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# Enhancing Optical Properties of Triple Layered Core-Shell Nanostructures

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## ABSTRACT

In this mini review, the effect of parameters on the optical properties of triple layered core-shell nanostructure is addressed. Optical absorbance of cylindrical triple layered core-shell nanoparticles are analyzed based on quasi-statics approximation of classical electrodynamics which is embedded in the active host-medium. In this geometry, two set of plasmonic resonance are observed: in visible region associated with inner interface of gold (spacer@gold) and near/in infrared spectral region associated with outer interface of gold (gold@medium). Optical response of the system, depend on the core size, dielectrics function and thickness of spacer, shell thickness, size of the composite, filling factor, and dielectrics function of host-medium. By optimizing materials parameter to the 'desired' values, such type of composite which are highly enhanced and tuned, are recommended for various applications like senor, photocatalysis, biomedical, nano-optoelectronics.

**Keywords:** Core-shell, Spacer, Host-medium, Filling factor, Enhancement factor, Dielectrics function

## INTRODUCTION

Core-shell nanoparticles (CSNPs) consist of one core and one or more than one shell nanomaterial by using encapsulation process in different geometry and size to obtain new materials with combined and/or other unique properties neither shown by constituents [1]. CSNPs can be consisting from metal, semiconductor, dielectrics or organic/inorganic materials one is a core and another or the same material is a shell [2,3]. Among core-shell nanostructures, metallic shell nanoparticles have unique or new properties. These new or unique properties mainly arise from the interaction of metallic (plasmonic) shell materials with the electromagnetic field which is greatly intensified by a phenomenon known as the Surface Plasmon Resonance (SPR) and the interaction of Plasmon of the metallic shell with inner materials [4].

Two layered core-shell nanostructure (CSNS) is widely studied either experimentally or/and theoretically [1,5]. To fabricate new or modify optical properties and application of two layered nanoparticle, the best alternative is inserting a new material as a spacer. To the best of my knowledge, Triple layered CSNS like ZnO@M@Au (M=vacuum, water, dielectrics, semiconductor) is not further studied yet. In addition to this, the present review provides a very conceptual framework, including specific cases previously investigated. In such system, there is an interaction between exciton-exciton/polariton-plasmon in the nanoinclusion which is very interested for new properties and various applications.

In this review paper, the author reported the optical response of the composite consists from the most applicable materials like ZnO as a core and Nobel metal Au as a shell as well as other different material as spacer. The shell metal Au NP has been investigated most extensively because of its high catalytic, universal biocompatibility, optical sensitivity, facile preparation, resistance to oxidation and Surface Plasmon Resonance (SPR) band that can absorb and scatter visible light relative to other noble metals [6]. The plasmonic resonance of Au nanoshell tuned from visible to near-infrared (N-IR) spectral region [7]. ZnO NP is wurtzite zinc oxide has wide band gap (3.37 eV), high exciton binding energy (60 meV) at room temperature (RT) and high dielectric constant and it is reliable material for visible and near-UV applications [8,9]. ZnO-NP has attractive extensive attention due to its potential application in laser diodes, solar cell, field emission display, optoelectronics devices, gas sensor, photocatalysis, ultraviolet laser [8-10]. Due to this noble properties and applications of ZnO and Au NPs, core-shell combination of these materials is a desirable way to

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generate new/unique properties and enhanced applications [11].

## THEORETICAL MODEL

Consider this triple layered core-shell nanoparticle (NP) consisting of a semiconductor core (*ZnO*) of dielectric function $\varepsilon_c$, spacer (*M*) $\varepsilon_d$ and a metallic (*Au*) shell of DF $\varepsilon_s$ embedded in a non-absorptive host matrix having a real DF $\varepsilon_m$. The radius of core, spacer and shell is $r_c$, $r_d$ and $r_s$, respectively, in which the volume fraction spacer to spacer+core and shell to composite is $\beta_1=1-(r_c/r_d)^2$ and $\beta_2=1-(r_d/r_s)^2$, respectively. When the composite of triple layered CSNP is irradiated (placed in) with an electromagnetic radiation, electric field is induced in the system due to polarization.

This composite (ensemble) has its own dielectrics function called effective dielectrics function ($\varepsilon_{eff}$). The effective dielectrics function of the system written as [3]:

$$\varepsilon_{eff} = \varepsilon_m[1 + 3f\alpha/(1 - f\alpha)] \quad (1)$$

known as Maxwell-Garnett equation and where $f$ is the filling factor which tell us how much the array of composite is embedded in the host- medium and α is the polarizability of composite.

Some of the metal properties, including optical properties can be described with the simple free-electron gas Drude-Sommerfeld model of dielectric function. In the framework of this model, by applying an external field, the conduction electrons move freely between independent collisions occurring at the average rate of the frequency dependent dielectric function $\varepsilon(\omega, r_{eff})$ predicted by the Drude-Sommerfeld model [8,12,13].

$$\varepsilon_s(\omega,r_{eff}) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega(\gamma_{bulk} + A\, v_F/r_{eff})} \quad (2)$$

where $\varepsilon_\infty$ is the phenomenological parameter describing the contribution of bound electrons to polarizability, $\omega_p$ is the bulk plasmon frequency, $\gamma_{bulk}$ is the damping constant of the bulk material, $v_F$ is the electron velocity at the Fermi surface, $A=0.25$ [8] is an empirical parameter. For Au, $\varepsilon_\infty=9.84$, $\gamma_{bulk}=0.072\ eV$ and $\omega_p=9.02\ eV$ [12], $v_F=1.38\ M\ m/s$ [14].

$r_{eff}$ is the effective mean free path of collisions, i.e., determines the broadness of Plasmon resonance and can be calculated from [8,14],

$$r_{eff} = 0.5[(r_s - r_d)(r^2 - r^2)]^{1/3} \quad (3)$$

## RESULTS AND DISCUSSION

Optical properties of matter are a consequence of reflect, transmit and absorb of coming light. In many optical problems, the complex refractive index of material is the basic parameter. The refractive index of the medium related to its dielectrics function which describes the electronic interaction of the medium with incident light wave of frequency. The response of a medium to an incident light wave may be described by a complex refractive index (n˜) which for a nonmagnetic medium is expressed as:

$$n^{\sim} = \sqrt{(\varepsilon_{eff})} \quad (4)$$

Incident light, in general, propagating in the composite is attenuated both by absorption and by scattering [15]. However, for NPs that are much smaller than the wavelength of incident light, scattering effects may be neglected so that only the absorption significant to the attenuation. By considering this phenomenon into account, this review paper focused on optical absorbance of nanoinclusion by optimizing the parameters. It brushed up one of author's research work [3] by incorporating new investigations.

**Figure 1**, depicts optical absorption of triple layered CSNS as a function of wavelength by using Eq. 4 for different parameters: filling factor, DF of spacer and host medium, core size, shell thickness. **Figure 1A** depicts the optical absorbance of quantum wire by increasing shell thickness (i.e., the shell concentration is 36.00%, 55.56%, 67.35%, 75.00%, 80.25% and 84.00%) and the other parameters is kept constant (i.e., $f$=0.01, $\varepsilon_m$=2.25, $\beta_1$=0.44). As shown in the figure, the optical absorbance is increased and the two peaks are closed each other when the shell thickness increasing. Similarly, the optical response of quantum wire CS is illustrated in **Figure 1B** by increasing the core size from 12 nm to 32 nm with the range of 4 nm for a fixed spacer and shell thickness. When the core size increased, correspondingly the shell concentration is decreased (i.e., 84.00%, 75.00%, 64.00%, 51.00%, 36.00% and 19.00%). As shell concentration decreased, the two interface resonances are decreased and but the second resonance is shifted to IR spectral region. For the concentration of metallic shell arranged to 19%, the outer interface resonance located at 13000 nm wavelength. In this resonance, the red shift of the absorption edge represented the change in the nanoparticles energy gap. It means that since the band gap of semiconductor materials will increase with the decrease in particle size, the so-called quantum size effect, it leads to the shift of the absorption edge towards high energy [9].

The optical absorbance of the given composite is also depending on the number of array embedded in the given matrix. To clarify this effect, the effect of filling factor is illustrated in **Figure 1C** for a fixed spacer and shell concentration 43.75% and 36.00%, respectively. As shown in the figure, when the filling factor is increased the optical absorbance of the composite is enhanced without shifting the peaks position. In addition to the above parameters, the optical absorbance of nanoinclusion is affected by DF of hot matrix and spacer. In the **Figure 1D**, I tried to explain the effect of spacer's DF. The intensity of both interface's resonance are decreased when DF of spacer increasing but the second resonance is shifted to higher wavelength. The first resonance of quantum wire CS is decreased when the dielectrics function of the spacer increasing. These resonances may be attributed to near band edge absorption (NBA) due to free exciton recombination. As discussed by Kassahun [3], both interface resonances are decreased when the spacer thickness increasing for a fixed core size and shell thickness.

The resonance peak for a single ZnO and Au nanoparticle is exist at visible region [16], but by combining them and by sandwiching other materials between them for the same size, the absorbance is enhanced and shifted to IR region that is interested phenomena for biological, photocatalysis and other various application.

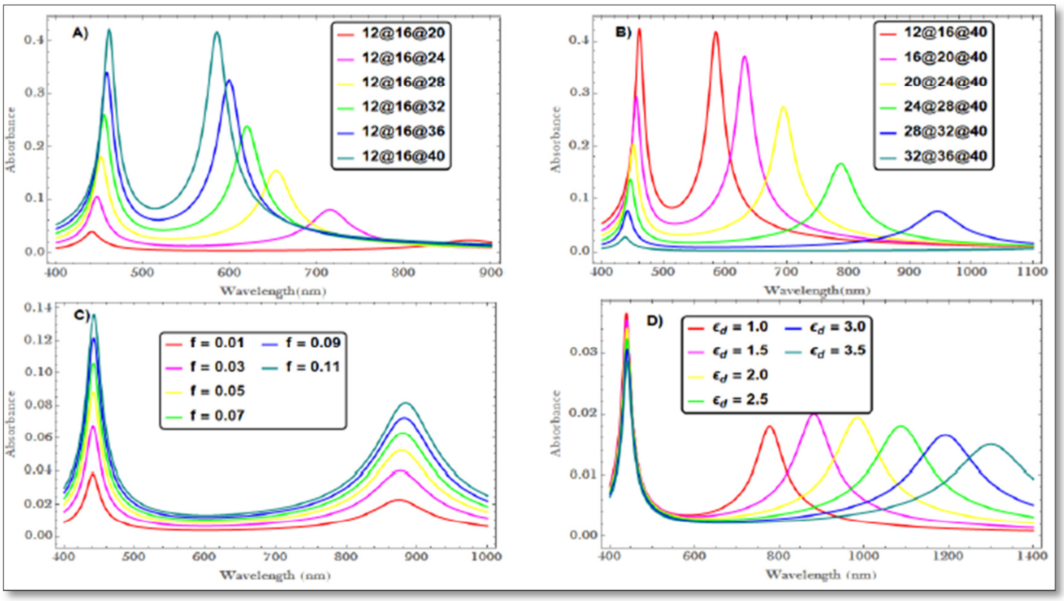


**Figure 1.** (Color online) Optical absorbance of nanoinclusion as a function of wavelength for $SiO_2$ spacer (A) effect of shell thickness (B) effect of core size (C) effect of filling factor (C) effect of DF of spacer.
*Note: 12@16@20=*$r_c@r_d@r_s$

## CONCLUSION

In this mini review paper, the effect of parameters: core size, shell thickness, DF of spacer, filling factor and size of composite on the optical absorbance of Zn@M@Au (m=spacer) quantum wire CS is addressed. By optimizing these and other parameters (not mentioned here), the optical response of nanoinclusion is enhanced and highly tuned and can be used for different applications. The enhancement in the optical properties is mainly attributed to strong coupling of the surface plasmon resonance of the Au shell and the energy gap of the inner part NPs, interaction of exciton-exciton/polariton-plasmon of the composite and interaction of the composite with it environment. Note that the results show triple layered core-shell nanostructures are composed of a semiconductor core of ZnO coated by thin Au NP with different spacer material can be ideal candidate for enhancing biological, solar-cell, catalysis application. Important remark can be pulled in this theoretical work, ZnO@M@Au core-shell nanostructures with large core absorbed more light.

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