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# The Effect of Surface Plasmon Resonances on Spherical Magneto-Plasmonic Fe304@Ag Core-Shell Nanoparticles

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## The Effect of Surface Plasmon Resonances on Spherical Magneto-Plasmonic Fe<sub>3</sub>O<sub>4</sub>@Ag Core-Shell Nanoparticles

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#### ABSTRACT

In this work, the scattering, absorption, and extinction cross-sections of  $Fe_3O_4$ @Ag core/shell spherical nanostructures embedded in a dielectric host matrix are investigated theoretically. Electrostatic approximation and Maxwell-Garnet effective medium theory are employed to obtain the effective electric permittivity and magnetic permeability, as well as the corresponding absorption, scattering, and extinction cross-sections. Likewise, for a fixed size of QDs (of radius  $a_s = 10$  nm) numerical analysis is performed to see the effect of varying the metal fraction ( $\beta$ ) and the permittivity  $(\varepsilon_h)$  of the host matrix on the magneto-plasmonic nanostructures. The results show that graphs of absorption, scattering, and extinction cross-sections as a function of wavelength have two sets of resonance peaks in the UV and visible regions. These sets of peaks arise due to the strong coupling of the surface plasmon oscillations of silver with the excitonic state of the semiconductor/dielectric at the inner ( $Fe_3O_4$ @Ag) and outer (Ag/host) interfaces. The absorption and scattering crosssections are blue-shifted in the first peak and red-shifted for the second set of peaks as  $\beta$  increases. Similarly, the extinction cross-section possesses two sets of resonance peaks which are enhanced for an increase in  $\varepsilon_h$  or decrease of  $\beta$ ; keeping one of these two parameters constant at a time. The results obtained may be utilized in applications that incorporates both the plasmonic and magnetic effects in core/shell nanostructures.

Keywords: Dielectric function, Extinction Cross-section, Core-shell

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#### 1. INTRODUCTION

A great attention has been given to the development of nanomaterials as they exhibit unique material properties as compared to their bulk counterpart. These unique properties includes optical, magnetic, specific heat, melting point, surface activities, chemical and biological properties [1]. Nanomaterials forms heterogeneous structures composed of a noble metal and a semiconductor. These peculiar type of systems offers to design materials with novel and unique physical chemistry properties. As isolated systems, the optical properties of semiconductor quantum dots (QDs) and noble metal nanoparticles (NPs) are characterized by excitons and plasmons, respectively. In both cases, the required wavelengths to produce such excitations are governed mainly by the nanoparticle nature, size, shape, and local environment [2].

Core-shell nanoparticles are essentially heterogeneous NPs composed of two or more materials (metal, element, or biomolecules); one nanomaterial acts as a core in the center while the other material behaves as a shell [3]. Core/shell composite nanostructures (NSs) exhibit many unique properties, including mono-dispersion, core/shell operability, stability and self-assembly. These materials have good surface plasmon resonance at their interface and the noble metal/semiconductor core/shell composite NS has been one of the most promising composite NSs of the recent decades [4].

Magnetic/plasmonic nanostructures demonstrate multiple properties not present in individual nanomaterials. Such materials offer the advantage of being manipulated by an external magnetic field, showing tunable optical properties being adjustable in accordance with modifying shell thickness. Experimental and computational studies by [5] shows that the higher the magnetization in magnetic core nanoparticles, the more is the suitable response toward the exposed magnetic field and the higher the effectiveness in nanomedical diagnostics. Magnetic-plasmonic core shell (NPs) possess dual magnetic and plasmonic properties and have widespread applications in biomedical fields. The magnetic cores such as iron-oxide (IO) are greatly desired for applications such as magnetic separation, magnetic resonance imaging or magnetic guided drug delivery. The IO-cores can be chemically stabilized by coating them with noble metals, which not

only provides a chemically inert surface, but also introduces interesting plasmonic properties which can be utilized for sensing, imaging, and photothermal therapy [6].

Many researchers have attempted to combine  $Fe_3O_4$  and Ag as nanocomposite devices. These attempts were challenged by the core/shell  $Fe_3O_4$ @Ag due to surface enhanced Raman scattering (SERS) effect and localized surface plasmon resonance (LSPR). The plasmon resonance wavelength, light scattering, absorption and extinction cross section of core/shell are affected by shell thickness, core diameter, electronic properties of shell and surrounding environment at the two different interfaces (outer interface between the surface and incident light, and inner interface between metal and semiconductor). LSPR causes some suitable characteristics such as enhancement of electric field, localization of energy at nanometer scale, and strongly enhanced absorption and scattering. In Ref. [7], it is reported that the synthesis and characterization of coreshell NPs with a magnetite core and a silver shell can be done by varying the concentration ratio of the reduction agent so that silver is deposited on the magnetite. Silver coating was achieved by adding butylamine as a weak reducing agent of AgNO<sub>3</sub> in foregoing solution.

Magnetic nanoparticles with a core/shell structure promises for many applications due to their multi-functionality including optical, electronic, and magnetic properties [8] and references therein. Iron-oxides nanoparticles play a major role in many areas of chemistry, physics and materials science.  $Fe_3O_4$  (Magnetite) is one of the magnetic nanoparticles. Different reports are demonstrating that magnetic  $Fe_3O_4$  can be used for waste water purification, such as to adsorb arsenite, arsenate, cadmium, nickel [9, 10], used to remove alkalinity and hardness, desalination, decolourisation of pulp mill effluent and removal of natural organic compounds. After adsorption, Fe3O4 can be separated from the medium by a simple magnetic process [8].

Noble metals nanoparticles, such as Ag and Au, strongly absorb light in the visible region due to coherent oscillations of the metal conduction band electrons in strong resonance with visible frequencies of light. This phenomenon is known as surface plasmon resonance (SPR) and is highly dependent on NPs size, shape, surface, and dielectric properties of the surrounding medium. Light absorbed by nanoparticles is readily dissipated as heat. Due to their large absorption cross sections, plasmonic NPs can generate a significant amount of heat and increase temperatures in their vicinities [10, 11, 12, 13, 14].

Silver NPs have been applied as a broad spectrum and highly effective bactericide. The antibacterial mechanism is associated to the release of silver ions. For medical applications,

an Ag@ $Fe_3O_4$  core-shell structure allows one to add a magnetic functionality to silver properties. Such nanostructure could lead to interesting advances to solve the lack of bio-compatibility of silver, eliminating its contact with tissues (iron-oxide can be considered biocompatible, at least up to the mg/ml range). However, an intriguing behavior was observed on Ag@ $Fe_3O_4$  NPs: its bactericidal efficiency is stronger than Ag –  $Fe_2O_3$  hetero-dimers or plain Ag [15, 16, 17].

Surface plasmon absorption has been observed for silver particles in various media, including aqueous solutions, gelatin and glass. Size effects exhibited by nearly spherical silver particles are similar to those for gold. While, extinction is the attenuation of an electromagnetic wave by scattering and absorption as it traverses a particulate medium. In homogeneous media the dominant attenuation mechanism is usually absorption. Comparison of extinction spectra for small particles of various sizes with absorption spectra for the bulk parent material reveals both similarities and differences [13].

To investigate the optical properties and response (absorption and scattering) of NPs with light (electromagnetic radiation) interaction, one has to measure the effective permittivity,  $\varepsilon_{eff}$ , and permeability,  $\mu_{eff}$ , [18]. In this paper, we studied the magneto-optical response of the theoretically modelled spherical  $Fe_3O_4$ @Ag coreshell NPs. Silver nanoparticle was selected as a shell on magnetite nanospheres, due to its nontoxic, strong absorption in the UV and visible spectrum [19] and surface plasmon resonance (SPR) which plays a great role in determining the optical response of nanoparticles.

The paper is structured as follow: In Section 2, the effective permittivity and permeability of the theoretically modelled magnetic-semiconductor/metal core/shell spherical NPs embedded in a dielectric host matrix are derived. In Section 3, equations for the effective polarizabilities, absorption cross-section and scattering cross-section are derived. The numerical results are presented and discussed in Section 4. Detailed analysis of the magneto-optical responses of  $Fe_3O_4$ @Ag core/shell NPs, namely the electric polarizability, absorption cross-section, scattering cross-section and extinction cross-section are presented. Finally, concluding remarks are presented in Section 5.

#### 2. THEORETICAL MODEL

In the present work, we considered a model of  $Fe_3O_4$ @Ag spherical core-shell NPs, which is composed of Magnetic-half metallic iron (III) oxide ( $Fe_3O_4$ ) core of radius ac and an outer metallic (Ag) shell of radius as embedded in a dielectric host matrix as shown in Fig. 1, where  $a_c < a_s$ . Because of the core material is magnetic with permeability,  $\mu \gg 1$ , the magneto-optical properties of the system requires determination of its effective permittivity  $\varepsilon_{eff}$  and permeability  $\mu_{eff}$ . Based on electrostatic approximation and the Maxwell-Garnet effective medium theory, theoretical analysis have been done to derive  $\varepsilon_{eff}$  and  $\mu_{eff}$ . Moreover, using these theoretically determined values, calculations has been done on the magneto-optical parameters such, as the electric polarizability, absorption and scattering cross-sections.

#### 2.1. Effective Permittivity and Permeability

In the previous work [20], we derived that the effective dielectric function of the core-shell composite material which is obtained to be:

$$\varepsilon_{I} = \varepsilon_{s} \frac{\varepsilon_{c} \left(\frac{3}{\beta} - 2\right) + 2\varepsilon_{s}}{\varepsilon_{c} + \varepsilon_{s} \left(\frac{3}{\beta} - 1\right)},\tag{1}$$

where,  $\beta = 1 - \nu_f$  is the volume fraction of the metal coated spherical core-shell nanoparticle, and  $\nu_f = \left(\frac{a_c}{a_s}\right)^3$ .

Here, we consider a system composed of a finite number of core-shell NPs uniformly dispersed in a host matrix



FIG. 1: Schematic of a core-shell spherical NPs embedded in a matrix. The permittivities and permeabilities are  $\varepsilon_c$ ,  $\mu_c$  for the core,  $\varepsilon_s$ ,  $\mu_s$  for the shell, and,  $\varepsilon_h$ ,  $\mu_h$  for the host matrix, respectively. Also,  $a_c$ ,  $a_s$  are the radii of the core and the shell, r = 2a is the diameter of core/shell, and a is the distance from the center of the NP to an observation point.

as shown in Fig. 1. Suppose N is the density number of the inclusions (NPs) in the system, then the effective polarizability and permittivity of the system can be described by using the Clausius-Mossotti relation together with the Maxwell-Garnet mixing formula. Accordingly, the electric polarizability and the effective permittivity are related by [21]

$$\frac{N\alpha}{3} = \frac{\varepsilon_{eff} - \varepsilon_h}{\varepsilon_{eff} + 2\varepsilon_h}.$$
(2)

Rearranging and carrying out some mathematical manipulation, the effective dielectric function "eff of the system and polarizability \_ are given by

$$\varepsilon_{eff} = \varepsilon_h \left( \frac{1 + 2f \alpha_{eff}}{1 - f \alpha_{eff}} \right), \tag{3}$$

where, f is the filling factor of the core-shell NPs defined by

$$f = \frac{4\pi r_s^3}{3} N, \tag{4}$$

and  $\alpha_{eff}$  the dimensionless effective electric polarizability of the inclusion given by

$$\alpha_{eff} = \frac{\varepsilon_I - \varepsilon_h}{\varepsilon_I + 2\varepsilon_h}.$$
(5)

Similarly, we previously derived [20] that the effective magnetic permeability of composite material and the dimensionless magnetic polarizability are found to be given by

$$\mu_{I} = \mu_{s} \left[ \frac{\mu_{c} \left( \frac{3}{\beta} - 2 \right) + 2\mu_{s}}{\mu_{c} + \mu_{s} \left( \frac{3}{\beta} - 1 \right)} \right].$$
(6)

Using the Clausius-Mossotti relation and the Maxwell-Garnet mixing theory, the magnetic polarizability and permeability are related by [21, 22, 23]

$$\frac{N\kappa_m}{3} = \frac{\mu_{eff} - \mu_h}{\mu_{eff} + 2\mu_h},\tag{7}$$

where  $\mu_{eff}$  is the effective magnetic permeability of the ensemble. After some manipulation, we obtained

$$\mu_{eff} = \mu h \left( \frac{1 + 2f \kappa_{eff}}{1 - f \kappa_{eff}} \right), \tag{8}$$

where  $f = 4\pi N a_s^3/3$  is the filling factor of the core-shell NPs and  $\kappa_{eff}$  the dimensionless magnetic polarizability which is given by

$$\kappa_{eff} = \frac{\mu_I - \mu_h}{\mu_I + 2\mu_h}.$$
(9)

#### 3. OPTICAL PROPERTIES OF Fe3O4@Ag NANOPARTICLES

In this Section, we present the equations for the optical parameters, i.e., the absorption, scattering, and extinction cross-sections with the help of the polarizability equations for a system composed of  $Fe_3O_4$ @Ag core-shell NPs embedded in a liquid/water medium. Hence, in order to get an explicit expression for the absorption and scattering cross-sections, we must fix the permittivities and effective electric and magnetic polarizabilities of the system that consists of the magnetic core, metallic shell, and host matrix.

The response of 'bare' metallic (Ag) shell to incident electromagnetic wave (EMW) is solely described by the dielectric function (permittivity) with the permeability being equal to unity ( $\mu_s = 1$ ). Therefore, we choose the frequency dependent complex dielectric function of the metallic (Ag) shell to have the Drude form given by

$$\varepsilon_s(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)},\tag{10}$$

where the constant  $\varepsilon_{\infty}$  is the permittivity at high frequencies,  $\omega_p$  is the plasma frequency, is the damping parameter, and  $\gamma$  is the frequency of the incident radiation. Further, separating the real and imaginary parts of Eq. (10), i.e.,  $\varepsilon_s = \varepsilon'_s + i\varepsilon''_s$ , we obtain the following:

$$\varepsilon_s'(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + \gamma^2},\tag{11}$$

And

$$\varepsilon_s^{\prime\prime}(\omega) = \frac{\gamma \omega_p^2}{\omega(\omega^2 + \gamma^2)},\tag{12}$$

where  $\varepsilon'_{s}(\omega)$  and  $\varepsilon''_{s}(\omega)$ , respectively, are the real and imaginary parts of  $\varepsilon_{s}(\omega)$ .

It was well understood that the dielectric function of metals, specifically that of noble and alkali metals, vary significantly as a function of the frequency of the incident light in the visible spectral region, but that of magnetite is constant or vary very little. Hence, we assumed that both the permittivity ( $\varepsilon_c$ ) and permeability ( $\mu_c$ ) of magnetite as well as the permittivity of the host ( $\varepsilon_h$ ) to be real constants independent of frequency.

#### 3.1. Effective Electric and Magnetic Polarizabilities

The effective (dimensionless) electric polarizability of the system is given by [24, 25]

$$\alpha_{eff} = 1 - \frac{3}{2} \left[ \frac{\varepsilon_c \varepsilon_h + \varepsilon_s \varepsilon_h \left(\frac{3}{\beta} - 1\right)}{\varepsilon_c \varepsilon_h + \varepsilon_s \varepsilon_h \left(\frac{3}{\beta} - 1\right) + \varepsilon_c \varepsilon_s \left[\frac{3}{2\beta} - 1\right] + \varepsilon_s^2} \right].$$
(13)

and the corresponding electric polarizability becomes

$$\alpha_e = 4\pi a_s^3 \alpha_{eff}. \tag{14}$$

Because  $\varepsilon_{eff}$  for the system is complex, the effective electric polarizability  $\alpha_{eff}$ , defined by Eq. (13) is also complex, which may be written as

$$\alpha_{eff} = \alpha'_{eff} + i\alpha''_{eff},\tag{15}$$

where  $\alpha'_{eff}$  and  $\alpha''_{eff}$  are its real and imaginary parts, respectively. Substituting  $\varepsilon_s = \varepsilon'_s + i\varepsilon''_s$  into Eq. (13), we get

$$\alpha'_{eff} = 1 - \frac{3}{2} \left[ \frac{(\varepsilon'_s \phi' + \varepsilon_c \varepsilon_h) \phi' + (\varepsilon''_s \phi') \psi}{\varphi^2 + \psi^2} \right],\tag{16}$$

and

$$\alpha_{eff}^{\prime\prime} = \frac{3}{2} \left[ \frac{(\varepsilon_s^{\prime} \phi^{\prime} + \varepsilon_c \varepsilon_h) \psi - (\varepsilon_s^{\prime\prime} \phi^{\prime}) \varphi^{\prime}}{(\varphi)^2 + \psi^2} \right],\tag{17}$$

Where

$$\begin{split} \phi' &= \varepsilon_h \left(\frac{3}{\beta} - 1\right), \\ \eta &= \phi' + \varepsilon_c \left(\frac{3}{2\beta} - 1\right), \\ \varphi' &= (\varepsilon_s)^2 - (\varepsilon_s'')^2 + \varepsilon_s \eta + \varepsilon_c \varepsilon_h, \\ \psi &= 2\varepsilon_s \varepsilon_s'' + \varepsilon_s''. \end{split}$$

Similarly, substituting Eq. (6) into (9), we find the effective magnetic polarizability to be

$$\kappa_{eff} = 1 - \frac{3}{2} \left[ \frac{\mu_c \mu_h + \mu_s \Delta}{\mu_c \mu_h + \mu_s \Delta + \mu_c \phi + \mu_s^2} \right],$$
(18)

where

$$\Delta = \mu_h \left(\frac{3}{\beta} - 1\right),$$

and

$$\phi = \mu_s \left(\frac{3}{2\beta} - 1\right)$$

In particular, for the case where  $\mu_c$  is a real constant and  $\mu_s = \mu_h = 1.0$  (nonmagnetic), we find that Eq. (18) for the dimensionless polarizability reduces to

$$\kappa_{eff} = 1 - \left[\frac{3 + \beta(\mu_c - 1)}{\mu_c + 2}\right],\tag{19}$$

and the corresponding magnetic polarizability becomes

$$\alpha_m = 4\pi a_s^3 \kappa_{eff} \,. \tag{20}$$

Note that both  $\kappa_{eff}$  and  $\alpha_m$  of Eqs. (19) and (20) are real constants.

#### 3.2. Absorption, Scattering, and Extinction Cross-Sections

The absorption cross-section,  $\sigma_{abs}$ , of the system consisting of spherical core-shell composite NPs embedded in a host matrix is given by [25]:

$$\sigma_{abs} = k \operatorname{Im}[\alpha_e + \alpha_m], \tag{21}$$

where  $k = 2\pi \sqrt{\varepsilon_h} / \lambda$ . Note that  $\alpha_m$  is a real constant.

In addition, we consider that the loss of electromagnetic wave upon propagation through the spherical nanoinclusions results by means of the generation of heat and scattering. The scattering cross-section,  $\sigma_{sc}$ , of the system can be shown to have the following form:

$$\sigma_{sc} = \frac{k^4}{6\pi} |\alpha_e + \alpha_m|^2 \,. \tag{22}$$

Furthermore, the extinction cross-section,  $\sigma_{ext}$ , of the system is given by

$$\sigma_{ext} = \sigma_{sc} + \sigma_{abs},\tag{23}$$

where  $\sigma_{sc}$  and  $\sigma_{abs}$  are given by Eqs. (21) and (22), respectively.

#### 4. NUMERICAL ANALYSIS

Next, we numerically analyzed the polarizability as well as the absorption, scattering, and extinction cross-sections of the theoretically modelled spherical  $Fe_3O_4$ @Ag core-shell NPs embedded in a dielectric host matrix. These optical parameters are analyzed by varying the material parameters  $\beta$  and  $\varepsilon_h$ ). For the numerical evaluations, we used Mathematica version 10 software. The following parameter values are used in the simulation:  $\varepsilon_{\infty} = 4.5$ ,  $\omega_p = 1.46 \times$ 

 $10^{16} rad/s$  and  $\gamma = 1.67 \times 10^{13} rad/s$  for the silver shell; and  $\varepsilon_c = 5.85$  and  $\mu_c = 9.0$  for magnetite.

#### 4.1. Electric Polarizability

Figure 2 depicts the real and imaginary parts of the frequency dependent complex electric polarizability ( $\alpha'_{eff}$  and  $\alpha''_{eff}$ ) of the spherical  $Fe_3O_4$ @Ag nanoinclusions as a function of the wavelength of the incident radiation for different values of the metal fraction,  $\beta$ , and fixed values of  $\varepsilon_h = 1.77$  and NPs size  $a_s = 10 nm$ . It is shown that



FIG. 2: The real a) and imaginary b) parts of the electric polarizability versus wavelength for different values of  $\beta$ ; with  $\varepsilon_h = 1.77$  and  $a_s = 10$  nm.

both  $\alpha'_{eff}$  and  $\alpha''_{eff}$  possess two sets of resonance peaks -the first in the UV region in the vicinity of the wavelength  $\lambda = 300$  nm and the second peaks in the visible spectral region above the wavelength of  $\lambda = 430$  nm. The first set of peaks for both real and imaginary parts are blue shifted as  $\beta$  decreases and second sets of peaks are red shifted as  $\beta$  decreases. The first and second sets of peaks arise due to the coupling of the surface plasmon oscillations of the silver shell at the inner semiconductor/metal ( $Fe_3O_4/Ag$ ) interface and outer (Ag/host matrix) interface, respectively.

Furthermore, it is found that the values of both  $\alpha'_{eff}$  and  $\alpha''_{eff}$  increases as the value of the core radius  $a_c$  is decreased (or equivalently as the metal fraction  $\beta$  is increased). Besides, the first set of resonance peaks are less intense than the second set of peaks. This may be explained with the fact that the surface area of the outer surface (Ag/host matrix interface) of the Ag shell is larger than that of the inner surface area (magnetite/Ag interface), and hence large number of carriers available at the outer interface than the inner.

Moreover, the analysis shows that when \_ is increased, the first set of peaks in the UV region are red-shifted which is mainly attributed to the decrease of the size of the NPs, i.e., the semiconducting  $Fe_3O_4$  core. Conversely, the second set of peaks are blue-shifted when  $\beta$  is increased, due to an increase in the thickness of the metallic shell. Certainly, the two resonance peaks corresponding to each NPs become closer and closer to each other as  $\beta$  is increased indicating that the metallic shell plays the dominant role in determining both the real and imaginary parts of the electric polarizability.





FIG. 3: The real a) and imaginary b) parts of the electric polarizability versus wavelength for different values of  $\varepsilon_h$ ; with  $\beta = 0.725$  and as = 10 nm fixed constant.

Similarly, the graphs of  $\alpha'_{eff}$  and  $\alpha''_{eff}$  as a function the wavelength of the incident EMW for the spherical nanoinclusions for different values of dielectric function of the host,  $\varepsilon_h$  and fixed values of  $\beta = 0.725$  and  $a_s = 10$  nm are shown in Fig. 3. From the Figures it is obvious that both  $\alpha'_{eff}$  and  $\alpha''_{eff}$  possess two set of resonance peaks - the first in the UV region in the vicinity of the wavelength  $\lambda = 300$  nm and the second peaks in the visible spectral region above the wavelength of  $\lambda = 450$  nm. The first and second sets of peaks are red-shifted as  $\varepsilon_h$  increases.

Likewise, it is found that the polarizabilities,  $\alpha'_{eff}$  and  $\alpha''_{eff}$ , increases in the second set of peaks, while no significant change take place in the first set of resonance peaks as the value of the  $\varepsilon_h$  increases. Besides, second set of resonance peaks are more pronounced than the first set of peaks. Note also that when  $\varepsilon_h$  is increased, the two sets of resonance peaks far apart each other, for both the real and imaginary parts of the polarizability (see Fig. 3), gets more pronounced in the second peaks than the first.

#### 4.2. Absorption Cross-Section

The absorption cross-section of  $Fe_3O_4$ @Ag core-shell spherical nanoinclusions are numerically analyzed using Eq. (21) together with the corresponding expressions for  $\alpha_e$  and  $\alpha_m$ , i.e., Eqs. (14) and (20). The absorption cross-section ( $\sigma_{abs}$ ) of the spherical nanoinclusions as a function of the wavelength of the incident EMW for different values of  $\beta$  and  $\varepsilon_h$  as shown in the Figs. 4a) and b). The graphs possess two sets of resonance peaks – the first set of peaks in both cases are located in the vicinity of  $\lambda = 300$  nm in the UV region which are attributed to the interaction at the inner ( $Fe_3O_4/Ag$ ) interface. The second set of peaks are found above the wavelength of  $\lambda = 450$  nm all in the visible spectral region, which are corresponds to the resonances at the outer (Ag/host) interface. As  $\beta$  increases, the two sets of peaks gets far apart from each other accompanied with a spectral shift towards lower wavelengths in the first set of peaks and shifted to the higher wavelengths in the second set of peaks (see Fig. 4a)). The peak values of  $\sigma_{abs}$  are found to be more pronounced in the second set of peaks than the first set of peaks.

As it seen from the graphs, the effect of a rapid onset of strong absorption, occurring in the UV regions for all dielectric medium/host  $\varepsilon_h$ , is dependent on the particles size. That is, when the value of  $\beta$  is increased, the absorption peaks sharply drops (less intense) for both the first and second peaks (see Fig. 4a) for a constant  $\varepsilon_h = 1.77$ . On the other hand, for a particular value of  $\beta = 0.725$ , the absorption cross-section for both the first and second sets of peaks sharply increases as  $\varepsilon_h$  increases and red-shifted as shown in Fig. 4b.





FIG. 4: The absorption cross-section versus wavelength a) for different values of  $\beta$  and b) for different values of  $\varepsilon_h$ ; with f = 0.003 and  $a_s = 10$  nm.

#### 4.3. Scattering Cross-Section

Figures 5a and b depict the scattering cross-section as a function of the wavelength of the incident EMWs for different values of  $\beta$  and  $\varepsilon_h$ . In each figures there are two sets of resonance peaks. The first set of resonance peaks positioned near to  $\lambda = 300$  nm in the UV region and is associated with the inner (magnetite/Ag) interface. The second set of peaks which are connected to Ag/host interface are located above the wavelength of  $\lambda = 450$  nm all in the visible spectral region. Figure (5a illustrate that, scattering of light is sharply increased (more scattering takes place) in the first set of peaks than the second set of peaks and gets sharply decreased as  $\beta$  increases. Furthermore, the two sets of peaks increases as  $\varepsilon_h$  increases as shown in the Fig. 5b. From both Figs. 5a and b, it is observed that the first resonance peaks are more pronounced than the second set of peaks. As the size of the system of core/shell nanoparticles gets smaller and smaller, the metal fraction,  $\beta$ , is also decreased. This leads to the decrease in the scattering cross-sections.



FIG. 5: The scattering cross-section as a function of wavelength a) for different values of  $\beta$  and b) for different values of  $\varepsilon_h$ ; with fixed values of f = 0.003 and  $a_s = 10$  nm.

In Fig. 5a, the two sets of resonances gets closer each other as  $\beta$  decreases accompanied by the shift towards the higher energy in the second peaks and emission spectral shift to lower energy in the first peaks. Both sets of resonance peaks are red-shifted (see Figs. 5) as  $\varepsilon_h$  increased. For both figures 5a and 5b there are no noticeable peaks found in the first sets of peaks at particular values  $\beta = 0.725$  and at  $\varepsilon_h = 1.50$ . This may be due to the fact that, the absorption is more likely to dominate over scattering processes at the particular values of  $\beta = 0.725$  and at  $\varepsilon_h = 1.50$ . On the other hand, the dielectric medium at the value of  $\varepsilon_h = 1.50$  in the host matrix may affect the propagation of the incident electromagnetic wave.

#### 4.4. Extinction Cross-Section

Figures 6 depict the graphs of extinction cross-section,  $\sigma_{ext}$  as a function of wavelength for different values of  $\beta$  and  $\varepsilon_h$  for the spherical nanoinclusions. As it is seen from the graphs, the extinction cross-section possess two sets of resonance peaks. The first set of peaks for Figs. 6a and 6b, the resonance peaks are located close to  $\lambda = 300$  nm in the UV region and the first set of peaks are due to resonances at the inner (magnetite/Ag) interface. The second set of peaks are those found above the wavelength of about  $\lambda = 450$  nm all in the visible spectral region.





FIG. 6: The extinction cross-section versus wavelength for different values of a)  $\beta$  and b)  $\varepsilon_h$ ; with fixed values of f = 0.003 and  $a_s = 10$  nm.

As Fig. 6a) depicts, the two sets of resonances gets closer to each other as  $\beta$  is decreased and the spectra shift towards lower frequencies in the first set of peaks, and shift toward higher frequencies for the second set of peaks. Both sets of resonance peaks are red-shifted (see Fig. 6b as  $\varepsilon_h$  is increased.

The extinction cross-section depends on the chemical composition of the particles, their size, shape, orientation, the surrounding medium, the number of particles, and the polarization state and frequency of the incident EMWs [13]. The system of spherical core/shell nanoparticles that is considered in this study is composed of two chemically dissimilar nanoparticles - one as the semiconducting core and the other as a plasmonic shell. We found that the extinction cross-section is dependent on the size and chemical composition of the semiconducting core or the metallic shell.

#### 5. CONCLUSIONS

In this study, we investigated the effects of varying parameters like the metal fraction and host matrix on the systems of spherical core/shell  $Fe_3O_4$ @Ag nanoparticles embedded in a dielectric host matrix. It is found that the real and imaginary parts of the polarizability, absorption cross-

section, scattering cross-section as well as the extinction cross-section of the system plotted for different values of  $\beta$  and  $\varepsilon_h$  as a function of wavelength possess two sets of resonance peaks in the UV (in the vicinity of  $\lambda \sim 300$  nm) and visible (above  $\lambda \sim 450$  nm) spectral regions. These sets of peaks arise due to the coupling of the surface plasmon oscillations of silver with the energy gap of the semiconducting core at the inner ( $Fe_3O_4/Ag$ ) interface and at the outer metal/dielectric (Ag/host matrix) interface. Moreover, when  $\beta$  is increased, the first set of peaks in the UV region are which is mainly attributed the decrease of the size of the semiconducting  $Fe_3O_4$  core, while the second set of peaks are blue-shifted with an increase of  $\beta$ , due to an increase in the thickness of the metallic shell for the graphs of the real and imaginary parts of the polarizability. On the contrary, for absorption and scattering cross-sections the resonance peaks are shifted towards higher frequencies in the first peak and red-shifted for the second set of peaks as  $\beta$  increases.

Furthermore, the graphs of the real and imaginary parts of the polarizability as a function of wavelength for different values of the dielectric function of the host matrix (for fixed  $\varepsilon_h = 1.77$ ) possess two set of peaks - the first in the UV (around  $\lambda \sim 300$  nm) and the second in the visible (above  $\lambda \sim 420$  nm) spectral regions. It is found that with an increase in the permittivity  $\varepsilon_h$  of the host, the resonance peaks of  $\sigma_{abs}$ ,  $\sigma_{sc}$  and  $\sigma_{ext}$  are enhanced accompanied with a red or blue shift. In this case, both sets of peaks are shifted to higher wavelength with an increase in  $\varepsilon_h$ .

Finally, the enhancement of the optical properties of the system (spherical core/shell  $Fe_3O_4$ @Ag nanoparticles embedded in a dielectric host matrix) is because of the strong coupling of the surface plasma oscillations of the silver shell with the energy gap of the magnetic semiconducting ( $Fe_3O_4$ @Ag) nano-core. It means that the silver nanoshell strongly modifies the optical properties of  $Fe_3O_4$  nanoparticles which correspondingly modify its potential applications. The results obtained may be utilized in device fabrication and applications that integrates the plasmonic effects of noble metals with magnetic semiconductors such as  $Fe_3O_4$  in core/shell nanostructures.

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## **Declaration of interests**

The authors declare that we have no major competing financial, professional or personal interests that might have influenced the performance or presentation of the work declared in this manuscript.

Sincerely

Mr. Kinde Yeneayehu Teshale

## Availability of data and material

Raw data were generated at the wolfram Mathematica language facility. Derived data supporting the findings of this study are available from the first author upon request. The output (figures) data that support the findings of this study will be available in wolfram notebook archive (<u>https://www.notebookarchive,org</u>) and with the ORCID identifier(s) <u>https://orcid.org/0000-0002-5697-4505</u>

### **Code availability**

The software codes supporting the findings of this study are available from the first author upon request and will be available at <u>https://www.notebookarchive,org</u>.

## **Authors' contributions**

All authors contributed to the study conception and design. Material preparation, and Numerical analysis were performed by Kinde Yneayehu Teshale, Teshome Senbeta Debela and Belayneh Mesfin Ali. The first draft of the manuscript was written by Kinde Yneayehu Teshale and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

## **Ethics approval**

This Section Not applicable

## **Consent for publication**

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## Highlights

- Varying magnetic core at a fixed size of metallic shell (of radius  $a_s = 10 \text{ } nm$ ) numerical analysis is carried out
- The effect of surface plasmonic resonance by varying the dielectric function of host medium and metal fraction on the optical properties
- Graphs of extinction cross-section possesses two sets of resonance peaks
- Two sets of peaks are shifted to higher wavelength with an increase in dielectric function of host medium ( $\varepsilon_h$ ).
- Resonance peaks are found to be enhanced

## References

- Chingsungnoen, P. Chaiyachate and T. Dasri, Composite Fe<sub>3</sub>O<sub>4</sub>@Au Core-Shell Nanoparticle: Tunable and Enhancement of Optical Absorption Property, ORIENTAL JOURNAL OF CHEMISTRY, vol.33, No.(4), pp. 1642-1647 (2017).
- [2] Ezequiel R. Encina, Manuel A. Perez, Eduardo A. Coronado, Synthesis of Ag@ZnO core/shell hybrid nanostructures: an optical approach to reveal the growth mechanism, Journal of Nanoparticle Research. 15:1688 (2013).
- [3] Mehrdad Khatami, Hajar Q. Alijani, Meysam S. Nejad and Rajender S. Varma, Core@shell Nanoparticles: Greener Synthesis Using Natural Plant Products, Appl. Sci. 8, 411 (2018).
- [4] Yan Zhao, Shuanghao Li, Yong Zeng, and Yijian Jiang, Synthesis and properties of Ag/ZnO core/shell nanostructures prepared by excimer laser ablation in liquid, APL. MATERIALS 3, 086103 (2015).
- [5] E. Kheradmand, R. Poursalehi and H. Delavari, Optical and magnetic properties of ironenriched  $Fe/Fe_xO_y$ @Au magnetoplasmonic nanostructures, Applied Nanoscience, (2020).
- [6] Shweta Bhardwaj, Jim Barr, Elise Chaffin, Xiaohua Huang, and Yongmei Wang, Near-field and far-field optical properties of magnetic plasmonic core-shell nanoparticles with nonspherical shapes: Adiscrete dipole approximation study, AIP Advances, 9, 025021 (2019).
- [7] Ahmad Yazdani, Mahdi Ghazanfari and Fatemeh Johar, Light trapping effect in plasmonic blockade at the interface of  $Fe_3O_4$ @Ag core/shell, RSC Adv., 5, 40989, (2015).
- [8] Poedji Loekitowati Hariani, Muhammad Faizal, Ridwan, Marsi, and Dedi Setiabudidaya, Synthesis and Properties of  $Fe_3O_4$  Nanoparticles by Co-precipitation Method to Removal Procion Dye, International Journal of Environmental Science and Development, Vol.4, No. 3, (2013).
- [9] Luciano Carlos, Fernando S. Garcia Einschlag, Monica C. Gonzalez and Daniel O. Martire, Waste Water – Treatment Technologies and Recent Analytical Developments: Applications of Magnetite Nanoparticles for Heavy Metal Removal from Wastewater, pp 63, (2013).
- [10] Ana Rita O. Rodrigues, Joana O. G. Matos, Armando M. Nova Dias, Bernardo G. Almeida, Ana Pires, Andr M. Pereira, Joo P. Arajo, Maria-Joo R. P. Queiroz, Elisabete M. S. Castanheira and Paulo J. G. Coutinho, Development of Multifunctional Liposomes Containing Magnetic/Plasmonic *MnFe*<sub>2</sub>*O*<sub>4</sub>/Au Core/Shell Nanoparticles, Pharmaceutics, 11, 10; (2019).

- [11] Kerker, M. The Scattering of Light and Other Electromagnetic Radiation, 1st ed.; Academic Press: New York, NY, USA, 1969; pp. 2796. ISBN 978-0-12-404550-7
- [12] Papavassiliou, C.G. Optical properties of small inorganic and organic metal particles. Prog. Solid State Chem., 12, 185271, (1979).
- [13] C.F. Bohren and D.R. Huffman, Absorption and Scattering of Light by Small Particles, 1st ed.; Wiley-VCH: Weinheim, Germany, ISBN 978-0-47-129340-8 (1998).
- [14] U. Kreibig M. Vollmer, Optical Properties of Metal Clusters, 1st ed.; Springer: Heidelberg, Germany, 1995; pp. 3068. ISBN 978-3-642-08191-0
- [15] Maria Eugenia F. Brollo, Roman Lopez-Ruiz, Diego Muraca, Santiago J. A. Figueroa, Kleber R. Pirota and Marcelo Knobel, Compact  $Ag@Fe_3O_4$  Core-shell Nanoparticles by Means of Single-step Thermal Decomposition Reaction, Scientific Reports, 4, 6839, (2014).
- [16] Morones, J. R., Elechiguerra, J. L., Camacho, A., Holt, K., Kouri, J. B., Ramrez, J. T., and Yacaman, M. J. The bactericidal effect of silver nanoparticles. Nanotechnology, 16(10), 23462353. (2005).
- [17] Xu, R., Ma, J., Sun, X., Chen, Z., Jiang, X., Guo, Z., Gu, N. Ag nanoparticles sensitize IRinduced killing of cancer cells. Cell Research, 19(8), 10311034.(2009).
- [18] Challa S.S.R. Kumar, UV-Vis and PL Spectroscopy for Nanomaterials Characterizations, Springer-Verlag Berlin Heidelberg, pp. 240 (2013).
- [19] Vladimir V. Apyari, Stanislava G. Dmitrienko, Yury A. Zolotov, Unusual application of common digital devices: Potentialities of Eye-One Pro mini-spectrophotometer A monitor calibrator for registration of surface plasmon resonance bands of silver and gold nanoparticles in solid matrices, Sensors and Actuators B 188, 1109-1115 (2013)
- [20] Kinde Yeneayehu, Teshome Senbeta, and Belayneh Mesfin, Enhancement of the Optical Response of  $Fe_3O_4$ /Ag Core-shell Nanoparticles, Physica E: Low-dimensional Systems and Nanostructures, 134, 114822, (2021).
- [21] S.E. Starodubtcev, N.V. Korolev, A.F. Klinskikh, and P.A.Meleshenko, Reduced polarizability and local-field effect in selfassembled ensemble of nanoparticles, J. Nano-Electron. Phys., Vol. 5, No. 1, pp. 1-5 (2013).
- [22] J.D. Jackson, Classical Electrodynamics, J. Wiley and Sons Inc. 3rd. Ed. (1999).

- [23] H-M. Chang and C. Liao, A Parallel Derivation to the Maxwell-Garnett Formula for the Magnetic Permeability of Mixed Materials, World Journal of Condensed Matter Physics, 1, 55-58 (2011).
- [24] Gashaw Beyene, Teshome Senbeta, and Belayneh Mesfin, Size dependent optical properties of *ZnO@Ag* core/shell nanostructures, Chinese Journal of Physics 58, 235-243 (2019).
- [25] Leta Jule, Vadim Malnev, Belayneh Mesfin, Teshome Senbeta, Francis Dejene, and Kittesa Rorro, Fano-like resonance and scattering in dielectric(core)metal(shell) composites embedded in active host matrices, Phys. Status Solidi B 252, No. 12, 27072713 (2015).