Simulation of Surface Plasmon Resonance on Different Size of a Single Gold Nanoparticle

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Abstract. In this work, the surface plasmon resonance wavelength position is calculated using metal nanoparticle boundary element method (MNPBEM) toolbox from Matlab classes. The surface plasmon resonance wavelength position is determined by full Maxwell’s equations. We present a simulation optical properties study of the dependence of the plasmon resonance spectrum of individual gold nanoparticles on the dielectric function and size change in the extinction efficiency spectrum. Previous studies have shown that the shift of the gold nanoparticle plasmon resonance wavelength increased when the size of gold nanoparticles was increased. However, the dielectric function of gold nanoparticle showed a different shifting when using a higher spectral range. In this work, the attention is focused on the size effects of gold nanoparticle on the position of the plasmon resonance wavelength. The aim of this work is to study the behaviour of the resonance position for different diameter size of gold nanoparticle by using boundary element method simulations. The gold nanoparticle diameter between 10 nm to 100 nm is used in determine the shifting of the surface plasmon resonance. The results in this work indicated that the position of the plasmon resonance wavelength for gold nanoparticle was redshift when the size of gold nanoparticle was increased. However, dielectric function measured by previous experiments show that the high spectral resolution gives the significant redshift to the extinction efficiency spectrum.

1. Introduction
Optical properties are closely related to the electrical and electronic properties of the material. There must be some other factors that can also be seen when dealing with optical properties. Optical properties usually can be referring to the interaction of electromagnetic radiation with matter. For instance, an electromagnetic wave of a single frequency entering a medium from a vacuum. This wave could be reflected, refracted or absorbed. There are only two possibilities phenomena that can occur when there is the interaction of a medium with electromagnetic radiation which is scattering and absorption. When we consider a wider spectrum of frequencies, then some part of the spectrum would be absorbed and the other frequencies would be scattered [1].

Gold nanoparticles interaction with light is strongly dictated by their environment, size and physical dimensions. Oscillating electric fields of a light ray propagating near a colloidal nanoparticle interact with the free electrons causing a concerted oscillation of electron charge that is in resonance with the frequency of visible light. These resonant oscillations are known as surface plasmons. By collective conduction band electron oscillation in response to the electrical field of the light radiation, the surface plasmon absorption dominate the optical properties of metal nanostructures in the visible region [2]. Also for particles that consist of alkali, noble, and various other metals the surface plasmon...
show themselves as pronounced optical resonances in the visible or UV parts of the spectrum. The resonance frequency of the oscillation such as surface plasmon energy is determined the dielectric properties of the metal and the surrounding medium and by the particle shape and size [3].

For this work, MNPBEM Matlab toolbox is used to calculate full Maxwell’s equation [4]. From this, we can predict the position of plasmon resonance. For this work, we choose to compare the dielectric function that are very common which is by Johnson and Christy with dielectric function of gold that the latest to be calculated which is by Olmon etc. Dielectric function of gold was measured by Johnson and Olmon are different since they approach different method in calculating the dielectric function of gold. For Johnson and Christy, they have calculated the dielectric function by using the index of refraction of films was measured by reflection and transmission from 0.50 to 6.5 eV (190 nm to 2.48 μm) in 1972 [5]. But for Olmon, in 2012 they performed precise spectroscopic ellipsometry measurements to determine the dielectric function across a broad spectral range (300 nm to 25 μm) 0.05-4.14 eV with high spectral resolution [6].

2. Modelling and simulations parameter
The work only focusing on the single particle model which have been calculated using MNPBEM toolbox (metallic nanoparticles using boundary element method) [4]. The size of the gold nanoparticles is ranged between 10-100nm. The particle is “comparticle” which is compound of particles in a dielectric environment and the shape of particle is describe by “trisphere” function which is load points on sphere from file and perform triangulation. The changing parameters for “trisphere” is diameter of the particles and the vertices. For this measurement, 144 vertices was used to calculate the interaction happened on the surface of the nanosphere. For the solver, the full Maxwell’s equations was used since we want to see the shifting of the extinction peak. The quasistatic plane-wave excitation and cross section was the parameters for “plane-wave-stat” function and the direction of E-field polarisation was along x-axis and light propagation was along z-axis. The wavelength range was between 400nm to 700nm. To have a smoother peak of extinction cross section 300 points was set to be calculated by the boundary element method solver [4], [7].

![Figure 1](image-url)  
Figure 1 Single gold nanoparticle in dielectric environment [4].

Where, \( \varepsilon_1 \) is the dielectric constant of medium and \( \varepsilon_2 \) is the dielectric function of gold nanoparticles. In this work, we compare two different dielectric functions of gold which are by Johnson and Christy; and Olmon etc. Johnson and Christy is widely used nowadays but Olmon etc. came out with the recent calculation of dielectric function which have a broad spectral range from 300nm to 25 μm (0.05-4.14 eV) with high spectral resolution in 2012. In 1972, Johnson and Christy measured the index of refraction of gold films with thicknesses 34 and 46 nm that were deposited onto fused-quartz substrates by reflection and transmission from 0.50 to 6.5 eV (190 nm to 2.48 μm) [6]. The dielectric function have a relation with refractive index given by:
\[ \varepsilon(\omega) = n^2 \]  

(1)

Where \( \varepsilon(\omega) \) is dielectric function and \( n \) is refractive index of gold nanoparticles [8]. To compare those two dielectric functions stated above, the bulk refractive index of the surrounding media was changed between air (\( n=1.00 \)) and water (\( n=1.33 \)) and the sensitivity of the bulk refractive index was calculated. The sensitivity is defined as:

\[ S = \frac{\Delta \lambda}{\Delta n} \]  

(2)

Where \( \Delta \lambda \) is the shift of the extinction peak and \( \Delta n \) is the refractive index change of the media [7]. From the comparison, we can determine which dielectric function is more significant for this kind of measurement. The signification was determined by which dielectric function have larger peak shift of extinction cross section.

3. Results and discussion

The normalised extinction cross sections (between air and water) simulated for two different dielectric functions of single-particles model with a diameter of 70nm are presented in Figure 2. Although, the peak wavelength between air for Johnson and air for Olmon is nearly the same. The peak shift (between air and water) of the two dielectric functions have 3nm in difference. From the previous calculation for Johnson and Palik, the difference was nearly the same [7]. From here, we can see that Olmon have longer peak shift (between air and water) compared to Johnson. Taking these observations into consideration, the Olmon dielectric function was used for further calculation.

Figure 2 Normalized extinction spectra of single 70 nm particles in water/air. Comparison of the two available tabulated gold dielectric functions (‘GoldJohnson’, ‘GoldOlmon’).

Figure 3 shows the normalized extinction efficiency of gold nanoparticles with diameter change from 10 to 100 nm. From the graph, we can see that the peak of wavelength is redshifted when the diameter of gold nanoparticles was increased. This redshift occurs due to the perturbation of the density of the conduction electrons in the particles. Therefore the redshift of the peak wavelength is size dependence. The other reason is due to the electromagnetic retardation which results from the depolarization of the light field across the particle surface. The peak wavelength of the extinction efficiency against wavelength was the results of surface plasmon resonance to occur. Besides the redshift, the peak also broadening when the size of the gold nanoparticles increase. The broadening of the peaks occurs due to the dephasing of the coherent electron oscillation. The large bandwidth corresponds to rapid loss of the coherent electron motion [9].
The absolute peak shifts of the extinction efficiency (between air and water) simulated for different diameter of single gold nanoparticle are presented in Figure 4. From here, we can see that when we change the dielectric constant of surrounding medium, the peak shift (between air and water) was increased when the diameter of the gold nanoparticles increased. The regression value also agrees with the increment of the gold nanoparticles diameter, where the wavelength peak shift increase. Since surrounding medium is one of the parameter of the shifting of plasmon resonance due to the boundary conditions which include the electric potential inside and outside the gold nanoparticles. This is because dielectric function of gold nanoparticles is the parameter that depends on frequency as the surrounding medium is a constant and real parameter [10].

![Figure 3](image1.png)

**Figure 3** Normalized extinction efficiency of 10-100nm particle diameter in water (n=1.33).

![Figure 4](image2.png)

**Figure 4** Peak shift (between air and water) against diameter of gold nanoparticles (10-100nm).

4. Conclusion
The plasmonic properties of single-spherical gold nanoparticle systems were investigated with MNPBEM Matlab toolbox. It was found that between Johnson and Olmon dielectric function of gold, Olmon have longer peak shift (between air and water) compared to Johnson. Olmon dielectric function
have been used to further the measurement. The surface plasmon resonance appears in the visible or near-infrared range for gold nanoparticle [10]. From the simulation, we can state that the diameter between 10 nm to 100 nm were in the visible or near-infrared range. Therefore, 70 nm of gold nanoparticles was in the good size for further measurement since it peak shift (between air and water) and the broadening of the peak was optimum. Meanwhile, different size of gold nanoparticle was applicable for different applications based on its requirement. The examples of application such as biosensor, catalyst application, and therapeutic agents [1].

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