Modeling of absorption and scattering properties of core-shell nanoparticles for application as nanoantenna in optical domain

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Abstract. The present paper describes the study of core-shell nanoparticles for application as nanoantenna in the optical domain. To obtain the absorption and extinction efficiencies as well as the angular distribution of the far field radiation pattern and the resonance wavelengths for these metal-dielectric, dielectric-metal and metal-metal core-shell nanoparticles in optical domain, we have used Finite Element Method based COMSOL Multiphysics Software and Mie Theory. From the comparative study of the extinction efficiencies of core-shell nanoparticles of different materials, it is found that for silica-gold core-shell nanoparticles, the resonant wavelength is greater than that of the gold-silver, silver-gold and gold-silica core-shell nanoparticles and also the radiation pattern of the silica-gold core-shell nanoparticle is the most suitable one from the point of view of directivity. The dielectric functions of the core and shell material as well as of the embedded matrix are extremely important and plays a very major role to tune the directivity and resonance wavelength. Such highly controllable parameters of the dielectric-metal core-shell nanoparticles make them suitable for efficient coupling of optical radiation into nanoscale structures for a broad range of applications in the field of communications.

1. Introduction
The concept of nanoantennas at optical frequency has recently opened up new fields of experimental and theoretical research in nanotechnology and antenna science. The growing interest in optical nanoantennas can be attributed to the ability of metal nanoparticles to support plasmon resonances. The strongly enhanced surface plasmon resonance of noble metal nanoparticles at optical frequencies makes them excellent absorbers as well as scatterers. It is well known that the plasmon resonance wavelength of metal nanoparticles is sensitive to the nanoparticle’s size, shape and the surrounding medium. The possibility of tuning the localized surface plasmon resonance wavelength, through the visible to near infrared region, makes metal nanoparticles very important and promising for the potential applications in the field of communication, quantum optics, information processing and in several linear and nonlinear optical processes. In addition to pure metal nanoparticles, in recent years, core-shell nanoparticles, in which nanoparticles of one material(dielectric/metal) are coated with a thin layer of another material(metal/dielectric), have received particular attention due to their many unique properties[1]. Oldenburg et al [2], from Mie scattering theory, obtained that for silica-gold core-shell nanoparticles of core radius (60±6)nm and shell thickness (11±4)nm, dipole plasmon resonance occurs at 830nm, whereas for core radius (135±6 nm) and shell thickness (15±4)nm, the dipole
resonance peak shifts to 1350nm. Dipole resonance peak having the highest scattering intensity out of all the other modes (quadrupole, octopole etc) is of great significance from the application point of view.

In the present study, metal-dielectric, dielectric-metal and metal-metal core-shell nanoparticles (eg. gold-silica, silica-gold, gold-silver, silver–gold) are modelled and simulation is done using COMSOL Multiphysics software to obtain the absorption and extinction efficiencies and the resonance wavelengths in the optical domain. The far field radiation patterns for the nanoantennas modeled by core-shell nanoparticles of different core to shell size ratios have also been studied using Mie theory [2]. Keeping in view the significance of dipole resonance and availability of characterization facilities in our lab for extending the present work to application domain, core size - shell thickness variation, for simulation, is limited within the range (66-30) nm - (5-41) nm.

2. Modeling and Simulation

2.1 Theoretical Background: The physical understanding of light scattering by small particles begins with the electric dipole concept. The polarization (i.e. the induced dipole) of materials exposed to electromagnetic fields is determined by dielectric function.

2.1.1 The dielectric function for metal particles are decomposed into two parts [3, 4]. One component is the Drude free electron term and the other part is the substantial contribution of the inter band electrons. The complex permittivity of bulk metal particles can be estimated by Lorentz-Drude model and is expressed as:

\[ \varepsilon_{\text{bulk}} = 1 - \frac{\omega_{pb}^2}{\omega^2 + i\omega\gamma_b} + \frac{\omega_p^2}{\omega_b^2 - \omega^2 - i\omega\gamma_b} \]  \hspace{1cm} (1)

where \( \omega_{pb} \) is bound electron plasma frequency, \( \omega_b \) is bound electron resonant frequency, \( \frac{1}{\gamma_b} = T_b \) is bound electron decay time, \( \omega \) is the angular frequency of the incident radiation and \( \frac{1}{\gamma_0} = T_0 \) is the free electron scattering time.

For metal nanoparticles of size smaller than the mean free path, the decay time (\( \gamma_f \)) has been proved to be size dependent. The size dependency can be realized by the relation

\[ \gamma_f = \frac{1}{\gamma_0} + \frac{2\nu_f}{d} \]  \hspace{1cm} (2)

\( \nu_f \) is the Fermi velocity and \( d \) is the diameter of the particle. Thus equation (1) can be modified to

\[ \varepsilon_{d,\omega} = 1 - \frac{\omega_{pf}^2}{\omega^2 + i\omega\gamma_f} + \frac{\omega_p^2}{\omega_b^2 - \omega^2 - i\omega\gamma_b} \]  \hspace{1cm} (3)

This modified mathematical expression for decay time can be used to calculate the complex dielectric function of metal nanoparticles of different sizes at different frequencies.

For estimation of complex effective dielectric function of core-shell nanoparticles, the Effective Medium Approximation models are generally used. Effective Medium Theories are physical models based on constitutive properties of individual components and their volume fractions in the composite. There are many Effective Medium Theories and each theory is more or less accurate under different conditions. In most of the works at the nanoscale till date, Maxwell-Garnett model, Bruggeman model and Loyenga model [5] below the percolation threshold are used. But in all these models, the coating of shell materials on the core materials are not taken into account and the core-shell nanoparticles embedded in a host matrix are considered as two component systems considering the dielectric function of core material only. In our study, we have used Hashin-Shtrikman model [5] to calculate the complex dielectric function of core-shell nanoparticle first and then the core-shell nanoparticles & the host matrix are considered as two component system thus making the system more realistic. In the
present work, Drude-Lorentz model is used for calculation of optical properties of metal nanoparticles first, and then the Hashin-Shtrikman bound for core-shell nanoparticles are applied, and based on the literature available on basic formulation of Rayleigh model [6], the Rayleigh model is finally used to calculate the effective complex dielectric function of the core-shell nanoparticle based nanocomposites.

2.1.2 The cross-sections for scattering ($C_{sc}$) and absorption ($C_{ab}$) are obtained from the scattering field radiated by this dipole, which is induced by the incident plane wave. The resulting expressions are

$$C_{sc} = \sigma_{geom} Q_{sc} , \quad Q_{sc} = \frac{8}{3} q^4 \left( \frac{\varepsilon_d - 1}{\varepsilon_d + 2} \right)^2 , \quad C_{abs} = \sigma_{geom} Q_{abs} \text{ and } Q_{abs} = 4qIm \left( \frac{\varepsilon_d - 1}{\varepsilon_d + 2} \right)$$

(4)

Where $\sigma_{geom} = \pi a^2$ is the geometrical crosssection, $a$ is the radius of the nanoparticle, $q = ka$ is the dimensionless size and $\varepsilon_d$ is the relative dielectric function. The extinction cross section is $C_{ext} = C_{sc} + C_{abs}$

(5)

2.2 Method: Modelling and simulation of the optical properties of core-shell nanoparticles are of great importance to achieve insight of the surface Plasmon phenomena. In this study, an analytical model based on an approximate Mie theory has been designed using Finite Element Method based COMSOL Multiphysics software. The simulation domain comprises of a core-shell nanoparticle with an air domain truncated by a perfectly matched layer (PML). The Maxwell’s equations for the scattering of electromagnetic radiation by spherical particles have been solved with the model. The model geometry is shown in figure1. In this model, the wavelength dependent optical properties such as scattering cross section and extinction cross section have been simulated. The far field calculations are done on the inner boundary of the PML. The model is nonuniformly meshed ensuring approximately 10 mesh points between the core-shell nanoparticles, the scattering and far field domain.

![Figure 1: Model Geometry](image)

The symmetry of the system is maintained by simulating half of the system. The simulation calculates the local electromagnetic field at every mesh point with an incident plane wave propagating in x direction with the electric field polarized along the z-axis. This imposes the following boundary conditions on the symmetry planes:

Symmetry in electric field:

$$nxH \big|_{y=0} = 0 \quad (PMC)$$

(6)

Symmetry in magnetic field:

$$nxE \big|_{z=0} = 0 \quad (PEC)$$

(7)

For the scattered field formulation, the background incident plane wave is defined as:

$$E_{inc} = \{0,0,E_0e^{-jkh_0x} \}$$

(8)

where $E_0$ is the plane wave amplitude, $k_0 = \frac{\omega}{c}$ is the wave vector in the air, $\omega$ is the circular frequency and $c$ is speed of light in air.
If a plane wave is incident on an object, then the wave amplitude from the scattering object, at a large distance, is given by:

$$\psi(r) \approx e^{i k x} + f(\theta) \frac{e^{i k r}}{r}$$

(9)

where $f(\theta)$ is the scattering amplitude which is a function of scattering angle $\theta$. COMSOL Multiphysics includes a built–in far-field computation node that calculates the far-field variables defined as:

$$E_{far} = \lim_{r \to \infty} r E_{sca}$$

(10)

where $E_{sca}$ represents the scattered electromagnetic wave.

3. Results and Discussions

We have modelled gold-silica, silica-gold, silver–gold, gold-silver core-shell nanoparticles with different core to shell size ratio as well as gold nanoparticles of varying size. The surrounding medium is considered as water. The resonance wavelength of the simulated extinction spectrum for single gold nanoparticle and for various core-shell materials are listed in table 1(a) to 1(e). Table 1(a) shows that for gold nanoparticles in water, resonance wavelength decreases with decreasing particle size. This theoretical finding is supported by experimental observations [7].

**Table 1:** Resonance Wavelength for different sizes (a) Gold (b) Silica Core - Gold Shell (c) Gold Core – Silica Shell (d) Silver Core – Gold Shell (e) Gold Core – Silver Shell nanoparticles.

| Table 1(a): Gold Nanoparticle | Table 1(b): Silica Core – Gold Shell |
|-------------------------------|--------------------------------------|
| Core Size (nm) | Resonance Wavelength (nm) | Core Size (nm) | Shell size (nm) | Resonance Wavelength (nm) |
| 66 | 556 | 66 | 5 | 980 |
| 60 | 552 | 60 | 11 | 720 |
| 50 | 537 | 50 | 21 | 550 |
| 30 | 520 | 30 | 41 | 650 |

| Table 1(c): Gold Core - Silica Shell | Table 1(d): Silver Core – Gold Shell |
|-------------------------------------|--------------------------------------|
| Core Size (nm) | Shell Size (nm) | Resonance Wavelength (nm) | Core Size (nm) | Shell Size (nm) | Resonance Wavelength (nm) |
| 66 | 5 | 680 | 66 | 5 | 600 |
| 60 | 11 | 500 | 60 | 11 | 650 |
| 50 | 21 | 720 | 50 | 21 | 620 |
| 30 | 41 | 200 | 30 | 41 | 700 |

| Table 1(e): Gold Core – Silver Shell |
|-------------------------------------|
| Core Size (nm) | Shell Size (nm) | Resonance Wavelength (nm) |
| 66 | 5 | 780 |
| 60 | 11 | 620 |
| 50 | 21 | 610 |
| 30 | 41 | 580 |
Table 1(a)-(e) reveal that for gold nanoparticles, variation in resonance wavelength is 36 nm for size variation of 36 nm, whereas, for core-shell nanoparticles, shell thickness variation of only 6 nm, keeping total size fixed at 71 nm, causes resonance wavelength variation of (50-260) nm. Thus, for core–shell nanoparticles, resonance wavelength is found to be very sensitive to shell thickness [8]. Moreover, it is found that out of all the core-shell configurations of Table 1, silica - gold core -shell nanoparticles of core size-shell thickness 66nm-5nm & 60nm-11nm show more shift in resonance wavelength with respect to corresponding gold nanoparticle. For silica-gold nanoparticles of core size 66nm-shell thickness 5 nm, resonance wavelength is found to be the highest (980nm), which falls in NIR region. For silica-gold core-shell nanoparticles, varying core size, keeping shell thickness fixed, it is found that for each case, highest resonance wavelength occurs for core size at ~ 66nm. Keeping core size fixed at 66nm and varying shell thickness, highest resonance wavelength is found to be at shell size ~ 5nm (not shown in tabular form). It is worth- mentioning that materials with resonance wavelength in the IR & NIR region are of great technological importance for a wide range of applications that include optical communications, medical imaging, treating tumours ,sensing, microscopy, spectroscopy, remote monitoring of industrial equipment etc.[9,10].

The normalized extinction efficiency for 66nm-5nm core-shell nanoparticles of table 1 is shown in figure 2. For gold–silver core-shell nanoparticle, extinction efficiency is slightly higher than that of silica-gold core-shell nanoparticle but the resonance wavelength is much lower.

Figure 2: The extinction efficiency vs. wavelength plot for different combinations of core-shell materials embedded in water when the size of the core is 66nm and shell thickness is of 5 nm.

Thus, getting some encouraging results with 66 nm-5 nm silica-gold core-shell nanoparticles, we have simulated the extinction spectrum for silica core - gold shell nanoparticles with varying core to shell size ratio, keeping total size fixed at 71 nm, some of which are shown in figure 3. Result of figure 3 is an added support to the usefulness of 66 nm – 5 nm silica-gold core-shell nanoparticles, from application point of view.

Figure 3: The extinction efficiency vs. wavelength plot for silica - gold core - shell nanocomposites for different core to shell size ratio.
The spatial distribution of scattered light intensity for gold & core-shell nanoparticles is also studied in terms of far field radiation pattern at resonance wavelengths specified in table 1(a) to 1(e) and two of them are shown in figure 4(a) and 4(b). Out of all the samples, directivity of silica-gold core-shell nanoparticles with 66nm core and 5nm shell size is found to be highest. Thus, it is found from the present study that by adjusting the core size and shell thickness precisely as well as by choosing proper material combination for core and shell, one can tune the directional pattern at the specified resonance wavelengths.

**Figure 4:** Far field radiation pattern for (a) single gold nanoparticle of size 66 nm (b) silica – gold core – shell nanoparticles with core size 66 nm and shell thickness 5 nm.

4. **Conclusion**

From this study, it can be concluded that by choosing different materials for core & shell as well as by varying the core to shell size ratio, one can obtain optimized size ratio, for the maximum shift in resonance wavelength with respect to single component nanoparticle. Again, from the comparative study of the extinction efficiencies of core-shell nanoparticles of different materials, it is found that for silica - gold core - shell nanoparticles, the resonant wavelength is greater than that of the gold –silver, silver – gold and gold - silica core - shell nanoparticles and also the radiation pattern of the silica – gold core – shell nanoparticle is the most suitable one from the point of view of directivity. The dielectric functions of the core and shell material as well as of the embedded matrix are extremely important and play a very major role to tune the particular directivity and resonance wavelength. Such highly controllable parameters of the dielectric - metal core - shell nanoparticles make them suitable for efficient coupling of optical radiation into nanoscale structures for a broad range of applications in the field of communications as well as in medical science.

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