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The effect of temperature on optical absorption cross section of bimetallic core-shell nano particles

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Abstract: In this paper, the temperature dependence on optical absorption cross section of the core shell bimetallic nanoparticles (NPs) is investigated in quasi static approximation. Temperature dependence of the plasmon resonance is important issue because of recent applications of NPs of noble metal for heat treating of cancer and the computer chips. The effect of temperature on surface plasmon resonance and spectral properties of spherical core-shell NPs are studied by using the Drude Lorentz model. As temperatures increases, the spectrum can be expanded, and thus it causes to expand plasmon resonance absorption and a weak red shift in core-shell NPs. In addition, the temperature dependent absorption cross section of the material depends on the type, structure and geometry of the NPs. The high sensitivity of surface plasmon resonance peaks causes that core shell NPs be completely suitable for medical and optical biosensor applications.

Key words: Nanoparticles, Optical Absorption Cross Section, Temperature.

1. Introduction

Metal nanoparticles (NPs) have unique optical properties such as resonance absorption and scattering of light that cannot be found in their volumetric counterparts [1]. Collective coherent oscillations of electrons in the conduction band that are known as surface plasmon resonance are responsible for the strong absorption and the dispersion of NPs. These intensifications are very sensitive to the size, shape and metal particles dielectric media. Because of this sensitivity, studying the interaction of light with metallic NPs includes widespread fields. Temperature dependence of the plasmon resonance is

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important issue because of recent applications of NPs of noble metal for the heat treating of cancer [2] and the computer chips [3]. A number of researchers have investigated the effect of temperature on the optical properties of NPs. Chiang et al. (1997) investigated the optical properties of the composite material as a function of temperature by the Maxwell-Garnett and Brugman models for the temperatures up to the melting point of the material [4]. Link and El-Sayed (1999) studied the size and temperature dependence of plasmon absorption of colloidal gold NPs [5]. Chuang et al. (2009) examined the optical properties of composites of metal nano- shell about the effects of temperature and classifying particles according to the effective medium theory [6]. Recently, Yashchenko et al. investigated temperature dependence of surface plasmon resonance in the spherical silver NPs embedded in the matrix of silica host in temperatures of 17-1700 ?C [7]. Zhu, studied the optical absorption properties of Au–Ag bimetallic nanospheres as a function of relative composition [8]. In this study, the effect of temperature on the cross section of the optical absorption of bimetallic core-shell NPs has been studied.

2. **Theory**

Fig. 1 shows a schematic representation of a core-shell NP. A core-shell NP consists an inner core of radius R_c and an outer shell of radius R_s surrounded by a continuum environment. The permittivities or dielectric constants of the core , shell and environment are ε_1, ε_2 and ε_3, respectively.

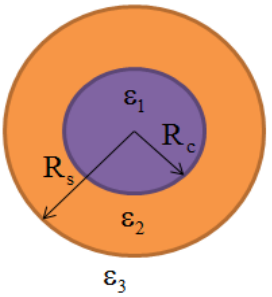

Fig. 1: A schematic diagram of the core-shell NP with inner core of radius R_c and an outer shell of radius R_s.

We consider the theoretical expressions for the electric fields and the polarizability of core-shell NP and then we present explicit formulas for the absorption cross sections of metal nanoshells. Furthermore, the dependence of the plasmon resonance on particle dimensions can be found in the polarizability. The optical properties can be understood with quasi-static theory. In our analysis we believe that the particle diameter is much smaller than the

wavelength of the incident field. Then the particle is subjected to an almost uniform field. The particle then oscillates like a simple dipole with polarization proportional to the incident field. Then the quasi-static approach can be employed in the calculation. In this approach the spatial variation of the electromagnetic field is neglected, while the temporal dependence is preserved [9].

The electric field in each region of the model could be derived from Laplace's equation. The general solution for the potential in each region in spherical coordinates is given by[10]:

$$\varphi_j = A_j\, r\cos\theta + \frac{B_j}{r^2}\cos\theta, \tag{1}$$

Where A_j and B_j are the constants and j is the index of each medium and has a value from 1 to 3. After applying the boundary condition and determined constants in each medium, the absorption cross-section of core-shell NP is as following[10]:

$$\sigma_{abs} = \frac{8\pi^2\sqrt{\varepsilon_3}}{\lambda} R_s^3 \mathrm{Im}\left(\frac{\varepsilon_2\varepsilon_a - \varepsilon_3\varepsilon_b}{\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b}\right) \tag{2}$$

where

$$\varepsilon_a = \varepsilon_1(3-2P) + 2\varepsilon_2 P \tag{3}$$

$$\varepsilon_b = \varepsilon_1 P + \varepsilon_2(3-P) \tag{4}$$

$$P = 1-\left(\frac{R_c}{R_s}\right)^3 \tag{5}$$

On several occasions authors have stated that the dielectric function of the Drude model adequately describes the optical response of metals only for photon energies below the threshold of transitions between electronic bands. For some of the noble metals, interband effects already start to occur for energies in excess of 1 eV. While the Lorentz model is used to describe an interband transition. The complex dielectric functions of a metal consisting of a Drude term and a Lorentzian term, which describes the response due to an interband transition. Physically, the Drude and Lorentzian terms are related to intraband (free-electron) and interband (bound-electron) transitions, respectively. Furthermore, the temperature dependence of permittivities of core-shell NPs would affect the absorption spectrum of the system. In fact, the increase in the temperature changes the real and imaginary parts of the complex dielectric function. Thus, the temperature-dependent dielectric function for gold and silver can be expressed as the sum of free electron and interband contributions as given by the Drude Lorentz form[11]:

$$\varepsilon^{DL}(\omega, T) = 1 - \frac{\omega_{pf}^2(T)}{\omega^2 + i\omega\gamma_{cf}(T)} + \frac{s\omega_{pb}^2(T)}{\omega_0^2 - \omega^2 - i\omega\gamma_{cb}(T)} \tag{6}$$

where ω, ω_0, s, ω_{pf}, and $\omega_{pb}(T)$ are the incident wave frequency, the transition frequency, the oscillator strength, the plasma frequency, and the bound-electron resonant frequency ($\omega_{pj}(T)=\omega_{p0}[1+\beta(T-T_0)]^{-1}; j=f,p$), respectively, while ω_{p0} is the plasma frequency at the room temperature, T_0 is the room temperature, and β is the volume thermal expansion coefficient of gold. Also, $\tau_{cf}=\frac{1}{\gamma_{cf}}$ is the relaxation time of the free-electron $\tau_{cp}=\frac{1}{\gamma_{cp}}$ is the bound-electron decay time (the damping constant is related to the lifetimes of all electron scattering processes). In fact, the collision frequency (the damping constant of plasma oscillations) is a sum of contributions of three different processes: the electron-phonon scattering (γ_{ep}), the electron-electron scattering (γ_{ee}), and the surface scattering (γ_s). Thus, they can be expressed as[11]:

$$\begin{cases}\gamma_{ep}(T)=\omega_0\left(\frac{2}{5}+4\left(\frac{T}{\theta}\right)^5\int_0^{\frac{\theta}{T}}\frac{z^4dz}{e^z-1}\right)\\ \gamma_{ee}(T)=\frac{\Gamma\Delta\pi^3}{12\hbar E_F}\left(\frac{\hbar^2\omega^2}{4\pi^2}+k_B^2T^2\right)\\ \gamma_s(T)=\frac{AV_F}{R_{ST}(T)-R_{CT}(T)},\end{cases} \tag{7}$$

Where k_B, θ, V_F, and A are the Boltzmann constant, the Debye temperature, the Fermi velocity of metal, and a geometrical factor, respectively. It is to be noted that, the volume of a NP is changed when the temperature rises $V=V_0(1+\beta\Delta T)$ [10].

3. Numerical Results

Several calculations were implemented for core-shell NPs. Since the optical response of metal nanostructures has an important role in plasmonics and biotechnology; thus, the metal intended for core or shell NPs is the gold, because the solid gold NPs show a different resonance that widens with increasing temperature. In numerical calculations, we also used $\beta=4.17\times10^{-5}\,K^{-1}, V_F=1.3\times10^6\,m/s, \Gamma=0.55, E_F=5.53, \Delta=0.7$ for gold NP and $\beta=5.67\times10^{-5}\,K^{-1}, V_F=1.39\times10^6\,m/s, \Gamma=0.54, E_F=5.49, \Delta=0.73$ for silver NP. In Figure 2, the dielectric function of gold NP for different amounts of temperature depending on the wavelength of Drude-Lorentz model is shown. As it can be seen from the Figure 2, the dielectric function is changed in Drude-Lorentz model due to the inter-bands transitions in the visible region, and at high

wavelengths, the temperature changes show more themselves. The variation of dielectric function with temperature comes from the temperature dependence of the collision frequency in Eq. (6), which accounts for the electron-phonon, electron-electron, and the surface collision process in the metal.

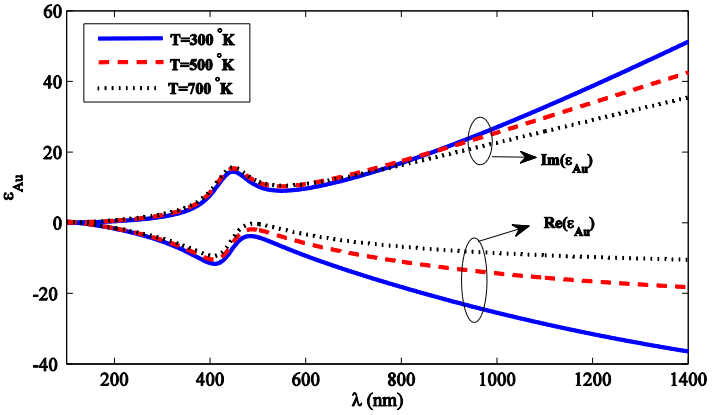

Fig. 2: The dielectric function of gold for different temperatures versus wavelength of Drude-Lorentz model

The absorption cross section of gold-silver bimetallic sphere in terms of wavelength for different values of temperature based on the Drude-Lorentz model in Figures 3 and 4 are plotted. In Figure 3, a gold-silver bimetallic sphere is considered, which the core radius is equal to $R_c = 10\,\mathrm{nm}$ and the total radius is equal to $R_s = 15\,\mathrm{nm}$. According to Figure 3, when temperature increases, the peak of absorption cross section of the bimetallic sphere is reduced and shifted to higher wavelengths. When Drude-Lorentz model is used, given that the gold may be affected inter-bands transitions in the visible region, and Lorentz model predicts these transitions, as can be seen from figures shown in the box, a peak is observed in this region which for the visible region according to the Figure, peak increases with increasing temperature.

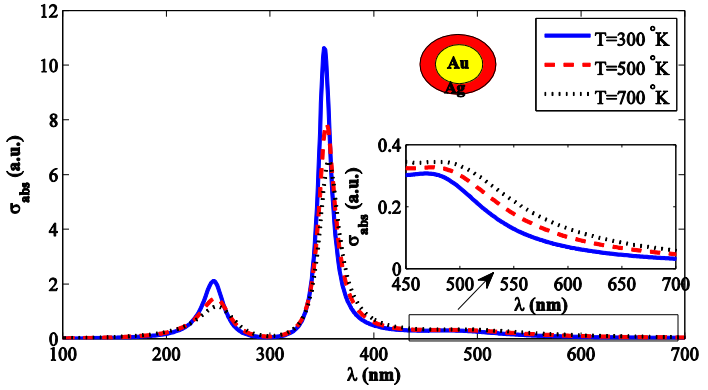

Fig. 3: The absorption cross section of gold-silver bimetallic NP in terms of wavelength for different values of temperature based on the Drude-Lorentz model.

In Figure 4, the absorption cross section of silver-gold bimetallic NP with core radius is equal to $R_c = 10\,\text{nm}$ and the total radius is equal to $R_s = 15\,\text{nm}$ for different temperatures is plotted versus wavelength. According to this Figure, it is observed in sub-visible region when the temperature increases, the absorption at wavelengths are reduced around $150\,\text{nm}$ and $R_c = 290\,\text{nm}$ and shift towards higher wavelengths. However, in the visible region, absorption peak increases with increasing temperature. In comparison with Figure 3 absorption peaks occur at lower wavelengths, and are also smaller in size. The third peak in the visible region is also created due to the inter-band transitions of gold in this region.

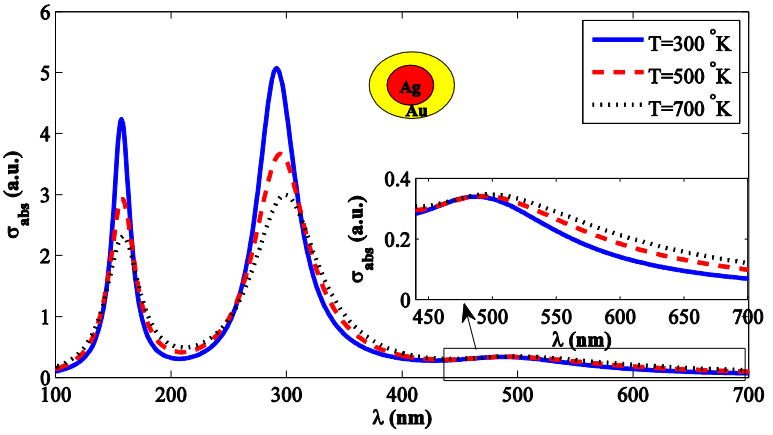

Fig. 4: The absorption cross section of silver-gold bimetallic NP in terms of wavelength for different values of temperature based on the Drude-Lorentz model.

In Figures 3 and 4, the optical properties of NPs depend on the temperature. The increase in the temperature causes changes in the spectrum intensity, spectral width and a weak red-shift of the plasmon absorption band. The optical response of metal NPs is related to the electron and phonon temperatures. As the temperature increases, the volume of NP increases and, thus, the rate of electron-phonon and also the rate of electron-electron increase with the temperature. There is a decrease in amplitude and broaden in width of absorption as the temperature increases and, thus, the optical absorption width increases with temperature.
Figure 5 shows contour plot of the absorption cross section in gold-silver bimetallic NP in term of geometrical parameters and wavelength. It is observed that, when the core radius increases, the peak of absorption cross section is reduced, and toward red shift.

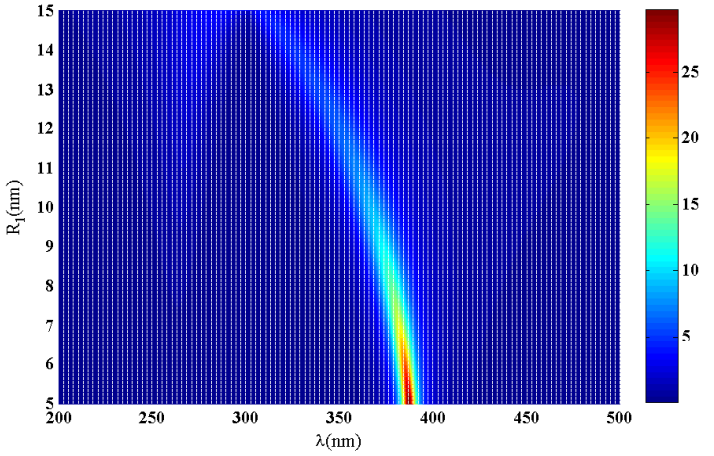

Fig. 5: contour plot of the absorption cross section in gold-silver bimetallic NP in term of core radius and wavelength.

In Figure 6, contour plot of the absorption cross section in gold-silver bimetallic NP versus shell radius and wavelength is shown. As this figure can be seen, when the shell radius increases, the peak of absorption cross section is increases, and toward blue shift. Contour plot of the absorption cross section in gold-silver bimetallic NP in term of core radius and wavelength.

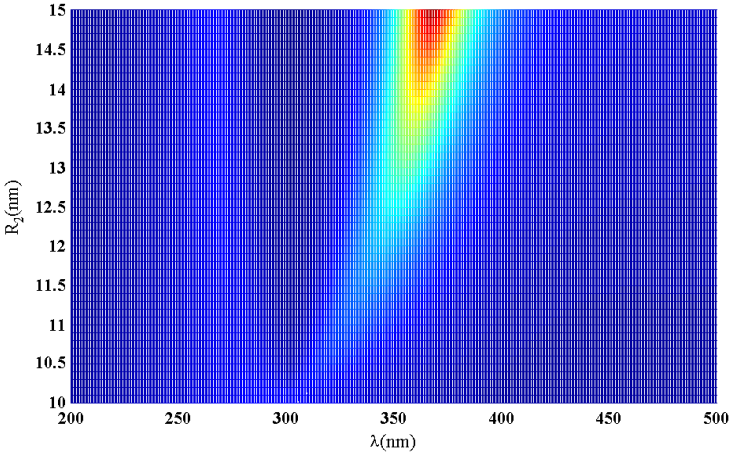

Fig. 6: contour plot of the absorption cross section in gold-silver bimetallic NP in term of shell radius and wavelength.

Figures 5 and 6 show that, the absorption cross section is sensitive to the shell thickness, the core radius. This means that the surface plasmon peak position, spectral width and resonance frequency of core-shell NP can be tuned by controlling the core radius and shell thickness.

4. **Conclusion**

In this paper, the effect of temperature on the absorption peak of bimetallic core-shell NP was investigated. One of the parameters affected on the alterating of plasmon resonance is temperature and for different structures, absorption cross section decreases with increasing temperature. As a result, by increasing the temperature, the spectrum can be broadened and, thus, leads to broadening of the resonance plasmon absorption and a weak red-shift in the core-shell NPs. In addition, temperature-dependent absorption also depends on the type of material, structure, and geometrical shape of the NPs. In addition, the temperature-dependent absorption of the material depends on the type, structure and geometry of the NPs. Another important consequence is the appearance of a new and weak absorption at long wavelengths. The appearance of this peak is due to the interband transitions. The high sensitivity of surface plasmon resonance peaks causes that core-shell NPs be completely suitable for medical and optical biosensor applications.

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