doi:10.20944/preprints202104.0435.v1

Article

Plasmonic Properties of Bimetallic Quantum Dot Ag@Au Core-Shell Nanostructures Embedded in Non-Absorptive Host Medium

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Abstract: **T**his studies the plasmonic properties of the bimetallic quantum dot Ag@Au core-shell nanostructures embedded in the non-absorbent host medium. Local field enhancement factor and coefficient of absorption of Ag-core and Au-shell are primarily studied based on quasi-static approximation of classical electrodynamics for 6-10 nm composite radius. In this quantum dot geometry, two set of plasmonic resonances in visible spectral region are observed: the first resonance associated with inner interface of gold (Ag@Au) and the second resonance associated with outer interface of gold (Au@medium). The two plasmonic resonances are close each other and enhanced when the size of composite decreased for a fixed core size while shifted to in opposite direction and the amplitude of peak decreased when the core size is increased for a fixed composite size. For the optimized size of core/composite or shell thickness and other parameters to the desired values, such type of composites are recommended for various applications like; photocatalysis, biomedical, nano-optoelectronics.

Keywords: *Core-Shell, Spacer, Host-Medium, Bimetallic, Enhancement Factor, Dielectrics Function*

1. Introduction

Core-shell nanoparticles (CSNPs) are a composite form consisting of more than one material: one as a core and the other as a coat using encapsulation process with different geometry and sizes for a particular application in order to acquire new materials with combined and/or other specific properties not shown by the components [1-5]. The core or/and shell martials can be one of the following materials: metal, semiconductor, dielectrics or organic/inorgamnic materials [2, 6, 7]. From different combination of core-shell nanostructures, metal@metal core-shell nanocomposites have novel properties for various applications. This new or special characteristics arise mainly from the interaction between metallic (plasmonic) materials and the incident electromagnetic field, which is very important Enhanced by the so-called surface plasmon resonance (SPR) phenomenon and the interaction of metal shell plasmons with metal interior material [8]. At the SPR frequencies, the collective oscillations of the conducting electrons in the metallic nanoparticle are driven by incident resonant light, which act as electric radiating dipoles.

Two layer of bimetallic core-shell nano-structure (CSNS) is studied for the desire applications either experimentally [9-11] and theoretically [12, 13]. Due to their peculiar properties and possible applications in catalysis, electronics, optoelectronics, information storage, bio-sensors, optical sensor, and surface enhanced Raman spectroscopy, bimetallic core-shell nanostructures have attracted tremendous attention. Metallic core-shell nanoparticles of quantum dot size have optical features due to the SPR excitations. In the present study, the author reported the plasmonic response of the composite consists from the most applicable and has noble properties materials: Ag as a core and Au as a shell for a quantum dot size. There is an investigation into the properties and applications of nobel metal@metal to the best of our knowledge, but there is no further investigation into the local filed enhancement factor and the absorption coefficient for Ag@Au CSNSs of quantum dot size. Monometallic nanoparticles have a drawback for a certain or appropriate applications; so, to modify or generate new properties for the desired applications it should be combined with other noble materials. By considering the noble properties and potential/versatile applications into account, the efforts are being made for plasminic properties of Ag coated by one of noble metal Au. Ag and Au NPs were most extensively investigated for their high catalytic, universal bio-compatibility, optical sensitivity, simple preparation, oxidation resistance, and surface plasmon resonance (SPR) band that can absorb and scatter visible light relative to other noble metals [10, 14, 15]. The plasmonic resonance of small size bimetallic Ag and Au tuned from visible to near-infrared (N-IR) spectral region [10, 16, 17]. Due to this noble properties and applications of Ag and Au NPs, core-shell combination of these materials is a desirable way to generate new/unique properties and enhanced applications.

The paper is organized as follow: In Sect. 2, theoretical description of bimetallic quantum dot Ag@Au core-shell NPs is carried out using the electrostatic approximation. Numerical analysis and results are presented in Sect. 3. Finally, in Sect. 4 concluding remarks are given2. Materials and Methods.

2. Materials and Methods

Consider two layered core-shell nanoparticle (NP) consisting of a semiconductor core (Ag) of dielectric function (DF) ε_c, and a metallic (Au) shell of DF ε_s embedded in a non-absorptive host matrix having a real DF ε_m. The radius of core and shell is r_c and r_s, respectively, in which the volume fraction shell to the composite is $\rho = 1 - (r_c/r_s)^3$ as depicted FIG.1. When the composite of two layered CSNP is irradiated (placed in) with an electromagnetic radiation, electric field is induced in the system due to polarization.

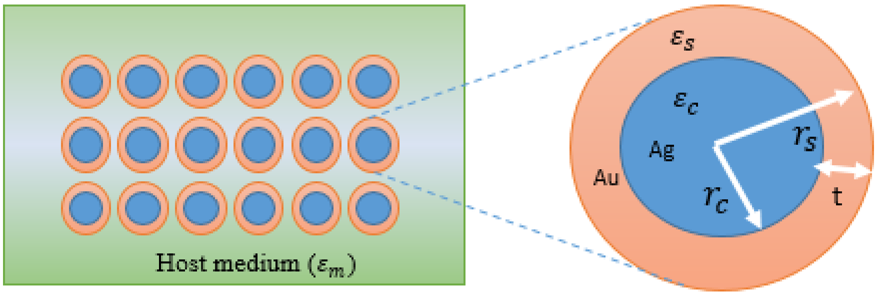

FIG. 5: (Color online) The array of Ag@Au CSNSs embedded in the non-absorptive dielectrics host medium (left side) and cross-sectional view of nanoinclusion (right side).

In a uniform external electric field, a metallic object becomes polarized. In far field, the polarized object can be approximated as an electric dipole because the higher order field components decay quickly as a function of distance [18].

The electric dipole movement of the composite can be expressed as [19],

$$\tilde{p} = \varepsilon_m \alpha E_0, \qquad \textbf{(1)}$$

where E_0 external applied electric field and α is the polarizability of the system (core-shell+host medium) given by,

$$\alpha = 4\pi \left[\mathbf{1} - \frac{3}{2} \left[\frac{\boldsymbol{\varepsilon_m} \left[\boldsymbol{\varepsilon_c} + \boldsymbol{\varepsilon_s} \left(\frac{3}{\boldsymbol{\rho}} - \mathbf{1} \right) \right]}{\boldsymbol{\beta}} \right] \right] \boldsymbol{r_s^3}. \qquad \textbf{(2)}$$

The variable in Eq.2 is

$$\beta = \boldsymbol{\varepsilon_s^2} + \boldsymbol{C\varepsilon_s} + \boldsymbol{\varepsilon_c\varepsilon_m}, \qquad \textbf{(3)}$$

where

$$C = \left(\frac{3}{2\rho} - 1\right)\varepsilon_c + \left(\frac{3}{\rho} - 1\right)\varepsilon_m \qquad (4)$$

For simplicity, from FIG. 1, assume a Drude model metal which will be adequate for certain simple and noble metals within the appropriate ranges of light frequencies**.** The Drude model provides an effective description of the free carrier response in metals. Hence, we can write the metal silver (Ag) and gold (Au) dielectric function from the Drude Model as [20]:

$$\varepsilon_s(\omega) = \varepsilon_\infty - \frac{{\omega_p}^2}{\omega[\omega + i\omega_0]} \qquad (5)$$

where ε_∞ is the phenomenological parameter describing the contribution of bound electrons to polarizability, ω_p is the bulk plasmon frequency, ω_0 is the damping constant of the bulk material, for Ag, $\varepsilon_\infty = 4.5$ **,** $\omega_0 = 0.072\ eV$ = and $\omega_p = 9.02\ eV$ [12, 19] and Au**,** $\varepsilon_\infty = 9.84$ **,** $\omega_0 = 0.011\ eV$ = and $\omega_p = 9.62\ eV$ [5, 21].

3. Results and Discussions

The quasi-statics approach method is ideal for measuring polarizability for the small dimension of composite less than the wavelength of incident light. Of small size composite, the incident electric field can be considered spatially uniform over the entry of the particle, such that the particle may be replaced by an oscillating dipole and this is called the quasi-static approximation.

3.1. Local Field Enhancement Factor

The intensity of applied electric field inside the core-shell nanocomposite can be enhanced due to the difference between the dielectrics properties of the two interfaces Ag/Au and Au/host-matrices as well as surface plasmon resonance of Ag/Au. The field enhancement factor is defined as the ratio of electric field intensity around the composite to applied electric field intensity. The local field enhancement factor (LFEF) ($|\eta|^2$) of the nano-composite is expressed as in the form [22],

$$|\boldsymbol{\eta}|^2 = \frac{|\boldsymbol{E}|^2}{|\boldsymbol{E_0}|^2} = \left|\mathbf{1} + \frac{\boldsymbol{\alpha}}{\boldsymbol{2\pi r_s^2}}\right| \qquad \mathbf{(6)}$$

where E is electric field inside the composite, E_0 is applied electric field and r_s is the radius of the composite.

Using Eq. 6, the local field enhancement factor (LFEF) is depicted in FIG. 2. by optimizing the size of core and composite. As shown in the figure, two plasmonic resonances are observed: associated with the inner and outer interfaces of plasminic shell from left to right [23], respectively. For a fixed composite size 10 nm FIG. 2(a), when the core size decreased i.e.; increased shell thickness (t) with the corresponding volume fraction 0.27, 0.33, 0.39, 0.44, 0.49; the first resonances correspond to Ag@Au interface are enhanced and red-shifted and the second resonances correspond to Au@medium interface are decreased without shifting. The plasmonic response of the composite is also vary by changing the size of composite, when the composite size decreased for a fixed core size 8 nm as depicted in FIG. 2(b), the first resonances are decreased and shifted towards higher energy and the second resonances are enhanced without shifting. When the size of nanocomposite decreased for a fixed core size simultaneously the shell thickness (t) decreased and the correspondence volume fractions are 0.49, 0.45, 0.40, 0.35, and 0.30.

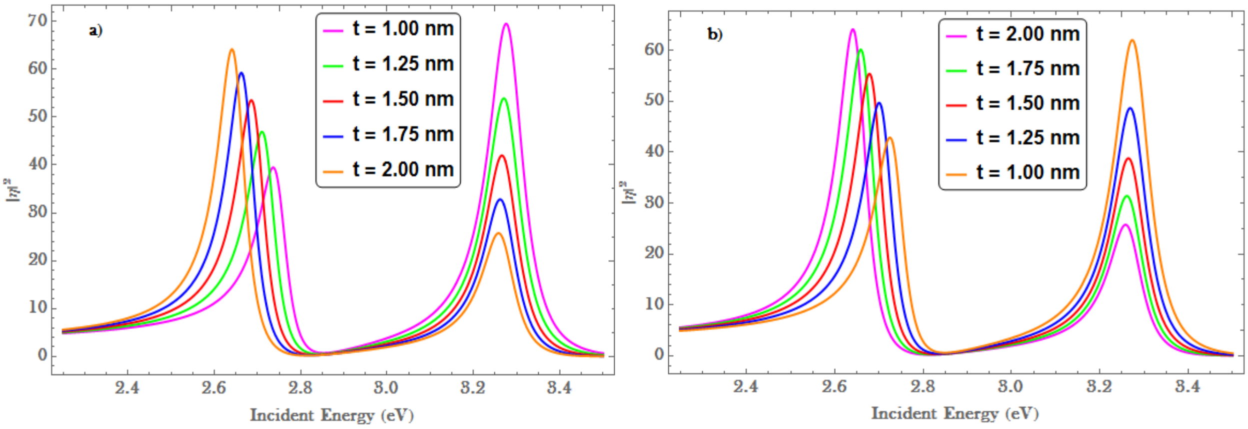

FIG. 2: (Color online) Local filed enhancement factor of Ag@Au core-shell nanostructures, (a) a decreasing core size for a fixed composite size and (b) a decreasing composite size for a fixed core size.

Among different parameters which affect the plasmonic response of core-shell nanostructures are dielectric function of host medium and the concentration of shell material (ρ, volume fraction of shell material to the composite) on the core. As depicted in FIG. 3(a), when the concentration of shell Au increased ($\rho = \sim 1$, the composite is pure Au) the first resonance is become diminished while the second resonance is enhanced. This indicates that, there is only one interaction at the interface of Au and the host medium. The other important parameter is DF of host medium which highly determine the plasmonic property of core-shell nanostructure. As shown in FIG. 3(b), all dielectrics materials including air and water are incorporated. As shown in this figure, the first resonance is more enhanced and red-shifted but the second resonance is slightly decreased.

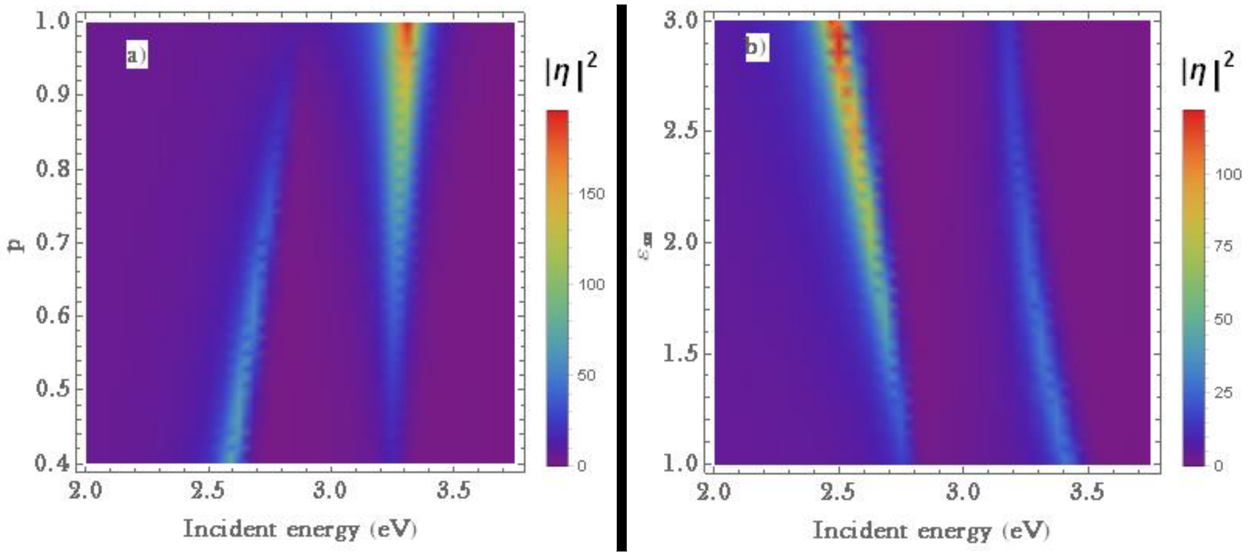

FIG. 3: (Color online) Local filed enhancement factor of Ag@Au core-shell nanostructures, (a) as a function of shell material concentration for a fixed ε_m value and (b) as a function of DF of host medium for $t = 2\,nm$.

From the result, we understood that the applied electric field is enhanced and shifted to infrared spectral region for the host medium which has high DF. The nanocomposites which have enhanced electric field near infrared spectral region can be applicable in different application areas.

3.2. Absorption Coefficient

By considering the quasi-static limit approximation method, the absorption (σ_{abc}), scattering ((σ_{scc}) and extinction coefficient ((σ_{exc}) can be modeled as the optical response and have the following relation [24],

$$\sigma_{abc} = \frac{k}{\pi r_s^2} Im[\alpha] \tag{7}$$

$$\sigma_{scc} = \frac{k^2}{6\pi^2 r_s^2} |\alpha|^2, \tag{8}$$

$$\sigma_{exc} = \sigma_{abc} + \sigma_{scc}, \tag{9}$$

where $k = 2\pi\sqrt{\varepsilon_m}/\lambda$ [2].

Incident light, in general, propagating in the composite is attenuated both by absorption and scattering [21]. The coefficient of nanocomposite depends on the size and other parameters; the absorption coefficient is more enhanced than the scattering coefficient for small size composite [25]. The diameter of Ag@Au core-shell nanostructure (20 nm) is less than the incident wavelength, so that, the absorption coefficient dominated scattering coefficient. For the quantum size core-shell nanoparticles, extinction coefficient is almost equal to absorption coefficient.

Simply the plasmonic properties core-shell nanostructure is varied due to the shell thickness or the size of core/composite. By considering these parameters in account, the paper is focused on the plasmonic response of novel material composite by optimizing core/composite size simultaneously the shell thickness.

The absorption coefficient of Ag@Au core-shell nanostructures is depicted in FIG. 4, as shown in the figure, the absorption coefficient is varied due the size of core/composite. Figure 4(a) depicted that, the first plasmonic resonances are enhanced and peak position is shifted to lower energy (red-shifted) and the second resonances are decreased without shifting when the core size decreased for a fixed composite size 10 nm. In the other hand, when the composite size decreased for a fixed core size 8 nm, the first plasmonic resonances in the visible spectral region are decreased and shifted towards higher energy (see FIG. 4(b)). The volume fractions of FIG. 4(a) and (b) for corresponding shell thickness are the same with FIG. 2(a) and (b), respectively.

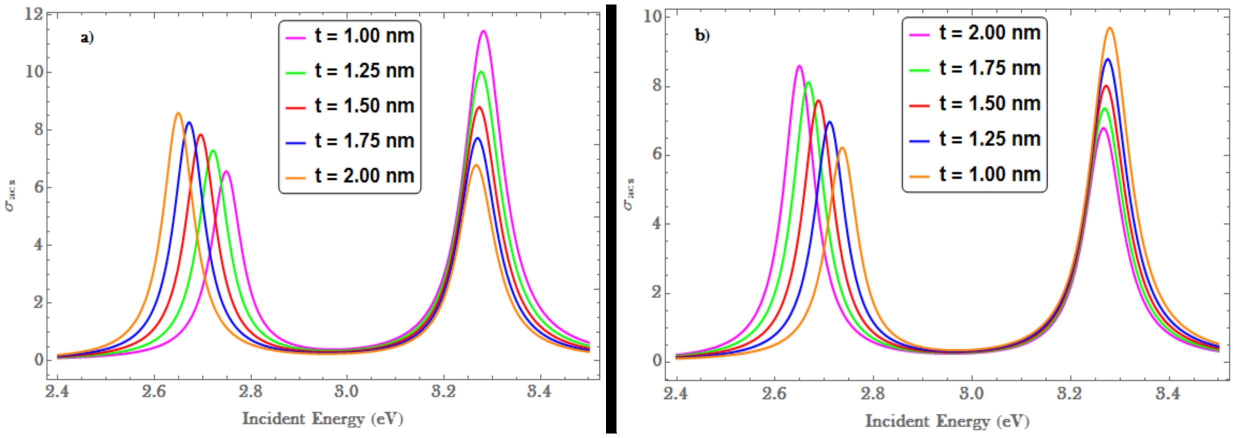

FIG. 4: (Color online) Extinction coefficient of Ag@Au core-shell nanostructures, (a) a decreasing core size for a fixed composite size and (b) a decreasing composite size for a fixed core size.

In the other case, we plotted absorption coefficient of the bimetallic core-shell nanocomposite by varying the radius of the system for a fixed shell thickness 1.0 nm. As shown in FIG. 5(a), when the dimension of Ag@Au CSNSs is decreased (from 6 nm to 10 nm), the first absorption coefficient resonances are slightly increased and shifted to higher incident photon energy. But, the second resonances in this case are enhanced without shifting. As explained in the above section, the nature of host medium is affected the plasmonic properties of bimetallic core-shell nanostructure of the absorption coefficient. When the DF of host-medium is changed the plasminic properties correspondingly its application is changed. As shown in the FIG. 5(b), the peak position of the two absorption coefficient resonances is red-shifted when the dielectrics function of host-medium is increased from 1 to 3 with range of 0.5. Similar to FIG. 3(b), the resonances associated with inner interface of Au are enhanced and more shifted than the resonances associated with outer interface.

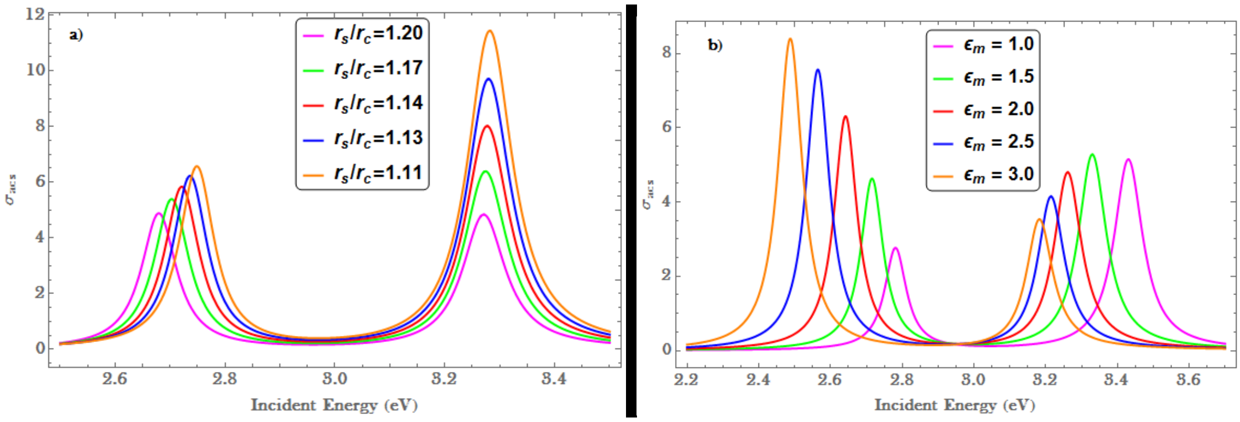

FIG. 5: (Color online) Extinction coefficient of Ag@Au core-shell nanostructures for a fixed shell thickness $t = 1.0\,nm$ (a) and the effect of dielectric function of the host-medium on the plasmonic response for a shell thickness $t = 2.0\,nm$ (b).

4. Conclusion

In this paper, by using the electrostatic approximation, I investigated local field enhancement factor (LFEF) and the absorption coefficient of Ag@Au CSNSs embedded in non-absorbent host-medium. Local filed enhancement factor and absorption coefficient as a function of incident photon energy possess two plasmonic resonances correlated with interior interface from 2.60 eV to 2.75 eV and external interface about 3.30 eV of metallic Au shell. In both cases, the first plasmonic resonances are enhanced and moved towards higher energy as the core size for a fixed composite size decreased. But, when the composite size decrease for a fixed core dimension, it decreased and shifted in the opposite direction. The second plsmonic resonances, for decreasing core size and decreasing composite size, are decreased and enhanced respectively. The first and second resonances of plasmonics are decreased and enhanced for both LFEF and the absorption coefficient when the volume fraction is increased, respectively. As the dielectric function of the host medium increases, the first plasmonic resonances of LFEF and the absorption coefficient are red-shifted and enhanced, while the second resonances are reduced and red-shifted. Note, that the results showed two layered bimetallic core-shell nanostructures are composed of a metal core Ag coated by tick Au NP can be ideal candidate for enhancing biological, solar-cell, catalysis, optical sensor, and information storage application.

Acknowledgement: This work is supported financially by the Adama Science and Technology University (ASTU).

Conflicts of Interest: The author declare no conflict of interest. The funders had no role in the design of the study; in the collection, analysis, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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