

CHAPTER 3

Theoretical Calculations for Appropriate Size Range of Silver and Gold Coated Fe₃O₄ Nanoparticles

3.1 Introduction

The shape and size of nanoparticles are important decisive factors for application of a material as multimodal imaging agent. The desirable optical property i.e. Surface Plasmon Resonance (SPR), which is an important criterion for multimodality, is exhibited by the nanoparticles in a certain size range only. This localized SPR, which arises due to collective oscillation of conducting electrons at optical frequencies on metal surface, makes these nanoparticles an exquisite absorbers and scatterers of visible light. Before synthesis of the nanoparticles, it is essential to determine the exact regime in which the nanoparticle will exhibit SPR in desirable wavelength region. Several investigations have been carried out using theoretical models such as Mie theory, ray-optics approach and Monte-Carlo simulations to obtain absorption, extinction and scattering coefficients [32,65,164]. Out of all these theories, Mie theory is found to be the most reliable and complete to study the absorption properties of the materials. Gaustav Mie, in 1908, worked on computation of the electromagnetic wave scattering

through homogeneous dielectric sphere [61]. A theoretical treatment by use of Maxwell equations and their solutions available in the literature has been provided by Mie to obtain surface plasmon absorption spectra in case of gold colloids [67]. The absorption bands were found to be heavily dependent upon the size of gold colloids which explained the reason behind the variation in the observed colours for different colloidal sizes varying from 20 nm to 1600 nm. A report with description of numeric computation for Mie scattering and Mie absorption programs is documented for nanoparticles [66]. For these Mie calculations in case of homogeneous spheres, the computation of Mie coefficients which involve the scattered field amplitudes has been done by making the use of spherical Bessel functions of the higher order. The MATLAB programs for computation of Mie coefficients were written in double-precision Bessel functions which were found to work well for size parameters $\left(\frac{2\pi x}{\lambda}\right)$ upto 10000, where x and λ represent nanoparticle radius and wavelength in ambient medium, respectively [66].

Apart from being optically active in visible region, the nanoparticles should exhibit magnetic characteristics to be implemented as multimodal imaging agent. To fit into the requirement, the nanomaterials with integrated magneto-plasmonic behaviour have been focused from past few years. Levin and group have shown that nanocores comprising wustite with gold coating retain their magnetic properties [165]. They obtained the extinction spectra for same effective core radius with varying shell thickness and different core dielectric permittivities using theoretical calculations which matched well with their experimental data. The theoretical analysis of SPR tunabilities for distinct geometries and core permittivities allows estimation of the dielectric behavior for mixed oxide magnetic nanocores from plasmonic properties of coated nanostructures. An optical modelling of experimentally obtained magneto-optically active nanoshells with

core size 9.5 ± 1.4 nm covered by a gold layer of 6.3 ± 2.5 nm was reported by Ghazanfari and Khosroshahi [166]. The modelling was carried out using MATLAB and further experimental validation has been done.

For this thesis work, a core-shell nanostructure with magnetite as magnetically active core and silver as shell material exhibiting excellent SPR properties has been theoretically investigated as a potential multimodal agent. In this chapter, we have calculated the absorption spectra for gold and silver nanoshells with magnetite core for core size varying from 1 to 50 nm with shell thickness 1 and 2 nm. The size of core and shell thickness of the nanoparticle for SPR peak to lie in the visible range has been determined.

3.2 Theoretical Calculation Methods

The optical properties of gold / silver nanoshells over magnetite core were determined in terms of their absorption efficiency and SPR peak calculated using Mie theory and MATLAB programs. The Mie theory has been reported for single nanoparticle system with uniform composition [32,66].

For gold and silver nanoparticles, the value of absorption efficiency Q_{ab} were computed using Mie functions derived for homogeneous dielectric spheres. The Mie absorption efficiency Q_{ab} was calculated using the energy conservation relation which states

$$Q_{ex} = Q_{sc} + Q_{ab} \quad (3.1)$$

implying $Q_{ab} = Q_{ex} - Q_{sc}$ (3.2)

The value of scattering and extinction efficiency, Q_{sc} and Q_{ex} results from extinction theorem leads to

$$Q_{ex} = \frac{2}{a^2} \sum_{q=1}^{\infty} (2q + 1) \text{Re}(x_q + y_q) \quad (3.3)$$

$$Q_{sc} = \frac{2}{a^2} \sum_{q=1}^{\infty} (2q + 1) (|x_q|^2 + |y_q|^2) \quad (3.4)$$

These expressions are infinite series which are curtailed over q_{\max} terms, where $q_{\max} = a + 4a^{1/3} + 2$. This value of q_{\max} was proposed by Bohren and Huffman in 1983 [167].

The value of Mie coefficients x_q and y_q are given as

$$x_q = \frac{m\psi_q(ma)\psi'_q(a) - \psi_q(a)b'_q(ma)}{m\psi_q(ma)\xi'_q(a) - m\xi_q(a)b\psi'_q(ma)} \quad (3.5)$$

$$y_q = \frac{m\psi_q(ma)\psi'_q(a) - \psi_q(a)b'_q(ma)}{m\psi_q(ma)\xi'_q(a) - m\xi_q(a)b\psi'_q(ma)} \quad (3.6)$$

where m represents the refractive index of n^{th} sphere relative to the surrounding medium, size parameter expressed as ' a ' in form of $2\pi R/\lambda$ where R is the radius of q^{th} sphere in an ambient medium of wavelength ' λ '. ψ_q and ξ_q are spherical Bessel functions of order q and prime denotes derivative with respect to the argument. The

Bessel function is given as $\psi_q(z) = \sqrt{\frac{\pi}{2z}} \Psi_{q+0.5}(z)$, with Ψ as Bessel function of the first kind. For values of $n = 0$ and 1 , the value of spherical Bessel function can be written as $\psi_0(z) = \frac{\sin z}{z}$ and $\psi_1(z) = \frac{\sin z}{z^2} - \frac{\cos z}{z}$, respectively. The numerical computation of Mie Series has been executed for wavelengths ranging between 310 to 700 nm in case of homogeneous gold and silver metallic nanospheres to obtain the absorption spectra curves.

The complex index of refraction at different wavelength is amongst the major parameter required in order to calculate the Mie coefficient and efficiency. These values for optical constants have been obtained from the reports by P.B. Johnson and R.W. Christy [168].

3.2.1 Theory for Obtaining Absorption Spectra for Gold/Silver Coated Magnetite Core-Shell Nanoparticles

The calculation of absorption efficiencies for gold and silver shells coated on the magnetite core nanoparticles has been done using MATLAB codes for homogeneous nanoparticle system with suitable modification for core-shell nanostructures. The

modified program to calculate the absorption efficiency for the magnetite core- (Au/Ag) shell nanostructures is given in Appendix-I.

The expressions used for coefficients which appear in extinction and scattering efficiencies were modified accordingly using the expressions already reported as follows [32]:

$$x_q = \frac{\left(\frac{\tilde{D}_q + q}{n_2 + \frac{q}{b}}\right)\psi_q(b) - \psi_{q-1}(b)}{\left(\frac{\tilde{D}_q + q}{n_2 + \frac{q}{b}}\right)\xi_q(b) - \xi_{q-1}(b)} \quad (3.7)$$

$$y_q = \frac{\left(n_2 \tilde{G}_q + \frac{q}{b}\right)\psi_q(b) - \psi_{q-1}(b)}{\left(n_2 \tilde{G}_q + \frac{q}{b}\right)\xi_q(b) - \xi_{q-1}(b)} \quad (3.8)$$

where

$$\tilde{D}_q = \frac{D_q(n_2 b) - A_q \chi'_q(n_2 b) / \psi_q(n_2 b)}{1 - A_q \chi_q(n_2 b) / \psi_q(n_2 b)} \quad (3.9)$$

$$\tilde{G}_q = \frac{D_q(n_2 b) - B_q \chi'_q(n_2 b) / \psi_q(n_2 b)}{1 - B_q \chi_q(n_2 b) / \psi_q(n_2 b)} \quad (3.10)$$

$$A_q = \psi_q(n_2 a) \frac{m D_q(n_1 a) - D_q(n_2 a)}{m D_q(n_1 a) \chi_q(n_2 a) - \chi'_q(n_2 a)} \quad (3.11)$$

$$B_q = \psi_q(n_2 a) \frac{D_q(n_1 a) / m - D_q(n_2 a)}{D_q(n_1 a) \chi_q(n_2 a) / m - \chi'_q(n_2 a)} \quad (3.12)$$

In the equation, n_1 represents the refractive index of the core material which has distinct values at different wavelengths. The term n_2 implies complex refractive index of the used nanoshell material whereas ‘ a ’ and ‘ b ’ are size parameters for the inner and outer nanospheres, respectively. D_q indicates logarithmic derivative for ψ_q and χ_q is the Bessel function. The code implementation requires nanocore and nanoshell radii values R_1 and R_2 along with the values of refractive index for magnetite and gold/ silver metals at different wavelengths.

3.3 Theoretical Calculation of Absorption Spectra

The optical characteristics of gold and silver nanospheres as well as gold and silver coated magnetite nanoparticles were computed in terms of their absorption efficiency and maximum plasmon resonance wavelength calculated using MATLAB code written for core-shell structure.

The first step in our calculation was to perform a validity check of these modified codes. In order to validate the modified codes, the absorption spectra for a core-shell nanoparticle system with magnetite core diameter 0.002 nm and silver/ gold shell thickness 1, 2 and 4 nm is obtained. Ideally, the smaller dimension core will behave as vanishing core and thus the effective size of the nanoparticles is equal to 2, 4 and 8 nm. The optical behaviour of this nanoparticle system with vanishing core should be similar to that for gold/ silver nanoparticle system with particle size equal to 2, 4 and 8 nm

3.3.1 Gold and Silver Nanoparticles

Figures 3.1(a) and 3.1(b) shows spectra of absorption efficiency for the nanoparticles using MATLAB code written for core-shell structure with vanishing core. The peaks are obtained at 506 and 355 nm for gold and silver coated nanoparticles, respectively. The value is in total agreement with the calculated value of Q_{abs} and SPR peak obtained by using the established MATLAB program written for homogeneous dielectric sphere (Figure 3.1(c) and 3.1(d)), with some maximum value restriction on size parameter for steady and precise computation of Mie scattering [66]. Thus, the validation of code is proved by comparing the results obtained for vanishing cores with those calculated using Mie code for homogeneous sphere. Link and El-Sayed had published UV- Visible absorption spectra for gold nanoparticles of sizes varying from 9 to 99 nm which shows plasmon resonances in the range of 520 to 580 nm [169]. The results obtained by simulations are in good agreement with the experimental values reported for the

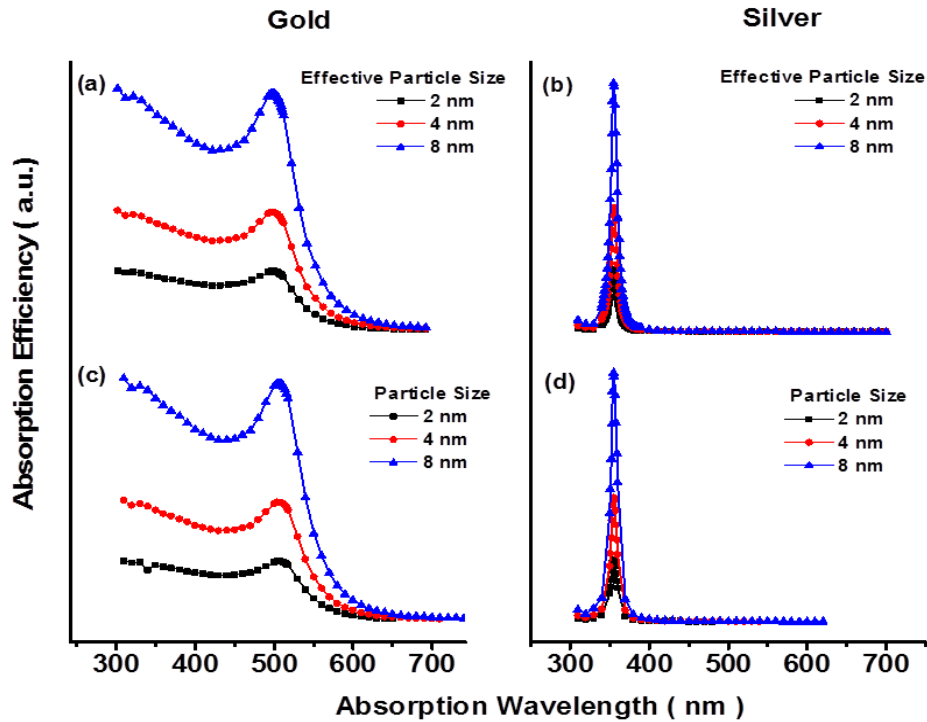


Figure 3.1 Calculated spectra of absorption efficiency Q_{abs} for nanoshells with vanishing magnetite core of $D = 0.002$ nm with nanoshells of varying thickness (a) 1, 2, 4 nm thick gold nanoshells (effective particle size = 2, 4 and 8 nm respectively), (b) $D = 1, 2, 4$ nm thick silver nanoshells (effective particle size = 2, 4 and 8 nm respectively) (c) $D = 2, 4, 8$ nm gold nanoparticles with no core (d) $D = 2, 4, 8$ nm silver nanoparticles with no core.

nanoparticle having size < 100 nm [67,71]. It is observed that the size dependence of maximum plasmon absorption of gold nanospheres is very weak, as it hardly changes when size is increased in small size region as reported by other groups. This can be clearly observed in Figure 3.1. Jain and Lee discussed the absorption properties of gold nanospheres of diameter 20, 40 and 80 nm using Mie theory and discrete dipole approximation [67]. The calculated values were obtained between 520 to 580 nm as same as experimentally identified by Link. Similarly, for silver nanoparticles, Evanoff and Chumanov have reported the absorption efficiencies for sizes varying from 29 to

136 nm using experimental measurement [71]. The spectrum shows very minute shift of 20 nm in resonance peak for a larger size variation of 29 nm to 136 nm, which is too limited for in vivo applications.

3.3.2 Gold and Silver Nanoshells with Monodispersed Magnetite Core

The studies have proved that by changing the structure of nanoparticles, their embodiment into distinct matrices and functionalization with several proteins and dyes enhances their utility in biomedical applications [2,23,28]. By varying the shape and size of a nanoparticle, its optical properties can be modified to a considerable extent. The absorption efficiency spectra for different sized magnetite core with 1 and 2 nm thick gold and silver nanoshells is shown in Figures 3.2, 3.3, 3.5 and 3.6, respectively for the core size of 1, 2, 4, 8, 12, 16, 20, 24, 30, 32, 40 and 50 nm.

It is worth mentioning that Jain and Lee have also performed the calculation for gold nanoshells with silica core for different core-shell ratios with core sizes > 40 nm and shell thickness > 10 nm. The plasmon resonance peak obtained for this size range is beyond visible range of electromagnetic spectrum [67]. Nghien and co-workers reported the absorption spectra for silica core of size 140 nm with increasing gold surface coverage. The SPR peak can be tuned from 550 to 1000 nm of the electromagnetic spectrum by adjusting the physical properties of nanoparticles [170]. Use of magnetite nanoparticle as a core material helps in overcoming the drawbacks of silica nanoparticles such as its potential carcinogenicity for humans and lack of desirable magnetic behaviour which allows them to be used as multimodal imaging agents.

From the absorption spectra observed in Figures 3.2, 3.3, 3.5 and 3.6, we notice that the reliance on size increases to a much considerable extent when core-shell structures are taken into account instead of homogeneous nanospheres (Figure 3.1).

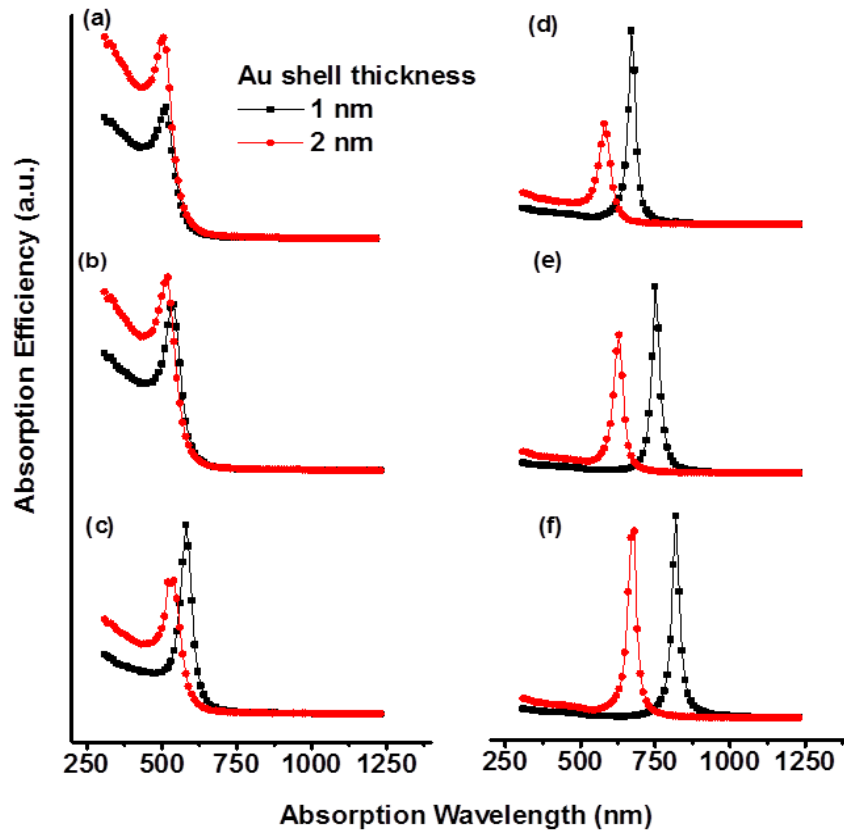


Figure 3.2 Absorption spectra of gold nanoshells of thickness 1 and 2 nm with magnetite core of size (a) $D = 1$ nm, (b) $D = 2$ nm, (c) $D = 4$ nm, (d) $D = 8$ nm, (e) $D = 12$ nm, (f) $D = 16$ nm.

The plasmon peak for 8 nm core size and 1 nm gold nanoshell is obtained at 670 nm [Figure 3.2(d)] which is otherwise obtained at 520 nm simply by reducing the core size to 1 nm [Figure 3.2(a)]. This reduction in the value of plasmon resonance is attributed to the change in density of electrons and charge distribution shapes. As the size of the core is further increased to 40 nm, the resonance wavelength spans a region of 520 nm and is observed at 1190 nm [Figure 3.3(e)].

The SPR absorption wavelength spectra for other intermediate core sizes 1, 2, 4, 8, 12 and 16 nm are shown in Figure 3.2 whereas Figure 3.3 represents the spectra for sizes 20, 24, 30, 32, 40 and 50 nm for the sake of complete study.

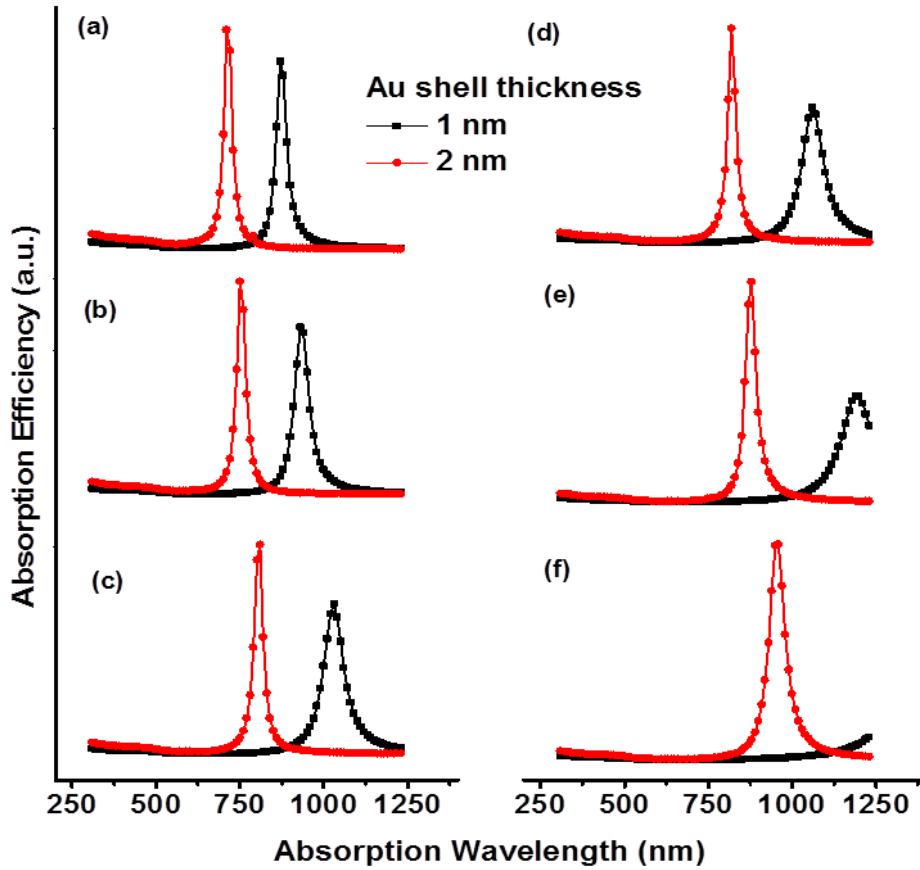


Figure 3.3 Absorption spectra of gold nanoshells of thickness 1 and 2 nm with magnetite core of size (a) $D = 20$ nm, (b) $D = 24$ nm, (c) $D = 30$ nm, (d) $D = 32$ nm, (e) $D = 40$ nm, (f) $D = 50$ nm.

Wang and Luo synthesized and assembled monodispersed gold coated magnetite nanoparticles of core sizes 4.5 ± 0.5 nm and 5.2 ± 0.4 nm with whole particle sizes on coating as 6.3 ± 0.5 nm and 6.6 ± 0.4 nm, respectively. They investigated their optical properties using UV-visible spectroscopy and found a shift of nearly 30 nm in absorption peak for such small difference in sizes [171]. Cui and Hong have synthesized gold nanoshells with magnetite core having diameter between 14 to 19 nm. The SPR peak is observed around 525 nm and 545 nm for gold nanospheres and gold-coated magnetite nanoparticles, respectively [172]. The range of resonance wavelengths obtained by the group match well with our calculated values of SPR wavelengths.

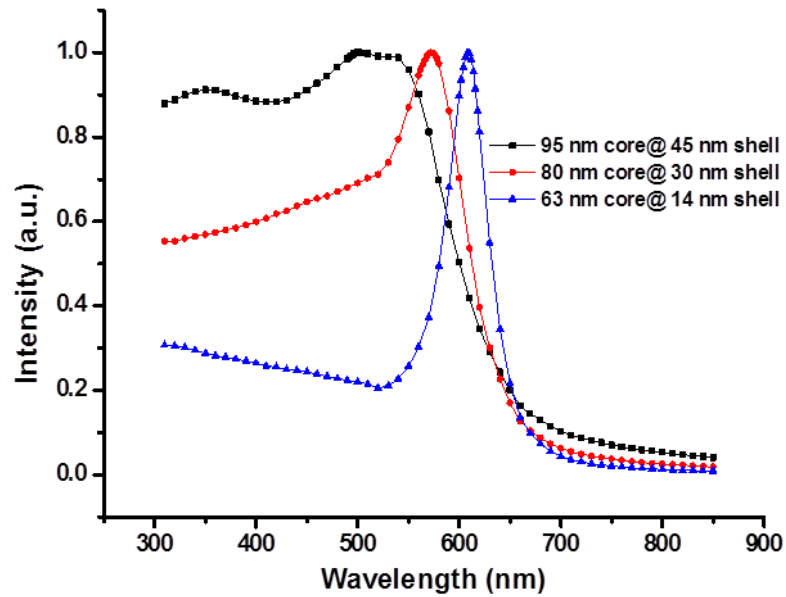


Figure 3.4 Optical absorption Spectra calculated for particles of core sizes 63 nm, 80 nm, 95 nm coated with gold nanolayers of thickness 14 nm, 30 nm, and 45 nm respectively.

Recently, the ability of Fe₃O₄@Au nanoparticles to act as a signal enhancing agent in SPR spectroscopy was investigated. The characteristic absorption peaks for 16 nm gold nanoparticles were obtained at 518 nm whereas the peak is observed at 548 nm for 25 nm gold coated magnetite nanoparticles [173]. The peak values can also be optimized by varying the concentration of gold and silver salts used during synthesis [174]. Goon et al have fabricated gold coated magnetite composite nanoparticles of particle size range 50-150 nm using Polyethyleneimine (PEI) as attaching agent [175]. The use of PEI has been employed to avoid aggregation of magnetic nanoparticles and to enhance their chemical stability. An SPR peak emerging at 550 nm is observed in UV-Vis spectra for Fe₃O₄-PEI-Au seed and Fe₃O₄-PEI-Au coated completely, the range of which nearly matches the data reported through our theoretical calculation. In recent year, synthesis and properties of magnetically active core- plasmonic shell nanoparticles

has been reported by Kwizera and co-workers [176]. They had synthesized octahedral shaped magnetite cores with coated with gold nanoshell of distinct morphologies and measured their optical and magnetic properties. The nature of UV-Vis absorption spectra obtained for particle sizes of 77 nm, 110 nm and 140 nm having gold layer of 14 nm, 30 nm and 45 nm respectively matches well with our theoretically calculated value (Figure 3.4). The values corresponding to the absorption peaks vary due to difference in shape of the core as well as particle size distribution. Since for spherical core the value of resonance peak shows a red-shift with increasing core-shell ratio, the absorption peak for particle with nanocores size of 63 nm and gold layer 14 nm is obtained at 609 nm. From the spectra, we also observe that the peak becomes broader as nanocores and nanoshells get bigger in size. After excitation, the plasmon oscillations, due to electron-phonon interactions, get damped by non-radiative absorption or by radiative resonant scattering process. The proportionate contributions from two processes are heavily dependent on the particle size. The resonance peak for 1 nm silver nanoshell on 40 nm magnetite core is obtained at 1090 nm [Figure 3.6 (d)]. This value of λ_{spr} can be brought upto 380 nm by reducing the core size to 1 nm which can otherwise also be reduced to a value of 350 nm just by increasing the shell thickness to 2 nm [Figure 3.5(a)] which was obtained at 520 nm for gold nanoshells of same dimension. The plasmon resonance peaks for sizes 2, 4, 8, 12, 16, 20, 24, 30 and 32 nm with 1 nm silver coating are obtained at 405, 470, 580, 670, 750, 810, 860, 940 and 970 nm whereas for 2 nm shell thickness they were obtained at 380, 410, 470, 530, 580, 630, 680, 730 and 750 nm, respectively. These values clearly explain the excellent tunability of optical properties of silver nanoshells over magnetite core in comparison with gold.

Xu and group had also reported the absorption properties of gold coated magnetite further coated onto by silver shell of thickness 0.5 nm, 1 nm and 2 nm. From their

experimental measurement, the blue- shift of peaks is easily visible showing absorption peaks at lower wavelength for silver coated samples as compared to the gold coated particles [177]. Chin and Iyer have also synthesized magnetite nanoparticles with particle size 10-13 nm homogeneously coated with gold and silver nanoshells of

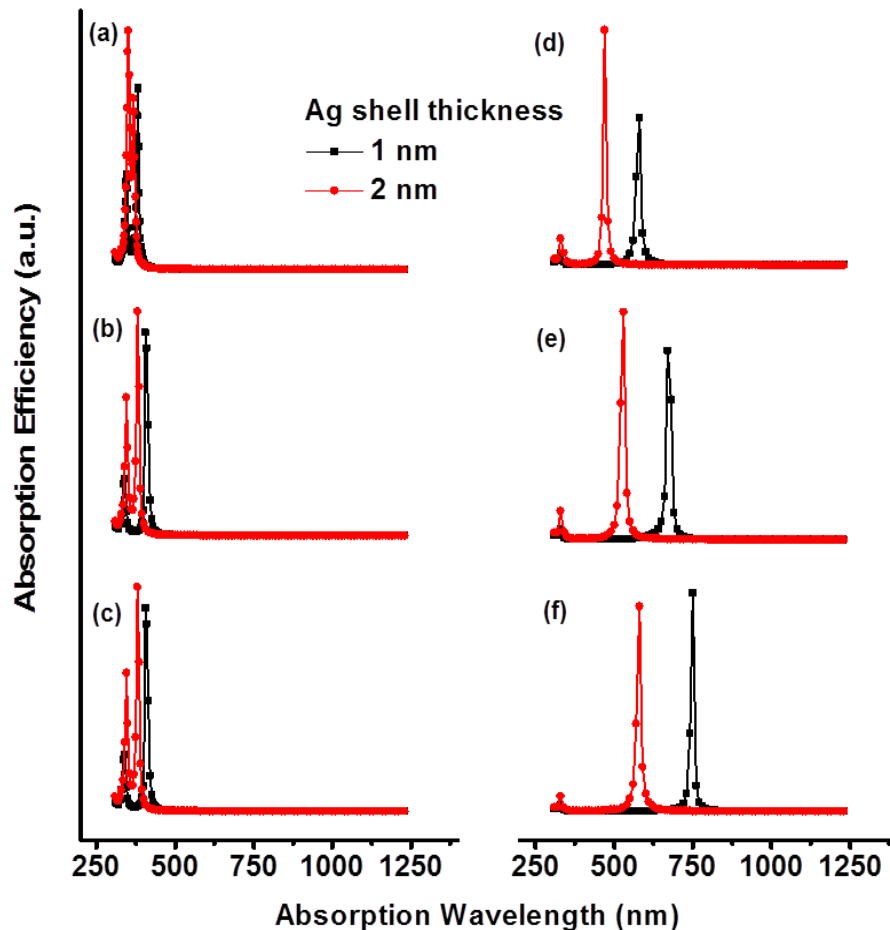


Figure 3.5 Optical Absorption Spectra of silver nanoshells of thickness 1 and 2 nm with varying magnetite cores of diameter (a) $D = 1$ nm, (b) $D = 2$ nm, (c) $D = 4$ nm, (d) $D = 8$ nm, (e) $D = 12$ nm, (f) $D = 16$ nm.

thickness 2-3 nm. The UV-Vis absorption spectra for the nanoparticles show a maximum around 460 nm for silver nanoshells whereas for gold coated particles, it is seen around 530 nm [178].

Tang et al developed functionalized magnetic core- silver shell nanoparticles for clinical applications. The core size was confirmed to be 40 nm with 6 nm silver shell around it.

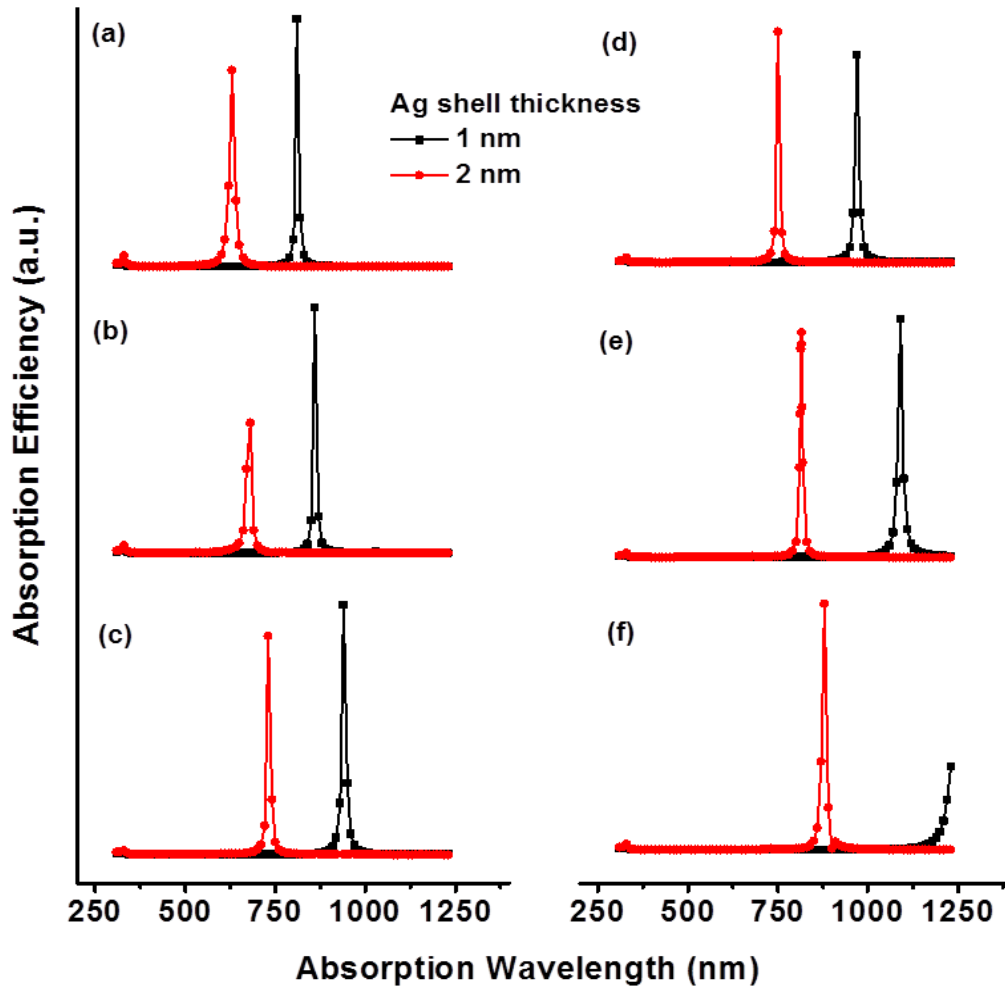


Figure 3.6 Optical Absorption Spectra of silver nanoshells of thickness 1 and 2 nm with varying magnetite cores of diameter (a) $D = 20$ nm, (b) $D = 24$ nm, (c) $D = 30$ nm, (d) $D = 32$ nm, (e) $D = 40$ nm, (f) $D = 50$ nm.

The absorption maximum for the Fe₃O₄@Ag nanoparticles was obtained around 400 nm [179]. The difference between energies for plasmon resonance and inter band transition for silver nanoparticles is higher as compared to other noble metals. This energy difference accounts for its tunable characteristics over a wider wavelength range than others. For silver nanoshell structure, an appreciable contribution from quadrupole coupling is also observed in addition to dipole coupling which is otherwise absent for gold nanoshells of same dimension.

The SPR peak value varies almost linearly with core- shell ratio for a given material. Further, the intercept of the SPR peak value curve with the core- shell ratio seems to be a function of the selected metal. The different absorption characteristics of the two nanoshells are attributed to the dielectric function of the metal and the medium. The local electric field effects induced due to collective oscillation of electrons near the surface of nanoparticles also play a significant role in SPR peak determination. For silver nanoparticles, the induced field value is up to ten times higher than the value of incident electric field [180].

3.3.3 Effect of Polydispersity on the Optical Properties of Coated Nanoparticles

Since the formation of monodispersed nanoparticles is practically quite complex, most of the synthesized particles are polydisperse in nature.

For calculation of absorption efficiencies in case of polydispersed nanoparticles-

1. The MATLAB program for monodispersed particles has been used to calculate the SPR spectra for an individual particle.
2. A frequency distribution has been plotted with particle size. The particle size weight fraction is obtained from the histograms depicting particle size distribution (PSD). The mean particle size and standard deviation is obtained by fitting the histogram using lognormal distribution function.
3. The absorption efficiency calculated using the following equation.

$$E_{pd} = \frac{\sum n_i E_{md}}{\sum n_i}$$

where, n_i is the weighted fraction of a particular particle size, E_{pd} and E_{md} are the absorption efficiencies of polydispersed and monodispersed nanoparticles, respectively.

The efficiency value obtained corresponding to particular wavelength for all particle sizes has been summed up and then plotted against the wavelength.

The effect on absorption properties of core nanoparticles due to polydispersion has been studied by taking an already reported experimental data. Xu and Hou had synthesized Fe₃O₄ nanoparticles and reported the average diameter of magnetic particles to be 10 nm [177]. Further, the magnetic nanoparticles were said to be coated with 2.5 nm gold shell. A particle size distribution is obtained for the TEM image provided in the literature. The histogram obtained is then fitted with lognormal distribution function given by following equation used by many groups for size analysis [166,175-176]:

$$y = y_0 + \frac{A}{wx\sqrt{2\pi}} e^{-\frac{\ln\frac{x}{xc}}{w^2}}$$

where variables xc and w represent the mean particle size diameter and standard deviation, respectively. The efficiency of polydispersed nanoparticles is then obtained using the following equation:

$$E_{pd} = \frac{\sum n_i E_{md}}{\sum n_i}$$

In this equation, n_i is the weighted fraction of a particular particle size, E_{pd} and E_{md} are the absorption efficiencies of polydispersed and monodispersed nanoparticles, respectively.

The absorption spectrum is theoretically calculated for the polydispersed nanoparticles and then compared to that of spectra obtained for monodispersed 10 nm particles coated with 2.5 nm thick gold nanoshells. The peak of absorption spectra for polydisperse nanoparticles is broader when compared with monodispersed particles but the peak profile remains constant irrespective of dispersity. The FWHM value corresponding to polydispersed and monodispersed nanoparticles are found to be 50 nm and 35 nm, respectively, suggesting the widening of absorption peak (Figures 3.7 (a) and (b)). The

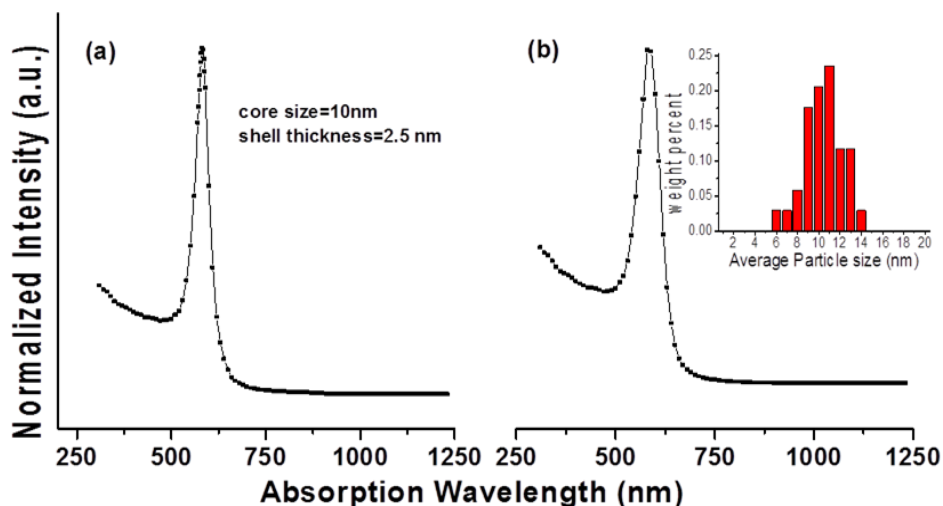


Figure 3.7 Calculated Absorption Spectra for polydispersed nanoparticles with average magnetite core size of 10 ± 4 nm with gold coating of 2.5 nm thickness.

experimental data, as per the quoted literature, shows a broadened UV-Vis absorption peak in range of 520-600 nm which nearly matches with our calculated data 540-620 nm with highest value lying between 570-580 nm. Thus, even polydispersed nanoparticles of this particular size range have its optical properties lying in the visible range of spectra which fulfils the essential criterion of multimodal agents for imaging and therapeutic purposes.

Figure 3.8 shows the SPR wavelength as a function of core to shell ratio calculated for gold and silver nanoshells with magnetite core. These theoretical studies illustrate that with varying ratio of core-shell, the optical resonances can be shifted to any values ranging from 1190 to 510 nm [Figure 3.2 & 3.3] and 1090 to 350 nm [Figure 3.5 & 3.6] using gold and silver shells, respectively, over magnetite nanoparticles of distinct sizes as shown in the figure as well in form of complete spectra.

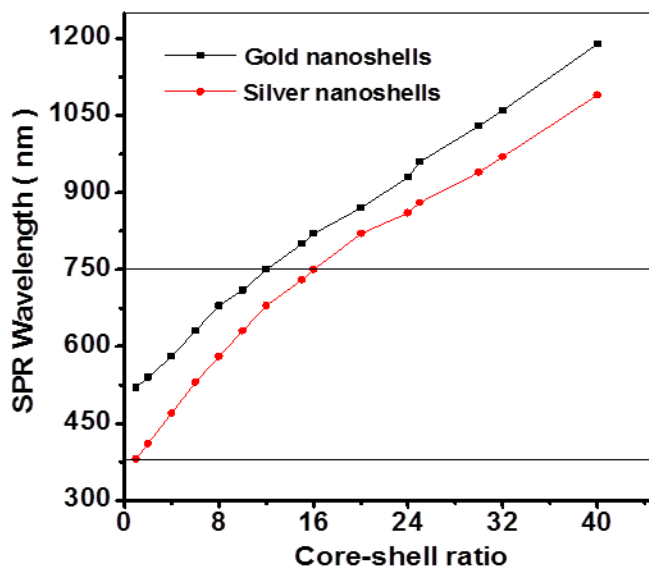


Figure 3.8 SPR peak as a function of core-shell ratio for gold and silver shells.

From our calculations performed for magnetite core sizes varying from 1 to 50 nm with noble metal shells of thickness 1 and 2 nm, we can observe that the absorption spectrum depends upon the core-shell ratios irrespective of core size and shell thickness. The crucial core-shell ratio varies from 1 to 12 and 1 to 16 for gold and silver coated magnetite nanoparticles, respectively (Figure 3.9) for resonance peak to lie in the visible region for their applicability as multimodal contrast agents. We can now specify the size range of gold and silver coated magnetite nanoparticles for which the SPR peak is obtained in visible range for its application as a multimodal agent in biomedical applications.

The critical core diameter identified for gold nanoshell is 12 nm (with shell thickness 1 nm) and 24 nm (with shell thickness 2 nm). In case of silver nanoshell, critical diameter is 16 nm and 32 nm with shell thickness 1 nm and 2 nm, respectively for SPR wavelength to lie between 370 to 750 nm. The SPR peak values has been plotted against the diameter of the magnetite core for gold and silver nanoshells with thickness of 1 and 2 nm for each separately in Figure 3.9. At smaller core size values, the SPR peak values

are convergent in nature for same noble metal with two different thick shells. The difference between the resonance wavelength values increase to a much considerable extent for increase in shell thickness just by 1 nm at higher core size values as seen in the Figure 3.9. From the graph, it can be concluded that when the core size is increased, the plasmon resonance peak shift towards the NIR and IR region of electromagnetic spectra. When the shell thickness is increased, the value of resonance peak shifts towards lower wavelength of visible region. The surface plasmon resonance is sensitive towards the particle size. For smaller size particles, the energy required to excite the motion of surface plasmon electron increases.

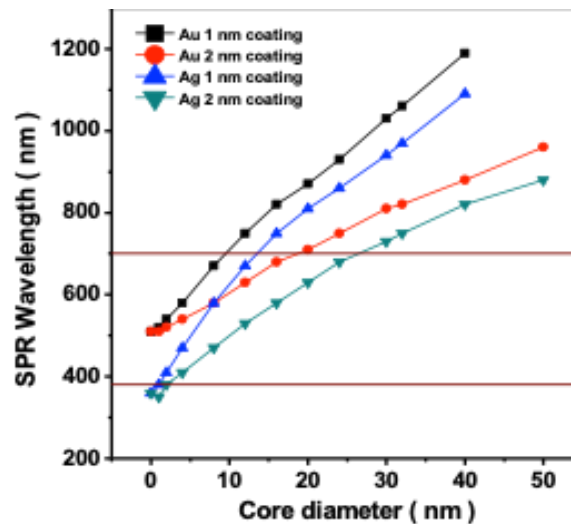


Figure 3.9 Plot of SPR peak values against the diameter of the magnetite core with gold and silver nanoshells of thickness 1 and 2 nm.

The plasmonic properties of gold and silver nanoshell are extremely sensitive to small variation in dimensions, i.e. shell thickness. For 1 nm core size, the SPR peak shows a shift of 10 nm when one increases the gold nanoshell thickness from 1 nm to 2 nm, whereas the same shift is 310 nm when the magnetite core size is 40 nm. Similarly, for

silver nanoshells, these shifts are 30 nm and 220 nm for core size 1 nm and 40 nm, respectively. The dependence of the position of SPR peak on the shell thickness becomes much weaker when the shells become thicker. It is also worth noticing that the difference between plasmon resonance wavelength values for 1 and 2 nm shell thickness is very minute for small core sizes.

The gap between the peak increases up to a considerable extent for larger core size. This behavior of plasmonic gold/ silver nanoshell is attributed to the separation between the neighboring particles. It is known that dipole- dipole coupling is responsible for the red-shift of plasmon band. For larger separation, i.e. thick coatings, dipole- dipole coupling is fully suppressed and the plasmon band is obtained at nearly same position for individual metal nanoparticle. Composite spherical nanoshells comprising of metallic shell and a dielectric core material could give rise to SPR modes with their wavelengths tunable over a wider range of electromagnetic spectrum. Plasmon resonance peaks of gold and silver nanoshells can be tuned over a broad range from the visible to near infrared region of spectra.

3.4 Conclusions

To summarize: theoretical investigation of SPR wavelength for the nanoparticles has been performed. A sequential study using MATLAB programs to acquire the trends in plasmon resonance wavelength with changing nanoparticle dimensions for gold and silver coated magnetite nanoparticles has been carried out. A strong dependence of SPR properties on nanoparticle dimensions has been found in case of core-shell nanostructures. We have identified the size range of core and shell for which the plasmon resonance peak lies in the visible range of electromagnetic spectrum. The critical diameter of magnetite core with 1 and 2 nm gold nanoshells for SPR peak to lie in the visible region of electromagnetic spectrum is 12 and 24 nm, respectively. This

critical diameter value for silver coated magnetite nanoparticles is 16 and 32 nm for 1 and 2 nm thick nanoshells, respectively. The SPR peaks of gold and silver nanoshells can be tuned by controlling the ratio of core radius to shell thickness. The wavelength of the SPR peak belonging to blue-green region lies between 450-560 nm. The corresponding particle size for silver coated magnetite nanoparticle having shell thickness of 1-2 nm turns out to be around 6 nm.

After the theoretical study to obtain the SPR wavelength of core-shell nanoparticles, an experimental study is much needed in order to verify the estimated absorption behavior of these nanoparticles in real systems where many factors such as shape anisotropy, local environment and interparticle interactions also affect these properties. In our study, we are concerned about the studies of physical, optical and magnetic properties of nanostructures with particle size lying only in this range. In order to study the effect of silver coating and increase in shell thickness on the structural and magnetic properties of magnetite nanoparticles with average size 6 nm, a series of sample with varying silver shell thickness has been synthesized using the method discussed in chapter 2 section 2.7 & 2.8. The magnetite nanoparticles with average diameter ~6 nm have been synthesized using single phase microemulsion technique at reaction temperature ~70⁰ C. The molar concentrations of ferrous and ferric salts were taken as 0.092 M and 0.184 M, respectively. The molar concentration of surfactant CTAB was taken to be 0.1 M. The 100 mg of so-obtained magnetite nanoparticles with size ~6 nm has been coated with ~1 nm, ~1.5 nm, ~2nm, ~3 nm, ~4 nm, ~8 nm and ~9 nm thick silver shells by using 100 mg, 125 mg, 150 mg, 200 mg, 300 mg, 500 and 700 mg of silver nitrate, respectively. Their optical, physical, magnetic properties and dynamics of magnetic spins have been discussed in the forthcoming chapters.