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Tunable Plasmonic Nanoparticles Based on Prolate Spheroids

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ABSTRACT

Metallic nanoparticles can exhibit very large optical extinction in the visible spectrum due to localized surface plasmon resonance. Spherical plasmonic nanoparticles have been the subject of numerous studies in recent years due to the fact that the scattering response of spheres can be analytically evaluated using Mie theory. However a major disadvantage of metallic spherical nanoparticles is that their resonance wavelength is independent of the particle dimensions.

In this paper, plasmonic resonance of spheroidal metallic nanoparticles is studied. Using the quasi-static approximation, the resonance condition for localized surface plasmon of spheroidal nanoparticles is derived. It is shown that unlike spherical nanoparticles in which the resonance wavelength is independent of the particle dimensions, the additional degree of freedom in spheroids allows for tuning the resonant wavelength. Additionally a formal approach to tune the surface plasmonic resonance of nano-spheroids to a wavelength of interest is presented. The results are confirmed by performing full-wave simulation for gold nanoparticles.

KEYWORDS

Localized Surface Plasmon, Plasmonics, Spheroidal Nanoparticles, Quasi-Static Approximation.

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1- INTRODUCTION

In recent years there has been immense interest in the optical and electromagnetic (EM) properties of metallic nanoparticles [1], [2], [3]. Metallic nanoparticles can exhibit very large optical extinction in the visible spectrum due to localized surface plasmon (LSP) resonance. Their unique properties make them great candidates for a variety of applications such as enhanced absorption with large angular tolerance for solar cells [4] , surface-enhanced Raman scattering (SERS) substrates [5], [6], and broadband plasmonic enhancement [7].

The LSP resonance of metallic nanoparticles are strongly dependent on the geometry of nanoparticle and the dielectric function of the metal [8], [9]. For nanoparticles of arbitrary shape, the LSP resonance must be determined using numerical simulations. Analyzing plasmonic structures using traditional full-wave finite-difference and finite-element techniques requires considerable computational resources even for relatively simple structures [10]. One method that is generally used to analyze plasmonic structures is the discrete dipole approximation (DDA) method [11].

One class of nanoparticles which have been the subject of numerous publications in recent years are spherical nanoparticles [12], [3]. This is due to the fact that the scattering response of spheres can be analytically evaluated using Mie theory [13]. Since Mie theory is a rigorous approach which provides a complete solution to Maxwell's equations it is far superior to the DDA method. Furthermore, it has been shown that in order to obtain accurate results for gold (Au) spheres with diameters on the order of 100 nm, in the near-IR region using the DDA method, about 10^7 dipoles per sphere are required. As it will be shown, a major disadvantage of metallic spherical nanoparticles is that the LSP resonance wavelength is independent of the nano-sphere dimensions. Changing the radius of the nano-sphere will change the scattering efficiency at the resonant wavelength, however it will not change the resonant wavelength.

In this paper, we study the LSP resonance of spheroidal nanoparticles. A spheroid is obtained by rotating an ellipse around its major (prolate) or minor (oblate) axis. The spheroidal coordinate system is one of the 14 curvilinear orthogonal systems in which the Laplacian operator is separable and thus the Helmholtz equation can be analytically solved [14]. Using the quasi-static approximation we derive the resonance condition for LSP. The quasi-static approximation is a great analytical tool for problems in which the solution domain is much smaller than the incident wavelength [14]. This assumption allows us to neglect the spatial field variations and essentially reduces the problem to an electrostatic problem which requires solving the Laplace's equation

$$\nabla^2\varphi = 0 \tag{1}$$

where φ is the electrostatic potential. Solving Eq. (1), allows us to derive the LSP resonance condition for very small spheroids. As it will be shown the LSP resonance condition for spheroids is a function of the aspect ratio of the spheroid and thus can tuned. We also propose a formal method to tune the LSP resonance to a wavelength of interest. Our derivations are confirmed by full-wave simulations.

2- QUASI-STATIC ANALYSIS OF SPHEROIDS

2-1- LSP RESONANCE OF NANO-SPHERES

Consider a single sphere of radius R with the relative dielectric constant ϵ_p embedded in a dielectric medium with relative dielectric constant ϵ_M and illuminated by a mono-chromatic z-propagating x-polarized plane wave with angular frequency ω. The electric field has a magnitude of unity and is of the form

$$E = \hat{x}e^{ikz} \tag{2}$$

where $k = \frac{2\pi}{\lambda}$ is the wave number and λ is the wavelength in the dielectric medium and we have assumed $e^{-i\omega t}$ time-variation. Using Mie theory [13], the expansion coefficients for the scattered fields, a_n and b_n are [13].

$$a_n = \frac{\psi_n(\chi)\psi_n'(m\chi) - m\psi_n'(\chi)\psi_n(m\chi)}{\Psi_n(\chi)\psi_n'(m\chi) - m\Psi_n'(\chi)\psi_n(m\chi)} \tag{3}$$

$$b_n = \frac{m\psi_n(\chi)\psi_n'(m\chi) - \psi_n'(\chi)\psi_n(m\chi)}{m\Psi_n(\chi)\psi_n'(m\chi) - \Psi_n'(\chi)\psi_n(m\chi)} \tag{4}$$

where $m = \sqrt{\frac{\epsilon_p}{\epsilon_M}}$, $\chi = kR$ and $\psi_n(z) = zj_n(z)$ and $\Psi_n(z) = zh_n^{(1)}(z)$ are the Riccati-Bessel functions of order n. The denominators in Eq. (3) and Eq. (4) can become very small and in essence form complex numbered poles. At these poles due to the large value of the expansion coefficient the scattered fields exhibit a resonant behavior. Considering the denominators in Eq. (3) and Eq. (4), the resonances are

$$m\frac{\Psi_n'(\chi)}{\Psi_n(\chi)} = \frac{\psi_n'(m\chi)}{\psi_n(m\chi)} \tag{5}$$

$$\frac{1}{m}\frac{\Psi_n'(\chi)}{\Psi_n(\chi)} = \frac{\psi_n'(m\chi)}{\psi_n(m\chi)} \tag{6}$$

For very small particles where $R \ll \lambda$ we can approximate the Riccati-Bessel functions using their first order approximations. In this case Eq. (5) and Eq. (6) will simplify to

$$\epsilon_p = -\frac{n+1}{n}\epsilon_M \tag{7}$$

$$\epsilon_p = -2\epsilon_M \tag{8}$$

The resonances resulting from Eq. (8) will lead to a trivial solution and are of no interest since the scattering by small spheres is dominated by TM^r modes [18]. For very small scatterers the dipolar term corresponding to $n = 1$ dominates the scattering response. Placing $n = 1$ in Eq. (7) leads to the well-known resonant condition

$$\epsilon_p = -2\epsilon_M \tag{9}$$

The resonance condition in Eq. (9) can also be derived using quasi-static approximation.

As an example here we consider an Au nano-sphere in free-space. The relative dielectric function of Au across the visible and near-IR range can be accurately modeled using a modified Drude model [15]:

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \tag{10}$$

where $\epsilon_\infty = 9$, $\omega_p = 13.8 \times 10^{15}\ s^{-1}$, and $\Gamma = 0.11 \times 10^{15}\ s^{-1}$. Figure 1 shows the real and imaginary parts of the modified Drude model shown in Eq. (10) over the 400 nm to 800 nm range. The plot also shows that the resonant wavelength at which $\Re(\epsilon) = -2$ is roughly 450 nm.

Figure 2 shows the extinction efficiency of three Au nano-spheres with radii of 10 nm, 15 nm, and 20 nm. As it can be seen from the plot changing the radius of sphere does not alter the resonance region. Also the resonance of all three nano-sphere occur around 450 nm as predicted from Figure 1.

2-2- LSP RESONANCE OF NANO-SPHEROIDS

A prolate spheroid is obtained by rotating an ellipse around its major axis. Figure 3 shows a prolate spheroid. The equation for a prolate spheroid with its major axis along the x-axis is

$$\frac{x^2}{a^2} + \frac{y^2 + z^2}{b^2} = 1 \quad , \quad a > b > 0 \tag{11}$$

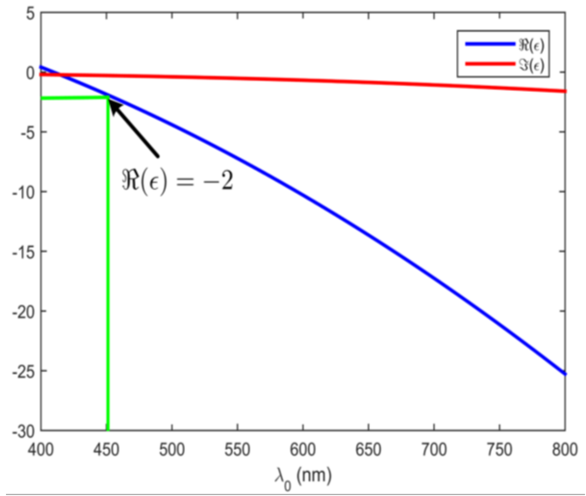

Fig. 1. Real and imaginary parts of the gold dielectric function according to Eq. (10). The green line shows the resonance condition for a nano-sphere in free-space which is $\Re(\epsilon) = -2$ is roughly 450 nm.

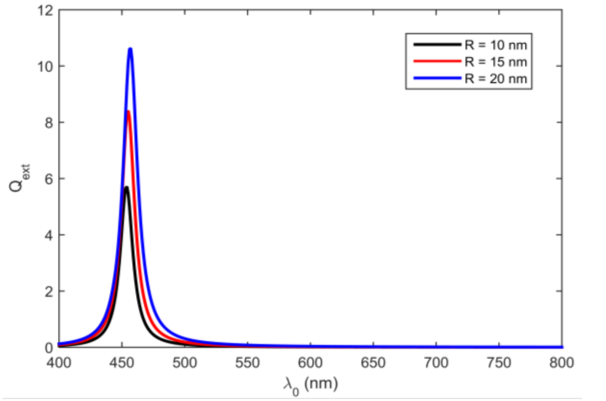

Fig. 2. Extinction efficiency of three Au nano-spheres with radii of 10 nm, 15 nm, and 20 nm. The resonance of all three nano-sphere occur around 450 nm as predicted from Fig. 1.

As it can be seen in the limiting case when $a \to b$, the spheroid becomes a sphere.

We consider the scattering response for very small prolate spheroid, incident by x-polarized plane wave such that the electric field is of the form

$$\mathbf{E}_{\text{inc}} = \mathbf{x}\, e^{i\mathbf{k}\cdot\mathbf{r}} \tag{12}$$

where $\mathbf{k}$ is wave vector and it lies in the yz-plane and $\mathbf{r}$ is the position vector. Assuming $\lambda \gg b$ the field variations along the ellipsoid are negligible and thus we can analyze it using the quasi-static approximation [14].

The quasi-static approximation requires us to solve the Laplace's equation for the spheroid which is a special case of an ellipsoid. The ellipsoidal coordinate system with coordinates (ξ, η, ζ) is one of the 14 curvilinear coordinate systems in which the Laplacian operator ∇^2 is separable and thus the Laplace's equation can be analytically solved [16].

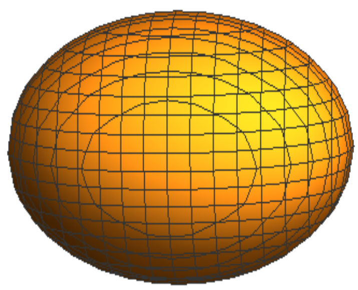

Fig. 3. A prolate spheroid obtained by rotating an ellipse around its major axis.

To solve the Laplace's equation, we consider a prolate spheroid with its major axis along the x-axis and relative permeability ϵ, surrounded by free-space. We also assume a constant electric field $\mathbf{E}$ directed along the x-axis. A complete derivation of the solution is provided in reference [16]. Here for the sake of brevity, we only state the results. Solving Eq. (1) for a prolate spheroid, leads to [16]

$$\varphi = \begin{cases} \varphi_0[1 + F(\xi)] & \text{outside spheroid} \\ c_2\varphi_0 & \text{inside spheroid} \end{cases} \quad (13)$$

where $\varphi_0 = -\mathbf{E}.\mathbf{r}$ is the potential of the unperturbed field and

$$F(\xi) = c_1 \int_\xi^\infty \frac{\mathrm{d}x}{(x+a^2)^{3/2}\,(x+b^2)} \quad (14)$$

Constants c_1 and c_2 are obtained by enforcing boundary conditions at the surface of the spheroid, which leads to

$$c_1 = -\frac{ab^2\,(\epsilon - 1)}{2\,[1 + L_a\,(\epsilon - 1)]} \quad (15)$$

$$c_2 = \frac{1}{1 + L_a\,(\epsilon - 1)} \quad (16)$$

where L_a is the *shape factor* defined as [16]

$$L_a = \frac{ab^2}{2}\int_0^\infty \frac{\mathrm{d}x}{(x+a^2)^{3/2}\,(x+b^2)} \quad (17)$$

Considering the expression for c_1 in Eq. (16), we conclude that a resonant be behavior occurs when

$$\epsilon = 1 - \frac{1}{L_a} \quad (18)$$

As $\epsilon \to 1 - \frac{1}{L_a}$, the potential outside the spheroid approaches infinity.

Now defining an aspect ratio α for the spheroid as $= \frac{a}{b}$, $\alpha > 1$, the expression for L_a is reduced to

$$L_a = \frac{a^3}{2\alpha^2}\int_0^\infty \frac{\mathrm{d}x}{(x+a^2)^{3/2}\left(x + \frac{a^2}{\alpha^2}\right)} \quad (19)$$

Here, without loss of generality, we set $a \equiv 1$ and express L_a as a function of α

$$L_\alpha = \frac{1}{2\alpha^2}\int_0^\infty \frac{\mathrm{d}x}{(x+1)^{3/2}\left(x + \frac{1}{\alpha^2}\right)} \quad (20)$$

Evaluating the integral in Eq. (20), we arrive at

$$L_\alpha = \frac{2\alpha\sin^{-1}(\alpha) - \pi\alpha + 2\sqrt{1-\alpha^2}}{2\,(1-\alpha^2)^{3/2}} \quad (21)$$

Since $\alpha > 1$, initially L_α seems complex, however upon closer inspection and after some manipulations we arrive at

$$L_\alpha = \frac{\sqrt{\alpha^2-1} - \alpha\ln\left(\alpha + \sqrt{\alpha^2-1}\right)}{\sqrt{\alpha^2-1}\,(1-\alpha^2)} \quad (22)$$

Using Eq. (18) and Eq. (22), we can now calculate the resonant condition as a function of the aspect ratio of the spheroid. Figure 4 shows the calculated resonant dielectric value of the nano-spheroid as a function of the aspect ratio of the particle. What is also notable about this plot is that at $\alpha = 1$ where the spheroid becomes a sphere we get the familiar resonance condition of $\epsilon = -2$. One point that is worth mentioning is that for both spheres and spheroids, we disregard the imaginary part of the dielectric constant.

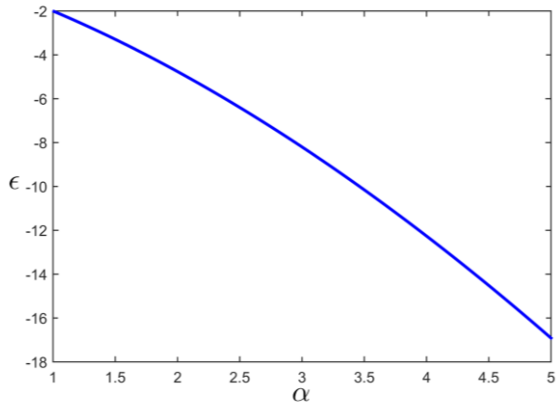

Fig. 4. Resonant dielectric value of the nano-spheroid as a function of the aspect ratio α of the particle.

3- TUNING THE LSP RESONANCE OF NANO-SPHEROIDS

Having shown that the LSP resonance of nano-spheroid is a function of its aspect ratio, the next step is to present a formal method to tune the LSP resonance to a given wavelength. We use the modified Drude model from Eq. (10) for the dielectric function of the metal. Separating the real and imaginary parts in Eq. (10) leads to

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i\frac{\omega_p^2\Gamma}{\omega\,(\omega^2+\Gamma^2)} \quad (23)$$

To satisfy the resonant condition Eq. (18), at a given wavelength λ_0 must have

$$1 - \frac{1}{L_\alpha} = \epsilon_\infty - \frac{\omega_p^2}{\omega^2+\Gamma^2} \quad (24)$$

where $\lambda_0 = \frac{2\pi c}{\omega}$. Substituting L_α from Eq. (22), we arrive at

$$\frac{\left(\alpha^2-1\right)^{3/2}}{\sqrt{\alpha^2-1} - \alpha\ln\left(\alpha+\sqrt{\alpha^2-1}\right)} - \epsilon_\infty + 1 + \frac{\omega_p^2}{\omega^2+\Gamma^2} = 0 \quad (25)$$

which must be solved numerically for α.

4- RESULTS

We consider designing Au nano-spheroids with LSP resonances at 500 nm and 550 nm and use the modified Drude model from Eq. (10) to model the dielectric function of Au. The corresponding aspect ratios which are obtained by numerically solving Eq. (25) are:

$$\alpha_{500nm} = 1.885 \quad , \quad \alpha_{550nm} = 2.733$$

To verify our results, we evaluate the extinction efficiency of two Au nano-spheroids. The extinction efficiency of a particle is its extinction cross section normalized by its geometric cross section. The simulations are performed using the full-wave commercial package CST MICROWAVE STUDIO [17]. For the first nano-spheroid with $\alpha_{500nm} = 1.885$, we set $a = 18.85\ nm$ and $b = 10\ nm$. The extinction efficiency of this nano-spheroid is shown in Figure 5. For the second nano-spheroid with $\alpha_{550nm} = 2.733$, we set $a = 27.33\ nm$ and $b = 10\ nm$. The extinction efficiency of this nano-spheroid is shown in Figure 6. As it can be seen in both cases the LSP resonances occur at the predicted wavelength.

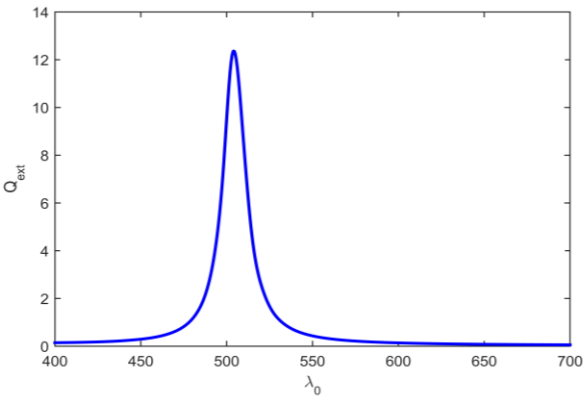

Fig. 5. Extinction efficiency of a prolate Au nano-spheroid with aspect ratio 1.885 designed to resonate at $\lambda_0 = 500\ nm$.

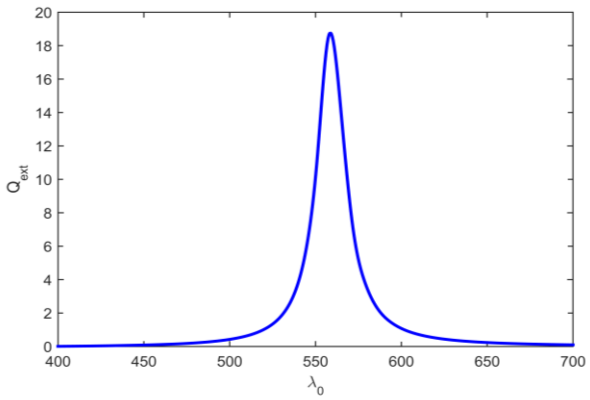

Fig. 6. Extinction efficiency of a prolate Au nano-spheroid with aspect ratio 2.733 designed to resonate at $\lambda_0 = 550\ nm$.

5- CONCLUSION

We analyzed the LSP resonance of plasmonic metallic spheroidal nanoparticles. Using quasi-static analysis we were able to derive analytical expressions for the resonance condition of these particles. Our derivations showed that unlike plasmonic nano-spheres in which the resonance condition is independent of particle dimensions, the resonance condition in spheroids is a function of the aspect ratio of the nanoparticle which allows for tuning the resonance. We also presented a formal method to tune the resonance of metallic nano-spheroids with modified Drude dielectric function. Finally to validate our results we presented a couple of examples and verified our theoretical predictions with full-wave numerical simulations.

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