Investigating of LSPR spectra on a hybrid Fe$_3$O$_4$-Au within core-shell structure

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Abstract. In this study, we have investigated the tunability of localized surface plasmon resonance (LSPR) spectra of the magneto-plasmonic system composed of Au-coated Fe$_3$O$_4$ (Fe$_3$O$_4$@Au) by public optical simulation, MNPBEM based on boundary element method calculation. The magneto-plasmonic system is modeled nanorod core-shell structure with three different core’s aspect ratio: 2.3, 4.3, and 6.3. The nanoparticle was immersed in water (1.33+0i). Then, we applied the electromagnetic field in parallel and perpendicular to the long axis of nanorod. Interestingly, the peak of LSPR spectra Fe$_3$O$_4$@Au shows blue-shifted at gold thickness toward around ~50 nm and as the gold-shell keep growing, a red-shifted can be occurred on greater than ~50 nm of thick gold-shell. The peak of LSPR spectra shows to shift to lower wavelength or blue-shift and produce narrow width spectra.

Based on the result, we believe our observation can be utilized for tuning LSPR spectra from visible range to near-infrared such as photocatalysis application and biosensing with well-controlled of thicknesses.

1. Introduction

In the last two decades, modifying the localized surface plasmon resonance (LSPR) of a composite system composed of noble metals (Au, Ag, and Cu) and ferromagnetic metals (nickel, iron, cobalt, and their alloys) has been extensively investigated [1]. LSPR phenomena have extraordinary potential applications ranging from bioscience, quantum optic, medicine, and imaging equipment such as magnetic resonance imaging [2], multimodal-imaging and cancer therapy [3]. In noble metals, the plasmonic resonance noticeable in visible to near infrared region, while not all ferromagnetic metals support plasmon resonance, specifically Iron(III)-Oxide (Fe$_3$O$_4$). However, Fe$_3$O$_4$ has a huge advantage such as can be easily changed the orientation by induced magnets for capture analytes [2], as an important key on magnetic resonance imaging [2,4], and sensor application with surface treatment [4] because of this element well-known to oxidize and corrosive.

Since the earlier discovery on the synthesis of Fe$_3$O$_4$ coating noble metal by Carpenter et al. [5,6], coating technique is an essential part in order to face the future challenging of both optical and magnetic properties. Meanwhile, these properties also might be achieved by altering size, shape, structure, and so forth. Many researchers have been dealing with ferromagnetic metal coating noble metal, Lingyan et al. develop a sequence synthesis method of gold shell in surface’s Fe$_3$O$_4$ with high
monodispersity and controllable [7]. Gole and co-worker did gold 1D nanostructure shielding of Fe₃O₄ [8], and Song et al. reported the synthesis of magnetoplasmonic (Ag-coated Fe₃O₄) nanochain aimed to tune their optical anisotropic band (longitudinal and transverse mode) in the range visible to near infrared by controlling interparticle gap [9].

Here, we report the computational studies of nanoparticle Au-coated Fe₃O₄ within core-shell structure to obtain the tunability of LSPR core-shell structure in the visible to near infrared. We used Fe₃O₄ within magnetite phase due to its possibility to utilize as a photocatalytic activity and biomedicine based on ferromagnetic material. Also, we provided the understanding of transition blue-shift to red-shift in two modes of excitation (longitudinal and transverse mode) to consider a minimum and effective shield of gold.

2. Simulation procedure
The calculation was carried out by electrodynamic simulation package, Metallic Nanoparticle Boundary Element Method (MNPBEM), developed by Hohenester et al. [10]. The geometry of nanoparticle presented in figure 1, where the aspect ratio (L/D) of core are 2.3, 4.3 and 6.3. Then, the thickness of shell come into 4 nm to 16 nm for small thicknesses and 20 nm to 100 nm for bigger thicknesses. Furthermore, the dielectric function of gold and Iron(III)-Oxide collected from Johnson & Christy experiment’s [11] and M. R. Querry’s work [12], respectively. The phase of Iron(III)-Oxide is magnetite. The nanoparticle core-shell structure immersed in water (1.33+0i). Then, we applied the electric field excitation in parallel and perpendicular to the long axis of nanorod. From this simulation, we have obtained LSPR spectra consist of scattering $C_{scat}$, absorption $C_{abs}$ and extinction $C_{ext}$ cross section follows equation (1)-(3). For this study, we used the extinction cross section to present LSPR spectra of nanorod model.

$$C_{scat} = n_b \oint_{\partial \Omega} \Re \{ \hat{n} (E \times B^*) \} \, da$$

$$C_{ext} = -\frac{1}{n_b} \oint_{\partial \Omega} \Re \{ \hat{n} (E \times B_{inc}^* + E_{inc}^* \times B) \} \, da$$

$$C_{abs} = C_{ext} - C_{scat}$$

where $n_b$ is background refractive index, $E$ and $B$ are scattered electromagnetic fields, $E_{inc}$ and $B_{inc}$ are incident electromagnetic fields of the planewave excitation.

![Figure 1](image.png)

**Figure 1.** The diagram illustration of nanorod core-shell system. The aspect ratio is the ratio of length (L) divided to diameter (D). The thickness of shell indicated by t (yellow color).

3. Result and Discussion
The spectra of extinction cross section of Fe₃O₄ nanorod with aspect ratio 2.3, 4.3, and 6.3 coating gold nanorod within core-shell structure was presented in figure 2. Increasing the thickness of gold-shell led to shift the resonance peak to lower wavelength or blue-shift and increased significantly intensity of Fe₃O₄. Nonetheless, as the gold-shell thicker the resonance peak shift to higher wavelength.
In fact, the red-shifted mainly due to increase the volume of particle (Fe$_3$O$_4$@Au) rather than increase the thickness of gold-shell, in other word, decreasing of the coupling plasmon resonance energy in the inner (a cavity between Fe$_3$O$_4$ and Au) and other shell (interface of gold and water) [13]. Prodan et al. reported on core-shell structure the resonance peak will split into two resonances as a manifestation of hybridization mode, coupled (red-shifted) and anticoupled (blue-shifted) plasmon resonance that appeared at outer shell and inner shell [14-16]. These mode energy strongly depends on the thickness of gold on both mode of excitation: Longitudinal Plasmon Mode (LPM) and Transverse Plasmon Mode (TPM). In this case, our spectra clearly seem correspond to dominant anticouple mode for LPM in range 10 nm to 50 nm of gold-thickness while coupled and anticoupled mode coexist on TPM for definite range of thickness.

Furthermore, an AuNR which have a similar size to Fe$_3$O$_4$ (AR 2.3) pure occurs at 659 nm for LPM and 518 nm for TPM. The LPM’s redshift will be observed by increasing the aspect ratio to 4.3 and 6.3 with peak maxima of 857 nm and 1057, respectively. On the other hand, a blueshift occurred at TPM with resonance peak 511 nm and 509 nm, respectively. Moreover, by increasing the gold thickness of Fe$_3$O$_4$@Au from 4 nm to 50 nm produce a blueshift of respective LPM and TPM from 1201 nm to 675 nm and 1029 nm to 594 nm for cores’s aspect ratio 2.3, 1248 nm to 697 nm and 880 nm to 561 nm for cores’s aspect ratio 4.3, and 1301 nm to 710 nm and 799 nm to 529 nm for core’s aspect ratio 6.3. Our results agree with previous studies by Prodan et al. [14], Prashant et al. [17], and Elyahb and co-worker both computational and experimental studies [18]. This result also suggests that coating Fe$_3$O$_4$ with noble metal can be enormously enhanced the absorption losses of ferromagnetic metal as show as increases its intensity of spectra [4]. From the calculation, the intensity coefficients TPM is twofold higher than LPM of Fe$_3$O$_4$@Au for gold-shell thickness from 4 nm to 50 nm.

Figure 2. The extinction spectra of Fe$_3$O$_4$@Au in longitudinal mode (upper-row) and transverse mode (lower-row) with various thickness of gold-shell. All spectra also compared with gold nanorod/AuNR (black line) and Fe$_3$O$_4$ pure (red line).
Figure 3. Fractional shifts of LSPR as a function of ratio gold-shell thickness \((t)\) and dimension of interest in longitudinal mode \((t/L)\) (upper row) and transverse mode \((t/R)\) (lower row) excitation. The simulation result and fitting denoted by dots and color lines, respectively. The inset figure shows the cut-off of gold-shell or the transition from blue-shift to red-shift denoted by vertical dash line.

In figure 3 shows the fractional shifts of resonance peak as a function of ratio gold thickness to core’s length \((t/L)\) for LPM and also gold thicknesses to core radii \((t/R)\) for TPM of Fe₃O₄@Au core-shell structure with three different aspect ratio of core. We have carried out fitting method using universal scaling equation to compare two excitation mode properties

\[
\frac{\Delta \lambda}{\lambda_0} \approx k e^{-\frac{x}{\tau}}
\]

where \(\frac{\Delta \lambda}{\lambda_0}\) is fractional plasmon shift and represents near-field coupling strength, while \(\lambda\) is associated with resonance peak of core-shell and \(\lambda_0\) is the pure-gold’s LSPR, \(k\) is constants represents the maximum plasmon shift, it constants does affect on properties of particles, \(\tau\) is a decay constant as reveal as near-field coupling depth, and \(x=t/L\) for LPM and \(x=t/R\) for TPM (\(t\) = thickness). The exponential fitting values depicted in the table 1.

| Aspect ratio (AR) | Constants \((k)\) | Decay length \((\tau)\) | Cut-off gold-shell (nm) |
|------------------|-------------------|------------------------|------------------------|
|                  | LPM               | TPM                    | LPM                    | TPM                    |
| 2.3              | 1.01              | 0.83                   | 0.050                  | 0.13                   | 59                     | 78                     |
| 4.3              | 0.90              | 0.73                   | 0.047                  | 0.22                   | 59                     | 59                     |
| 6.3              | 0.79              | 0.65                   | 0.046                  | 0.31                   | 56                     | 59                     |

Next, in table 1 shows the data calculation result from a fitting method using universal scaling equation. The two modes of excitation indicating that there was a slight difference of constant \((k)\) and noticeable value of decay length \((\tau)\). The constant \((k)\) are quite different in each aspect ratio and it
suggests that increasing aspect ratio’s core will decrease the maximum shift of LSPR coupled and anticoupled mode, consistent with the resonance spectra in figure 1 which are lower aspect ratio’s core more redshift than bigger one, indeed, TPM has smaller maximum shift than LPM. The decay length \( r \) of LPM does not many changes, it has value around \( \sim 0.05 \). Previous works did by Prashant et al., [17] and Nordlander et al. [19] also shown that decay length of complex structure (i.e. dimer, trimer, dimer core-shell, etc) have similar value around \( \sim 0.2D \) (\( D \) is dimension of disk/sphere/elongated-sphere), they conclude that decay length is independent to shape, size, and structure of particle. Interestingly, our works noticeable a significant decay length value, in which LPM (\( \sim 0.05 \)) has a very smaller decay length than TPM (\( \sim 0.2 \)). From the relation \( x=t/L \) and \( x=t/R \), we can derive the maximum thickness of gold-shell as shown in inset figure 3 using logarithmic scale on both \( y \) and \( x \) axis and present it on table 1. Based on our results, it shows that increasing aspect ratio, however, decreasing the cut-off gold-shell, then particle (\( \text{Fe}_3\text{O}_4@\text{Au} \)) becomes like gold pure.

4. Conclusion
In conclusion, we have successfully investigated the LSPR on magneto-plasmonic core-shell structure with raw materials gold (shell) and \( \text{Fe}_3\text{O}_4 \) (core). Gold-coated \( \text{Fe}_3\text{O}_4 \) can be enhanced the optical loss absorption of \( \text{Fe}_3\text{O}_4 \). A blue-shift of the spectra ranging from near infrared to visible range can be tuned by increasing the gold thickness. However, after gold-shell reach the maximum thicknesses, the LSPR will shift to lower energy. Moreover, aspect ratio (\( L/D \)) of core (\( \text{Fe}_3\text{O}_4 \)) has a crucial part in order to determine the cut-off thickness of gold-shell. This cut-off also implies coupling strength between surface and cavity plasmon resonance, in which to utilized for magnetic resonance imaging application.

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