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Abstract. We present a new analytical study of metallic nanoparticles, working in the infrared and visible frequency range. The structure consists of triaxial ellipsoidal resonating inclusions embedded in a dielectric environment. Our aim is to develop a new analytical model for the ellipsoidal nanoparticles to describe their resonant behaviors and design structures that satisfy specific electromagnetic requirements. The obtained models are compared to the numerical values, performed by full-wave simulations, as well as to the experimental ones reported in literature. A good agreement among these results was obtained. The proposed formula is a useful tool to design such structures for sensing applications. [DOI: 10.1117/1.OE.52.5.051205]

Subject terms: ellipsoidal nanoparticles; analytical models; localized surface plasmon resonance; biomedical applications.

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1 Introduction

In the last few years, many studies have been done on the electromagnetic properties of nanostructures, particularly on the interesting applications available from their use. The extraordinary optical properties of such structures derive from the strong local electromagnetic field enhancement: the so-called localized surface plasmon resonance (LSPR). Typically, the LSPR phenomenon can be described as the resonant collective oscillation of electrons, stimulated by an incident electromagnetic wave. The resonance condition is set up when the electromagnetic wave frequency matches the natural frequency of the oscillating electrons. In addition to the LSPR, a high localization of the electromagnetic field in the neighborhood of the nanostructure is obtained. As a result, the interaction between the electromagnetic field and the surrounding dielectric environment is restricted to a small area.[1] For this reason, these structures are very sensitive to any change in the local index of refraction, which causes the resonance conditions of the surface plasmon waves to modify. Such characteristics allow these structures to be suitable for several application fields, such as optical[2] and photonic ones,[3] biochemical sensing and detection,[4,5] protein analysis,[6,7] cell membrane function,[8] biomedical applications,[9,10] and food quality analysis.[11] They can also be used as contrast agents in cellular and biological imaging.[12,13] The nanoparticle effectiveness as a sensing or therapeutic tool depends on its optical properties: for instance, a high scattering cross-section is crucial for light-scattering microscopy-based imaging or sensing applications.[14] On the other hand, photothermal therapy requires a high nanoparticle absorption cross-section with low scattering losses for superficial and deep tumor treatment.[15]

The existing literature has mainly focused on the experimental evaluation of the nanoparticle electromagnetic characteristics, but it is almost silent on the development of proper analytical models and design methods describing their resonant behavior. It is known that the analytical closed-form electromagnetic solution exists only for a restricted number of particle geometries, such as sphere and cylinder,[16] cube,[17] disc and needle.[18] For any other arbitrary shapes, the electromagnetic solution is given by numerical approaches.[19]

To describe the electromagnetic behavior of the nanoparticles, it is useful to study the electromagnetic extinction cross-section properties in terms of scattering and absorption.

Separate evaluation of the absorption and scattering phenomenon is crucial to understand why certain structures are preferred to others for specific applications.

In order to describe the nanoparticle electromagnetic behavior using closed-form formulas, it is fundamental to correlate the electromagnetic properties, in terms of extinction cross-section, with the structural and geometrical parameters.

The aim of this article is to find out the analytical relation between the nanoparticle electromagnetic properties and its geometrical parameters. In particular, this research attempts to present a new design method for ellipsoidal nanoparticles with the desired electromagnetic properties, in order to satisfy specific requirements. In the fabrication of nanorod particles, we have chosen the ellipsoidal geometry, as it represents a good approximation for the realistically obtained shapes.

This article is structured as follows:

1. The electromagnetic properties of triaxial ellipsoidal nanoparticles, in terms of extinction cross-section (absorption and scattering), are evaluated. For this purpose, a new analytical closed-form formula is proposed, linking the geometrical parameters and the electromagnetic properties of the nanoparticle with its resonant frequency properties: position, magnitude, and bandwidth.
2. The analytical models are compared to the results obtained by full-wave simulations and to the experimental values existing in the literature.
3. Exploiting the proposed analytical model and the design methods, the sensitivity properties of the

nanoparticle were calculated and compared to the experimental values.

2 Analytical Models and Electromagnetic Properties of Ellipsoidal Nanoparticles

The structure under study consists of a metallic resonating inclusion embedded in a dielectric environment. Such a nanoparticle has a specific resonant wavelength in terms of magnitude, amplitude width, and position, depending on its geometrical characteristics (such as shape and dimensions) and on the metal optical properties. An electromagnetic source excites the nanostructure, and its electromagnetic properties are revealed in terms of absorption and scattering cross-section. To be more precise, when an impinging electromagnetic wave with an appropriate incident wavelength illuminates a metallic nanoparticle, free electrons of metal structure start oscillating collectively. Such oscillations lead to the propagation of strong surface waves.[20,21] The resonant optical properties of nanoparticles can be studied, starting with their polarizability expressions. It is well known[22] that the polarizability of an arbitrary shaped particle can be expressed as

$$\alpha = V\varepsilon_e \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_e + L(\varepsilon_i - \varepsilon_e)}, \tag{1}$$

where V is the particle volume, ε_e is the surrounding dielectric environment permittivity, ε_i is the inclusion dielectric permittivity, and L is the depolarization factor. The polarizability value strongly depends on the nanoparticle geometry, particularly on its size, shape, inclusion composition, and the surrounding dielectric environment refractive index. Assuming that the inclusion permittivity can be written as $\varepsilon_i = \varepsilon_{\text{real}} + j\varepsilon_{\text{imm}}$, the dipolar polarizability α is maximized (in other words, the nanoparticle is at its resonance condition) when

$$\begin{cases} \text{Re}[\varepsilon_e + L(\varepsilon_i - \varepsilon_e)] = 0 \\ \text{Im}[\varepsilon_e + L(\varepsilon_i - \varepsilon_e)] = 0 \end{cases}. \tag{2}$$

Therefore, the L factor of a nanoparticle plays a crucial role in the polarizability's resonant behavior for the enhancement of LSPR strength. In order to study the nanoparticle electromagnetic properties in terms of scattering and absorption cross-section, the following assumptions must be made:

- The particle size is much smaller than the operative wavelength in the surrounding medium.[22] In the limit of "electrically" small particles, the electromagnetic field is approximately constant over the particle volume. Therefore, the resonant behavior of the individual structure can be studied in terms of quasi-static approximation.
- The considered particle is homogeneous, and the surrounding material is a homogeneous, isotropic, and non absorbing medium.

Under such conditions, we can relate the nanoparticle macroscopic electromagnetic behavior to its polarizability. In this study, the structure is excited by an electromagnetic plane wave with the electric field parallel (and the propagation vector **k** perpendicular) to the nanoparticle principal axis, as depicted in Fig. 1, where the single particle is shown. In particular, in this study, the nanoparticles are triaxial ellipsoids with $a > b > c$, where a, b, and c are the semi-major axes aligned along the coordinate axes (x, y, z) (Fig. 1).

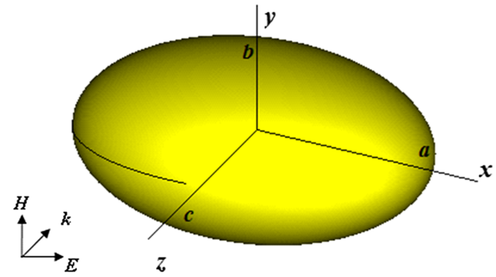


Fig. 1 Triaxial ellipsoidal nanoparticles geometry.

In this paper, the following is true:

- For metallic nanoparticles, experimental values[23] of the complex permittivity function have been inserted.
- The surrounding dielectric medium is considered to be water, with a complex refractive index $n = 1.33 + j0$ at all the considered wavelengths: $300 - 1000$ nm.

2.1 *Analytical Models of Ellipsoidal Nanoparticles*

In this section, the analytical models of ellipsoidal nanoparticles that link the electromagnetic nanoparticle properties to their geometrical and structural parameters are presented in order to describe their resonant behavior. Starting from the findings of Ref. 24, it is possible to develop new analytical closed-form formulas for the scattering (C_{sca}) and absorption (C_{abs}) cross-section of the aforementioned particles. The general corresponding expressions read, respectively,

$$C_{\text{abs}} = k\text{Im}[\alpha] \tag{3}$$

$$C_{\text{sca}} = \frac{k^4}{6\pi}|\alpha|^2, \tag{4}$$

where $k = 2\pi n/\lambda$ is the wavenumber, λ is the wavelength, and $n = \sqrt{\varepsilon_e}$ is the refractive index of the surrounding dielectric environment. For oblate and prolate ellipsoids, several closed-form formulas for the depolarization factor can be found, while for triaxial ellipsoids, a closed formula for the depolarization factor does not exist. Typically, such factors can be written in terms of tabulated functions.[25] In this study, a new closed-form analytical formula for the triaxial case is obtained. Considering the electric field polarization of the impinging plane wave and the particle geometry, the absorption and scattering cross-section formulas follow:

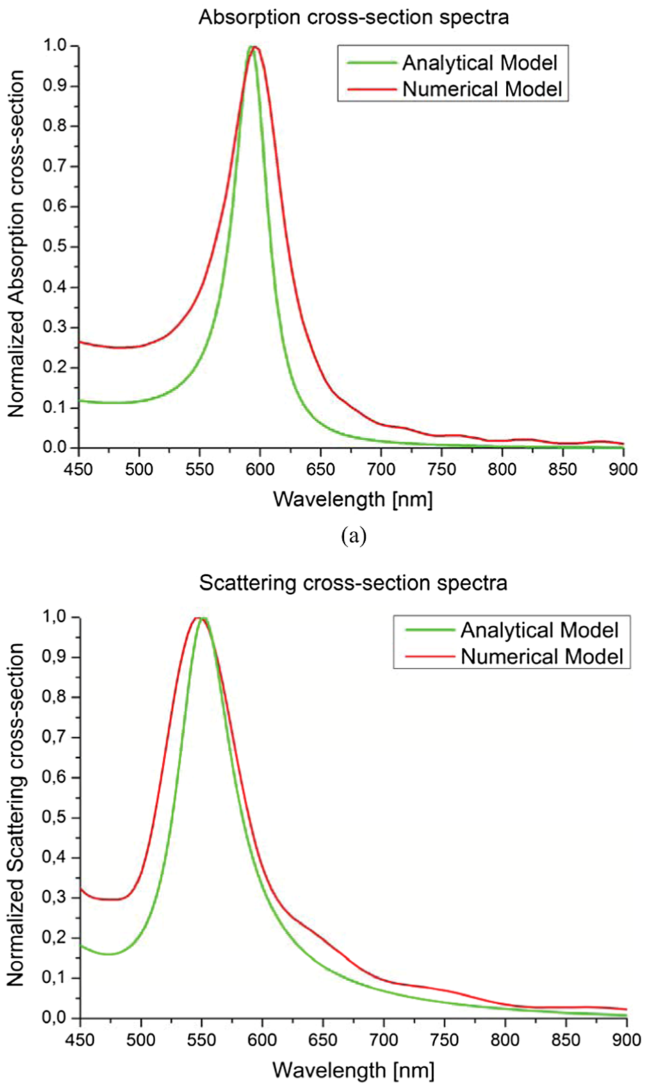
$$C_{\text{abs}} = \frac{2\pi}{\lambda}\sqrt{\varepsilon_e}\text{Im}\left[\frac{\left(\frac{4\pi}{3}abc\right)(\varepsilon_i - \varepsilon_e)}{[L_{\text{tri-axial}}(\varepsilon_i - \varepsilon_e) + \varepsilon_e]}\right] \tag{5}$$

$$C_{\text{sca}} = \frac{\left(\frac{2\pi}{\lambda}\sqrt{\varepsilon_e}\right)^4}{6\pi}\text{Abs}\left[\frac{\left(\frac{4\pi}{3}abc\right)(\varepsilon_i - \varepsilon_e)}{[L_{\text{tri-axial}}(\varepsilon_i - \varepsilon_e) + \varepsilon_e]}\right]^2, \tag{6}$$

where $L_{\text{tri-axial}}$ for triaxial ellipsoids ($a > b > c$) reads

$$L_{\text{tri-axial}} = \frac{7}{2\pi}\left(1 - \frac{\pi}{\sqrt{\frac{4b^2E(e^2)^2}{a^2} + \pi^2}}\right),$$
$$e = \sqrt{1 - \left(\frac{c}{b}\right)^2}, \tag{7}$$

where E is the complete elliptic integral of the second kind. It is worth noting that if the triaxial ellipsoid degenerates into a prolate/oblate ellipsoid or sphere, the depolarization factor coincides with the classical formulas existing in the literature (e.g., Ref. 25). In Fig. 2, a comparison among analytical and numerical models for absorption and scattering cross-section spectra of gold triaxial ellipsoids is presented.



(a)

(b)

Fig. 2 Analytical-numerical model comparison for $a = 40$ nm, $b = 30$ nm, $c = 20$ nm of absorption cross-section spectra (a) and scattering cross-section spectra (b).

2.2 *Comparison Among Analytical, Numerical, and Experimental Results*

Using the proposed analytical model, it is possible to describe the nanoparticle resonant behavior in order to predict its electromagnetic properties. In this subsection, the analytical results are compared to the numerical ones, performed by the finite-integration commercial code CST Studio Suite (CST, Framingham, MA), and to the experimental values of silver ellipsoids[26] and gold nanorods,[27] for several geometrical parameter values, as shown in Table 1. The surrounding dielectric medium is considered to be water with a complex refractive index $n = 1.33 + j0$ at all wavelengths. In order to verify the quality of the proposed models, the relative errors were calculated, and they are listed in Table 1, where it is clear that a good agreement among all three results was achieved.

2.3 *Electromagnetic Properties Analysis and Sensitivity Properties*

Starting from the proposed polarizability analytical model, it is possible to predict how the geometrical parameters, the metal electromagnetic properties, and the surrounding dielectric environment permittivity affect the nanoparticle resonant behavior in terms of position, magnitude, and bandwidth. The inclusion permittivity can be expressed as $\varepsilon_i = \varepsilon_{\text{real}} + j\varepsilon_{\text{imm}}$.

As the resonant behavior of the nanoparticle is reached when the denominator goes to zero in both its real and imaginary part [see Eq. (2)] and starting from the general polarizability expression,[28] the resonant condition reads:

$$L^2\left[\varepsilon_{\text{real}} - \left(\frac{(L-1)\varepsilon_e}{L} - \varepsilon_{\text{imm}}\right)\right] \times \left[\varepsilon_{\text{real}} - \left(\frac{(L-1)\varepsilon_e}{L} + \varepsilon_{imm}\right)\right] = 0. \tag{8}$$

By solving Eq. (8) with respect to $\varepsilon_{\text{real}}$ and by inserting the proposed depolarization factor [Eq. (7)], we can find the corresponding solution for the inclusion permittivity for which the polarizability of the overall structure rises to infinity (which is related to the nanoparticle resonant behavior):

$$\varepsilon_{real} = -\frac{\varepsilon_e\left[\pi^2a^2\left(\sqrt{\frac{4b^2E(e^2)^2}{a^2} + \pi^2} + \pi\right) + 2(2\pi - 7)b^2E(e^2)^2\right]}{14b^2E(e^2)^2} - \varepsilon_{\text{imm}}. \tag{9}$$

Exploiting Eq. (9), it is possible to tune the nanostructure resonance by changing its geometrical parameters in order to coincide with the spectral absorption characteristics of the sample under study. Such a condition is necessary for specific absorption measurements.

In addition, in this section, we analyze the designed nanoparticle sensitivity properties to optimize the single inclusion for sensing applications. The sensitivity is commonly defined as

$$S = \frac{\Delta\lambda}{\Delta n}, \tag{10}$$

Table 1 Comparison of resonant wavelengths for triaxial ellipsoid: analytical, numerical, and experimental values (silver ellipsoids:[26] $b = 55$ nm, $c = 50$ nm; gold nanorods:[27] w is the nanorod thickness and l is the nanorod length).

Nanoparticle geometry	Size (nm)	Resonant wavelength [λ (nm)]			Analytical-numerical error (%) $\lambda_{analytical} - \lambda_{numerical}/\lambda_{numerical}$	Analytical-experimental error (%) $\lambda_{analytical} - \lambda_{experimental}/\lambda_{experimental}$
		Analytical values	Numerical values	Experimental values[26,27]		
Silver ellipsoids[26]	$a = 120$	625	634	640	1.42	2.34
	$a = 130$	660	674	650	2.10	1.54
	$a = 150$	740	760	740	2.63	0
	$a = 180$	870	880	850	4.66	3.53
Gold nanorods[27]	$l = 40$ $w = 17$	645	637	653	1.3	1.2
	$l = 55$ $w = 16$	710	744	728	4.6	2.5
	$l = 74$ $w = 17$	840	838	846	0.3	0.7

Table 2 Comparison of the sensitivity values for the inclusions considered.

Metal nanoparticle	Sensitivity (nm/RIU)		
	Analytical sensitivity	Numerical sensitivity	Experimental sensitivity[29]
Silver[29]	450	400	425
$a = 62.5$ nm			
$b = c = 12.5$ nm			

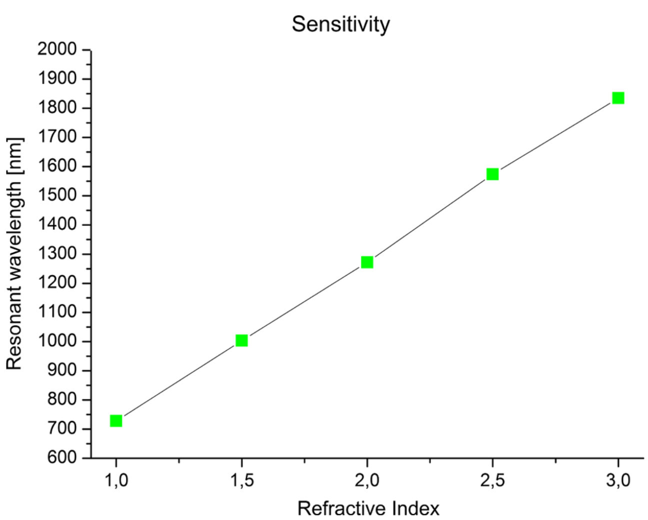


Fig. 3 Variation of the resonant wavelength as a function of the refractive index of the surrounding medium for the nanoparticle dimensions reported in Table 2.

expressed in nm/RIU (RIU = refractive index unit), where $\Delta\lambda$ is the wavelength shift and Δn is the refractive index variation. In Table 2, we report the sensitivity values for the inclusions considered in this paper. In particular, analytical, numerical, and experimental values[29] of sensitivity are compared.

A test material surrounding the nanoparticle with a varying refractive index n in the range of 1 to 3 was used. As shown in Fig. 3, the sensitivity is sufficiently constant over the range considered, as confirmed by analytical results. A good agreement among analytical, numerical, and experimental sensitivity values was obtained.

3 Conclusions

In this paper, a study on metallic nanoparticles electromagnetic modeling in the infrared and optical frequency regime was presented. The considered structures were triaxial ellipsoidal nanoparticles, embedded in a surrounding dielectric environment. In this regard, the electromagnetic properties of such structures, in terms of extinction cross-section (absorption and scattering), were evaluated by the use of a new analytical model.

Then the proposed model was compared to the results obtained by full-wave simulations and to the experimental values. A good agreement among analytical, numerical, and experimental results was achieved.

The ability to manipulate and control the electromagnetic phenomenon by exploiting the proposed analytical model on the nanometer scale opens up the possibility of using such structures for sensing applications.

For this reason, the nanoparticle sensitivity was studied. Sensitivity values obtained from the proposed analytical model were verified by full-wave simulations and compared to the experimental results, showing good agreement.

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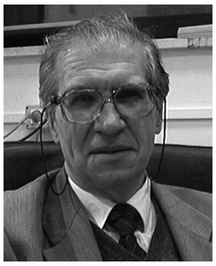

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