Nanoparticle Optical Properties: Size Dependence of a Single Gold Spherical Nanoparticle

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Abstract. The optical properties of a spherical gold nanoparticle have become our interest due to its remarkable characteristics when interacting with the light. In this work, the dependence of surface plasmon resonance on the size of the gold nanosphere has been studied with varying diameter from 20 to 100 nm. The optical spectra of the single isolated gold nanoparticles are simulated by employing the versatile MNPBEM toolbox. The wavelength corresponding to the maximum extinction, absorption as well as scattering redshifts (shift to longer wavelengths) were observed as the nanoparticle size increased. The rate of change of scattering (Δsca) and absorption (Δabs) relative to the extinction is calculated to correlate these two properties. For the nanoparticle with size less than 70 nm, Δabs is larger than Δsca, whereas for the diameter of nanoparticles above 70 nm, they show that Δsca is larger than Δabs. Due to this, it is found that absorption efficiency initially increases with nanoparticle size, which eventually reaches a maximum at a size of 70 nm and then begins to decrease with further increase in the nanoparticle diameter. The observed volcano trend of absorption efficiency is the result of electromagnetic retardation and radiative scattering. It can be concluded that the intermediate-size nanoparticle has the highest absorption efficiency with an optimal size of 70 nm for gold nanoparticles.

1. Introduction

Gold nanoparticles have unique optical properties that can be easily tuned, which are different from bulk gold. These intriguing characteristics provide a plethora of advantages in various fields particularly in the biomedical field as its optical properties can be applied in biosensing, drug delivery and diagnostic imaging [1,2]. One of the major attributes offered by nanoparticles is the interchange of light with electrons on its exterior. At a specific light wavelength, a phenomenon known as surface plasmon resonance occurs when the frequency of the incident photon is resonant with the collective electrons oscillations on the surface of the nanoparticle [3]. As the incident light with an electric field passed through the nanoparticle, there is a displacement of electrons, which located at the boundary of nanoparticles relative to the positive ionic lattice, leading to the net charge difference. In turn, it gives rise to Coulombic restoring force, which is responsible for restoring the system to its equilibrium state and results in the creation of dipolar oscillation of electrons or also called as surface plasmon oscillation [4]. Mie theory postulated by Gustav Mie in 1908 has been used to explain the color variation of colloidal gold with particle size. Mie calculated the surface plasmon resonance by solving Maxwell’s equation with appropriate boundary conditions for small sphere interacting with electromagnetic field [5]. When the size of the particles is much smaller than the wavelength of light (2r << λ), it is sufficient to consider only the dipole oscillation contributes to the interaction of the light-nanoparticle interaction (dipole approximation) and it is possible to employ the quasistatic approximation, means that the electric field...
of light is assumed to be constant [6-8]. Under this circumstance, the polarizability of the sphere, \( \alpha \) is given by Clausius-Mossotti relation as:

\[
\alpha = 3 \varepsilon_0 V \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2 \varepsilon_m} \right)
\]

where \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_m \) is the dielectric constant of surrounding medium, \( \varepsilon \) is the dielectric function of the metallic nanoparticle and \( V \) is the volume of spherical nanoparticle. This equation indicates that the polarizability of the nanoparticle directly depends on the size of the nanoparticle as \( V = \frac{4}{3} \pi r^3 \).

Generally, the size of the nanoparticle affects the spatial distribution of the polarization charges over the surface as well as the separation of positive and negative charges. Thus, this effect influences the peak maxima, plasmon resonance wavelength and plasmon bandwidth as shown by many researchers both theoretically and experimentally. Based on their works, however, the size effect of gold nanoparticles is either studied up to 80 nm of diameter or emphasizing on the extinction spectra only [9-12]. In date, the contribution of the absorption and scattering properties to the total extinction of a single gold spherical nanoparticle has not yet been investigated in detail. Therefore, in this present work, the size dependence of the gold nanospherical on the total extinction, absorption and scattering have been highlighted.

2. Methods and Parameters
In order to simulate the size dependency of gold nanoparticles on the surface plasmon resonance, the MNPBEM toolbox was used, provided by Ulrich Hohenester, in which has been described elsewhere in details [13-15]. Therefore, the most concise of introductions was provided. The major purpose of the toolbox is to compute Maxwell’s equations for dielectric nanoparticles with homogeneous dielectric properties, which are separated by sharp boundaries. This homogenous dielectric environment condition is advantageous as only the boundaries between different dielectric materials need to be discretized rather than the whole volume, eventually results in faster simulations as compared to DDA and FDTD method [16]. In this work, a spherical gold nanoparticle embedded in water of refractive index, \( n = 1.33 \) [17] was investigated. The diameter of the gold nanosphere was increased by 10 units from 20 to 100 nm, while other optical characteristics were fixed. The data of dielectric constant for gold was taken from the experimental data of Johnson and Christy [18]. Full BEM simulation (BEMret) was chosen as the most appropriate solver as it solves the simulations based on the full Maxwell equations which works perfectly for all cases. Moreover, this solver also takes retardation effect into account which is significantly important for large nanoparticles (in the case of gold, diameter greater than about 20 nm) [19].

3. Results and Discussion
Figure 1 illustrates the optical efficiency as a function of the wavelength for different values of the nanoparticle diameter, with Figure 1a presenting the extinction efficiency, Figure 1b the scattering efficiency and Figure 1c the absorption efficiency. It is worth mentioning that all results in Figure 1 are presented in terms of efficiency instead of cross sectional area for clearer and better understanding. From Figure 1a, the dipole plasmon resonance of the gold nanoparticle gives a peak in extinction at about 522 nm for the 20 nm gold particle which is in good agreement with previous works [10].

By increasing the size of gold spherical nanoparticles, there is a remarkable redshift in the position of the wavelength corresponding to the maximum extinction efficiency. Additionally, this pattern can also be perceived in scattering efficiency spectrum as shown in Figure 1b. These expected results are related to the dependence of free electron contribution to the dielectric function which can be modified by changing the size of the particle. Electromagnetic retardation which results from the depolarization of the light field across the particle surface causes the Coulombic restoring force on the
electron cloud becomes weaker. Hence, the frequency needed to initiate the surface plasmon oscillation is much lower (higher resonance wavelength). As depicted in Figure 1c, the size effect is strongly shown in the absorption efficiency, where two trends of intensity can be seen. As spherical nanoparticles get larger, the dipole resonance peaks redshifts from 521 to 543 nm. However, it is found that increasing the size of nanoparticles gives rise to an increase in the absorption efficiency, which eventually reaches a maximum and then begins to decrease with further increase in the nanoparticle diameter. For the sake of clarity, the plot of the absorption maxima against particle size is shown in Figure 2.

Figure 1a: The simulated extinction efficiency with different size as a function of wavelength.

Figure 1b: The simulated scattering efficiency with different size as a function of wavelength.

The observed trend resembles a volcano shape, which is the result of effects 1) radiative scattering and 2) electromagnetic retardation. To correlate the optical properties, namely absorption and scattering, the rate of change of scattering (Δsca) and absorption (Δabs) relative to the extinction is calculated. It shows that when the diameter of nanoparticles below 70 nm, Δabs is larger than Δsca, whereas nanoparticles with size greater than 70 nm, they show that Δsca is larger than Δabs.
At small size, the nonradiative absorption dominates, which is due to the collision of electron with the nanoparticle surface [19]. The total damping rate in small nanoparticles can be written as

\[ \gamma = \gamma_{bulk} + \frac{A v_f}{R} \]  

This damping is included in the dielectric function of the metal as shown in Equation 3:

\[ \varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{i \omega \gamma + \omega^2} \]

This contribution is valid if the size of the gold nanoparticle is smaller than its mean free path of electrons (for gold = 40 nm). At large size, the radiative scattering dominates in which its damping rate increases with increasing nanoparticle size as \((kR)^3\). There is more scattering as opposed to absorption. We can conclude that the nonradiative absorption dominates in small nanoparticle whereas the radiative scattering dominates in larger particle. Since the nanoparticle size approaches the wavelength of light, the electric field across the nanoparticle can no longer be considered as uniform. Thus, the incident light field is perturbed across the particle. This leads to electromagnetic retardation or dynamic depolarization in which causes damping for large particles. Theoretically, as the size of the
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nanoparticle is comparable to the wavelength of light, the nanoparticle is no longer homogeneously polarized by the light due to the electromagnetic retardation, results in the excitation of higher-order oscillation mode. The emergence of higher oscillation mode peak (quadrupole, octupole etc.) is always located at shorter wavelength relative to the dipolar one [7]. For a mode of order \(l\), the general resonance condition is given as Equation 4

\[ e_r = -\left(\frac{l+1}{l}\right)e_m \]  

(4)

where \(l=1\) for dipole, \(l=2\) for quadrupole and so on.

Figure 3 shows the dependence of a) extinction efficiency and b) ratio of scattering to the absorption on the nanoparticle size. It is shown that with an increasing nanosphere diameter, the extinction as well as the ratio of scattering to absorption \((C_{\text{sca}}/C_{\text{abs}})\) increase exponentially. From this figure, for 20 nm gold nanoparticle, total extinction is predominantly contributed by absorption. Gradually, scattering becomes important, but absorption still contributes significantly with diameter is increased until up to 70 nm in which scattering starts to be larger than absorption. Thus, for small nanoparticle, absorption dominates while scattering becomes significant for larger nanoparticle.

**Figure 3a:** The extinction cross-section of nanoparticles as a function of size.

**Figure 3b:** The ratio of scattering to the absorption as a function of size.

4. Conclusion
This work demonstrated the size dependence of gold nanospheres on the dipole plasmon resonance by using MNPBEM toolbox. It was found that the dipole plasmon resonance wavelength of the gold spherical nanoparticle redshifted (shift to longer wavelengths) with increasing of the nanoparticle size. Nevertheless, the absorption spectrum showed a distinct feature that is not possessed by extinction and scattering spectra, in which a significant damping in intensity had been observed for nanoparticle larger than 70 nm. Consequently, the plotted spectrum for absorption efficiency resembled a volcano shape with the maximum intensity at 3.92 for 70 nm gold nanosphere. Therefore, it can be concluded that the
intermediate-size nanoparticle has the highest absorption efficiency with an optimal size of 70 nm for an isolated gold spherical nanoparticle.

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