



Research articles

Surface plasmon resonance enhanced light absorption and wavelength tuneable in gold-coated iron oxide spherical nanoparticle

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ABSTRACT

Surface plasmon in nano-sized particles, such as gold, silver, copper and their composites, has recently attracted a great deal of attention due to its possible uses in many applications, especially in life sciences. It is desirable for application devices with a tenability of surface plasmon wavelength and optical properties enhancement. This article presents enhanced optical light absorption and tunable wavelength in gold-coated magnetite ($\text{Fe}_3\text{O}_4@Au$ core-shell) nanoparticles embedded in water using the theoretical method of discrete dipole approximation (DDA). The absorption spectra in the wavelengths from 350 to 900 nm were found to be the spectra obtained from $\text{Fe}_3\text{O}_4@Au$ core-shell nanoparticles, and when compared with pure Fe_3O_4 nanoparticles, the surface plasmon resonance can be enhanced and tuned over the entire visible spectrum (viz. 350–800 nm) of the electromagnetic spectrum by varying the Au shell thickness (2–5 nm). Similarly, the Faraday rotation spectra can also be obtained.

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1. Introduction

The size, shape and surrounding medium dependent physical and chemical properties of nanosized materials of various natures has stimulated many investigations. For example, plasmonic nanoparticles (NPs), especially gold (Au), silver (Ag) and copper (Cu), which possess a negative real and small positive imaginary dielectric constant in thin films or nanostructures, are potential candidates for many applications, such as sensors [1], organic light-emitting devices (OLEDs) [2], organic solar cells [3–5] and photothermal applications [6], due to their localized surface plasmon resonance (LSPR). LSPR is collective oscillations of a conductor's surface electrons at the interface between the metal NPs, which are much smaller than the incident light wavelength, and a dielectric medium under excited electromagnetic field that tends to trap optical waves near their interface [7]. The operation of the plasmonic nanoparticles in the above applications is affected by the refractive index of the metal and the surrounding medium, the particle size, and shape as well as the polarization direction of the incident light [8–13]. The metal gold is predominantly utilized as plasmonic particles for applications in life sciences due to its biocompatibility and resistance to oxidation [14,15]. In addition,

in the case of gold, there is a $d \rightarrow s$ interband transition that exhibits LSPR in the visible region and shifts it to the near-infrared region (NIR) of the electromagnetic spectrum [16]. Magnetic nanoparticles, for instance, magnetic iron oxide (magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles) are of a great scientific and technological interest. Fe_3O_4 NPs display superparamagnetic behavior and quantum tunneling of magnetization, and can be considered as single-domain particles [17]. Therefore, they offer high potential for several biomedical applications, such as magnetic resonance (MR) imaging [18]. However, a single component nanomaterial is usually limited to only the single unique property of the active ingredient. To obtain more properties, in recent years, fabrication of two different types of materials, such as nanoparticles composed of Fe_3O_4 cores with Au shell, is performed to bring them together into multifunctional structures [6,19–21]. This work will theoretically present the utilization of surface plasmon resonance by incorporating plasmonic material onto the surface of magnetic materials to enhance the magneto-optical effect and light absorption by means of discrete dipole approximation (DDA). It is one of the most frequently used numerical methods for computing optical properties, such as scattering and absorption by arbitrary size and shape nano-geometry [22]. This study will contribute to a better understanding of the uses of the multifunctional nanocomposites for enhancing optical absorption in specific applications.

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2. Computational details

DDA is a numerical method for calculating the optical properties of materials by approximating each nanoparticle as a point dipole [22]. When the coordinates and polarizabilities of the individual dipoles are known, the scattering, extinction and absorption cross-section spectra of the whole structure can be solved. The basis of the DDA method is that the polarization of the element due to interaction with a local electric field $\vec{E}_{\text{loc}}(\vec{r}_j)$ will be given by $\vec{P}_j = \tilde{\alpha}_j \vec{E}_{\text{loc}}(\vec{r}_j)$, where $\tilde{\alpha}_j$ is the polarizability tensor of the nanoparticle. The local electric field can be calculated using

$$\vec{E}_{\text{loc}}(\vec{r}_j) = \vec{E}_{\text{inc}}(\vec{r}_j) - \sum_{j \neq k}^N \tilde{A}_{jk} \vec{P}_k, \quad (1)$$

where $\vec{E}_{\text{inc}}(\vec{r}_j) = E_0 \exp(i\vec{k} \cdot \vec{r}_j - i\omega t)$ is the incident electric field. The second term in Eq. (1) is the sum of the electric field emitted by all neighboring dipoles at the point \vec{r}_j . After solving \vec{P}_j of each particle, the incident electric field can be obtained using the system of $3N$ linear equations

$$\vec{E}_{\text{inc},j} = \sum_{k=1}^N \tilde{A}_{jk} \vec{P}_k, \quad (2)$$

where \tilde{A}_{jk} is the interaction matrix,

$$\tilde{A}_{jk} = \frac{e^{ikr_{jk}}}{r_{jk}} \left[\kappa^2 (\hat{r}_{jk} \hat{r}_{jk} - \tilde{I}_3) + \frac{ikr_{jk} - 1}{r_{jk}^2} (3\hat{r}_{jk} \hat{r}_{jk} - \tilde{I}_3) \right]. \quad (3)$$

Here, r_{jk} is the distance between two particles of j and k , \hat{r}_{jk} is the unit vector in the direction of r_{jk} , κ is the wave number and \tilde{I}_3 is the 3×3 identity matrix. In case of $j = k$, the interaction matrix can be reduced to

$$\tilde{A}_{jj} = \tilde{\alpha}_j^{-1}. \quad (4)$$

Finally, the absorption cross-section can be obtained as following

$$C_{\text{abs}} = \frac{4\pi k}{|E_0|^2} \sum_{i=1}^N \left\{ \text{Im} \vec{P}_i \cdot (\tilde{\alpha}_i^{-1})^* \vec{P}_i - \frac{2}{3} k^3 |\vec{P}_i|^2 \right\}. \quad (5)$$

The symbol ** in Eq. (5) represents the conjugate of a complex variable and E_0 is the amplitude of incident electric field. In this paper, however, the DDA method was utilized to calculate the magneto-optic of Fe_3O_4 @Au core-shell NP embedded in water, shown in Fig. 1. The spherical nanocomposite materials consisting of a Fe_3O_4 core coated by a gold film with the shell thickness of t_{Au} .

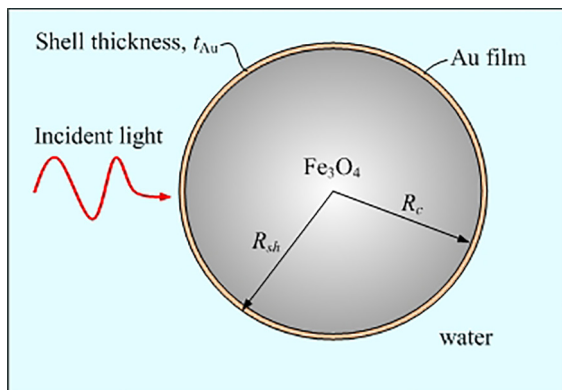


Fig. 1. Fe_3O_4 @Au core-shell structure and parameters.

The size of particles is assumed to be much less than the wavelength of light. R_{sh} and R_c are the radius of shell and core and ϵ_m is the dielectric constant of the surrounding medium, which throughout this work was assumed to be water with a dielectric constant of 1.77. In this calculation, the dielectric constants for Fe_3O_4 were taken from Ref. [23] and the dielectric constants for Au NP were obtained from Ref. [24]. The calculation process was as follows. Firstly, the composite particle's dielectric function $\tilde{\epsilon}$ was calculated using [25]

$$\tilde{\epsilon} = R_{\text{sh}}^3 \frac{(\epsilon_{\text{sh}} - \epsilon_m)(\epsilon_c + 2\epsilon_{\text{sh}}) + (1-g)(\epsilon_c - \epsilon_{\text{sh}})(\epsilon_m + 2\epsilon_{\text{sh}})}{(\epsilon_{\text{sh}} + 2\epsilon_m)(\epsilon_c + 2\epsilon_{\text{sh}}) + (1-g)(2\epsilon_{\text{sh}} - 2\epsilon_m)(\epsilon_c - \epsilon_{\text{sh}})}, \quad (6)$$

where g is the volume fraction of the shell layer $= 1 - R_c^3/R_{\text{sh}}^3$, ϵ_{sh} and ϵ_c are the dielectric constant of the shell and core.

The method of calculating results was based on Ref. [26]. The magneto-optical materials lie in the presence of antisymmetric off-diagonal components in the dielectric tensor. Therefore, off-diagonal components of the dielectric tensor are non-zero. For a magnetized direction parallel to the propagation direction of incident light, the dielectric tensor can be calculated using the following equation [26,27],

$$\tilde{\epsilon} = \begin{pmatrix} \epsilon_{xx} & i\epsilon_{xy} & 0 \\ -i\epsilon_{xy} & \epsilon_{xx} & 0 \\ 0 & 0 & \epsilon_{xx} \end{pmatrix}, \quad (7)$$

where ϵ_{xx} and ϵ_{xy} are the diagonal and off-diagonal components, respectively. In order to use the Claussius–Mossotti equation for determining the polarizability in the DDA method, the dielectric tensor in Eq. (7) must be diagonalized by transforming to the right-left (rl) circularly polarized coordinate system [26]:

$$\tilde{\epsilon}^{rl} = f^{-1} \tilde{\epsilon} f, \quad (8)$$

where,

$$\tilde{f} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 & 0 \\ -i & i & 0 \\ 0 & 0 & \sqrt{2} \end{pmatrix}. \quad (9)$$

Then, the Claussius–Mossotti principle for calculating the polarizability of the sphere in this coordinate system can be obtained [26] as

$$\alpha_{j,u}^{rl} = R_{\text{sh}}^3 \frac{\epsilon_{j,u}^{rl} - \epsilon_m}{\epsilon_{j,u}^{rl} + 2\epsilon_m}, \quad (10)$$

where subscript u represents the diagonalized component (right, left, and z). Transforming the matrix \tilde{A}_{jk} and the vectors \vec{P}_j and $\vec{E}_{\text{inc}}(\vec{r}_j)$ into the circular coordinate system with Eq. (9), Eq. (2) becomes

$$\sum_{k=1}^N \tilde{A}_{jk}^{rl} \vec{P}_k^{-rl} = \vec{E}_{\text{inc}}^{-rl}(\vec{r}_j), \quad (11)$$

with $\tilde{A}_{jj}^{rl} = (\tilde{\alpha}_j^{rl})^{-1}$. Solving Eq. (11) for the polarization \vec{P}_j^{rl} , an effective polarizability can be determined. The Faraday rotation spectra can be calculated from the dielectric components which were found by using the inverse of the Claussius–Mossotti relation [25–27]

$$\theta_F = \frac{\pi}{\lambda} \text{Re} \left(\frac{\tilde{\epsilon}_{xy}}{\sqrt{\tilde{\epsilon}_{xx}}} \right) \quad (12)$$

where $\tilde{\epsilon}_{xx}$ and $\tilde{\epsilon}_{xy}$ are the effective diagonal and off-diagonal components in Cartesian coordinates, respectively. Similarly, the absorption cross section can be calculated by using Eq. (5).

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