to the interpretation for the dielectric function due to the direct relation between the dielectric and refractive index (see equation 2-6 and 2-7).

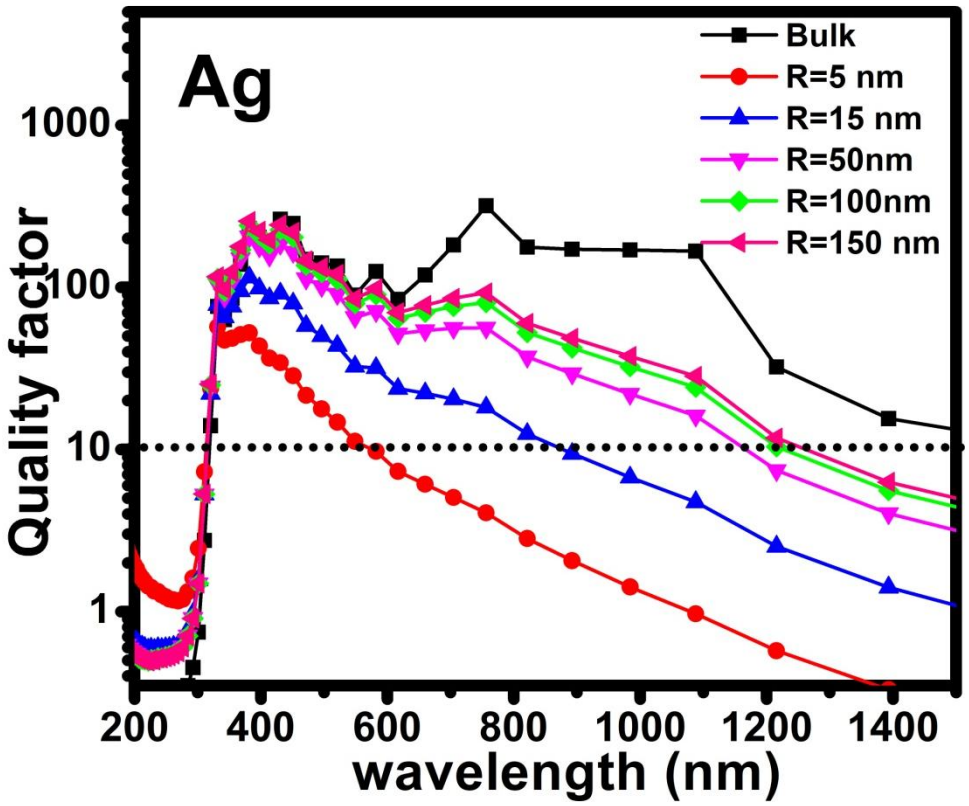


Figure 3.3. The quality factor (*Q*) of the LSPR for a bulk Ag/air interface compares to Ag with different sizes.

Figure 3.3 shows the quality factor of bulk Ag and Ag with different particle sizes. The quality factor is the factor that determines the field enhancement around nanoparticles. In general, the quality factor should be larger than 10 in most Plasmonic applications (Rycenga et al., 2011). To study the effect of particle size on the quality factor of Ag, the (Rycenga et al., 2011) quality factor of bulk Ag and of Ag with different sizes as the function of wavelength is plotted as shown in figure 3.3, using equation (2.19) and the dielectric constant data plotted in figure 3.1. It can be seen that the quality factor of Ag is depends on the particle sizes. Moreover, the quality factor for all particle sizes is above 10 in the visible range (maximum at 400 nm) and shift to infrared region when particle sizes increased.

3.1.2 Gold

Figure 3.1 shows the dielectric function (A) real and (B) imaginary part of gold metal as the function of photon energy for bulk and nanoparticles with different sizes. These results were calculated using Drude-Summerfeld model for free electrons (equation (2.13). The inset in figure 3.1 shows the deviation of real dielectric function for sizes 15, 50, 100 and 150 nm.

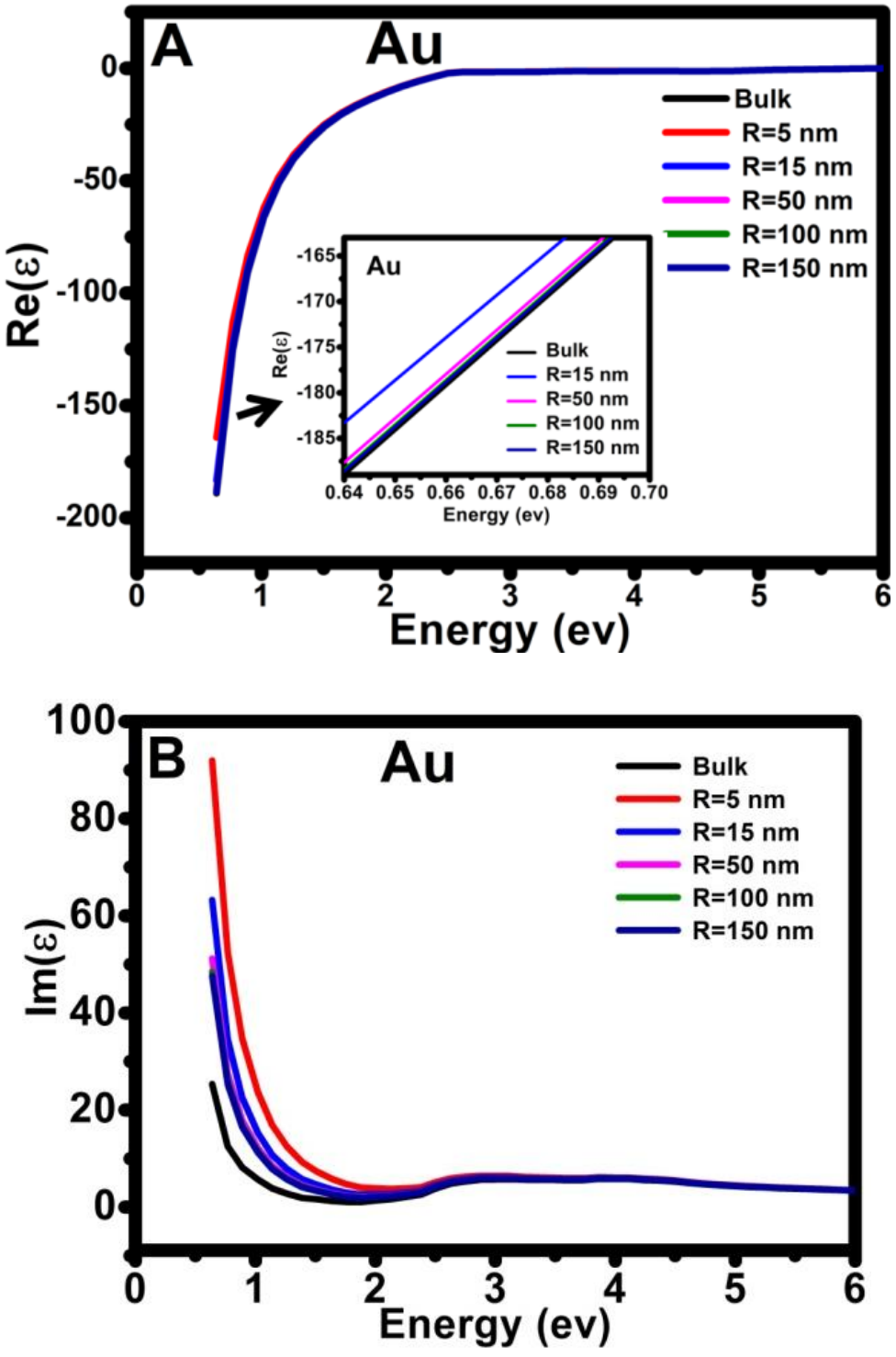


Fig. 3.4 shows the (A) real and (B) imaginary part of dielectric function of gold metal as the function of photon energy for bulk and nanoparticles with different sizes. The inset in Fig.3.4a shows the deviation in real dielectric of Au NPs having sizes of 15, 50,100 and 150 nm.

Fig. 3.4 shows the dielectric function (A) real and (B) imaginary part of gold metal as the function of photon energy for bulk and nanoparticles with different sizes. These results were calculated using similar equations that used for silver metal (see section 3.1.1). As can be seen both figures (3.4 A and B) looks similar in behavior compared to figures 3.1 a and b, except that the dielectric function of Au NPs departs from bulk value at 1~ eV and 2~ eV for real and imaginary parts respectively. Moreover, the interband transition for Au occurs at low energy (2.5 eV) compared to that of silver (4 eV).

Significant effect of particle sizes on the refractive index (*n*) and extinction coefficient (*k*) of gold can be seen clearly from figure (3.5 A and B). Another important note is that when the particle sizes reduced to nanoscale, the deviation in the dielectric function, refractive index (*n*) and extinction coefficient (*k*) form their bulk values is more pronounce in silver compared to the gold.

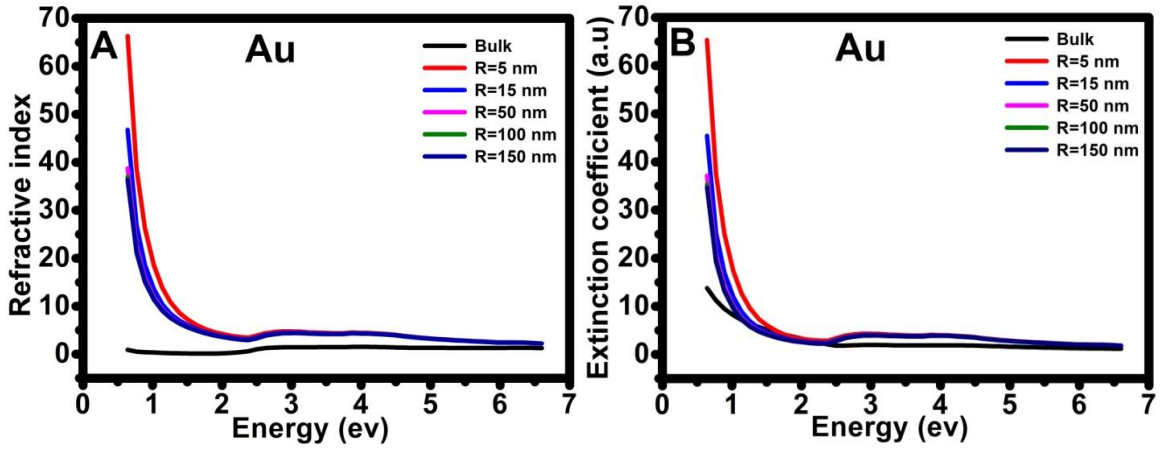


Figure. 3.5. The real (A) and imaginary (B) parts of the refractive index of gold metal as the function of photon energy for bulk and nanoparticles with different sizes.

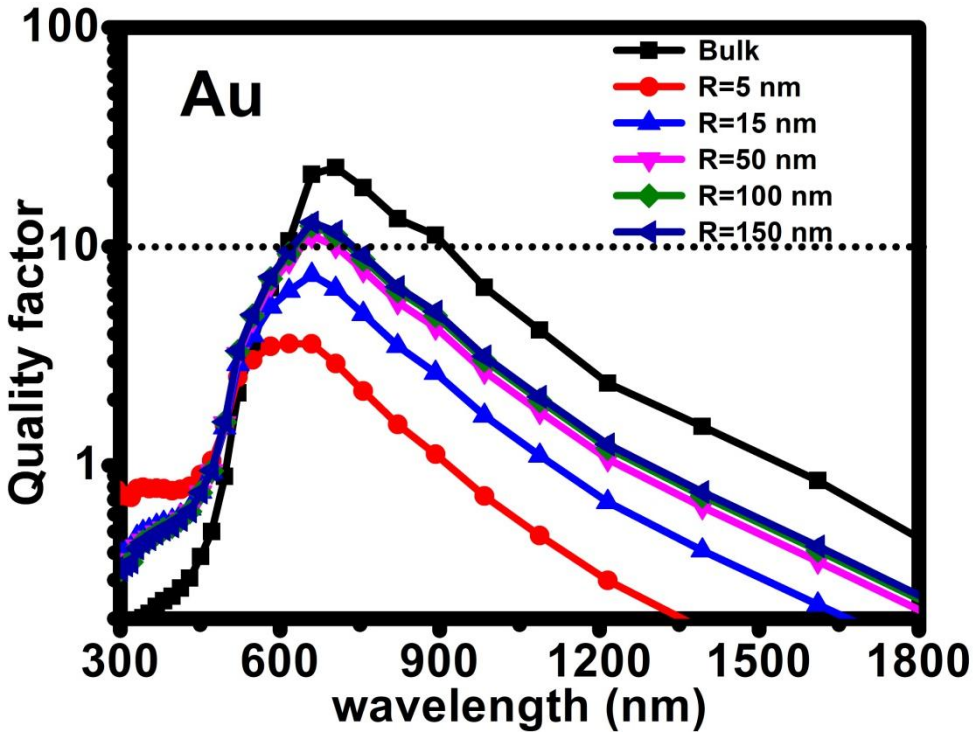


Figure 3.6. The quality factor (*Q*) of the LSPR for a bulk Ag/air interface compared to Ag with different sizes.

Figure 3.6 shows the quality factor of bulk Ag/air interface (as reported by Johnson) compared to Ag NPs with different sizes. As can be seen from Fig.3.6, the maximum of quality factor start at 600 nm for small size (5 nm) and then shift to the red side as particle sizes increase. Of interest is that the quality factor of Au for all sizes is less than 10 in both visible and NIR region. Comparing the quality factor of Ag with that of Au, it found that the Ag has a higher quality factor and therefore stronger Plasmon resonance. This is due the fact that the interband transition of Ag is occurs at higher energy (~3.8 eV) compared to the LSPR energy (~2.9 eV) (Wang, 2005) while Au exhibits LSPR at ~530 nm (2.3 eV) which is very close to the interband transition region (2.5 eV) (Wang, 2005).

According to the theoretical results shown in Figs. 3.1 and 3.4, it was found that for both Ag and gold there is a significant change in the dielectric function (Optical properties) when the size is decreased to the nano-scale. Moreover, for particle size above 100 nm, the dielectric function is well matched the bulk value, in agreement with the definition of nanoparticles which is define as particles having sizes between 1-100 nm (Ning, 2012). Furthermore, the effect of particle sizes on the dielectric function of Ag is found to be more pronounce in the visible region while for Au is lies in the near infrared window. In addition, significant difference in optical properties between Ag and Au can also be seen from figure 3.3 and 3.6

which are showed the quality factor as the function of wavelength for Ag and Au, respectively. The most important difference is that for all particle sizes, Ag showed high quality factor in both visible and near infrared regions while gold showed high quality factor only for size larger than 15 nm in near infrared region. This suggests that the Ag can be used in possible Plasmonic applications (for absorption or scattering enhancement) in both visible and near infrared regions while Au will be a good choice only in infrared region.

Chapter 4

Conclusion and recommendation

4.1 Conclusion

In this work, the effect of the particle sizes on the dielectric function and quality factor of silver and gold were investigated. Significant variation in dielectric function for both silver and gold was observed when the particle size becomes smaller than 100 nm. Therefore, it can be concluded that the nanoparticles can be defined as particle having sizes between 1-100 nm in agreement with the definition reported in literature.

For quality factor, the obtained results showed significant differences between silver and gold. Silver showed maximum quality factor in visible and infrared regions while for gold is shown only in infrared. This is very important results which can be used as key in plasmonic applications. Moreover, for all sizes silver showed higher quality factor compare to gold. This indicates that silver can produce strong field around nanoparticles (electric field enhancement). Therefore, it can be concluded that the silver the is best choice for plasmonic applications in both visible and near infrared regions.

4.2 Recommendation

Many different adaptations, tests and experiments have been left for the future due to lack of time. Future work will concern about:

- Synthesis gold and silver nanoparticles with different sizes and compare their optical properties with theoretical properties in this dissertation.
- Study the tuning of localized surface Plasmon resonance experimentally.
- Taking different metal into study.

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