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Shift of Optical Absorption Spectra of Anisotropic and Interacting Au and Ag Nanoparticles: Correlation between Shape Anisotropy and Interaction

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Abstract

The studies of Au and Ag Nanoparticles (NPs) nowadays find much importance due to their interesting optical properties in the visible range. In this article we have studied theoretically the optical absorption (OA) spectra of Au and Ag NPs considering the shape anisotropy and interaction between the particles separately using a simple model developed by Garcia et al. In the model we represent the shape deformation or anisotropy of the particles by a parameter β and interparticle interaction by a parameter K. In the calculation of OA spectra, the values of β have been varied from 0.05 to 1.0, considering K = 0 and two different values of particle radius. The spectra of anisotropic Au and Ag NPs exhibit redshift of surface plasmon resonance (SPR) peak. The similar shift of the SPR peak has also been observed in case of the OA spectra calculated by considering the variation of the interaction between the particles in both the systems. In both the cases an exponential type decay of SPR peak position with increase of β as well as $1/K$ has been observed. The similar nature of SPR peak variation when fitted we get an almost identical exponential equation. The observation gives a direct mathematical correlation between β and K which was not established earlier. This correlation is essential and helpful for different device applications of anisotropic Au and Ag NPs in plasmonic, photonics, optoelectronics and others.

Keywords: Surface plasmon resonance, anisotropy, interparticle interaction, redshift

1. Introduction

The optical absorption (OA) properties of anisotropic and or interacting Au and Ag nanoparticles (NPs) nowadays play an important role due to their various interesting optical absorption properties in different practical applications like plasmonics, photonics, catalysis, bio-sensing [1], and optoelectronics [2], surface enhanced Raman scattering (SERS) etc. The Au and Ag NPs show 'collective oscillations' of their conduction electrons when electromagnetic radiation incident on their surfaces. The phenomenon is known as surface plasmon resonance (SPR) and appears in the visible region [3]. The SPR of Au and Ag may also appear in the bulk which show a propagating nature and hence found to have less importance. In nanoscale, the SPR of both of these noble metals get localized and is known as localized surface plasmon resonance (LSPR) [4, 5]. The localized plasmon resonance has a unique property that it can be tuned by changing the particle size, shape, interparticle distance or interaction and also by changing its surrounding medium in which the particles are embedded. The LSPR results in significant enhancement of local electromagnetic fields near the surface of the NP than the incident fields. The enhancement of local field and strong scattering is found to be unique for bio-molecular manipulation, labeling, sensing and detection [6]. There are special cases of interest where the application of a single metal NP is of less importance. Hence, much attention has been given on the assemblies or arrays of metal NPs [7]. The studies of the OA properties of these arrays show that their plasmonic properties strongly depend on interactions between particles [8]. On the other hand the NPs are not always spherical, rather they are shape deformed i.e. elongated or cylindrical rod shaped. The shape deformation is known as shape anisotropy of the particles. When shape anisotropy comes into the particles they exhibit more interesting optical properties such as stronger and tunable plasmon absorption than the spherical NPs. Here we have first considered the non- interacting (i.e. K = 0) particles of radius 2 and 5 nm and taken the values of β as 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.20, 0.50, 0.75 and 1.00 for the calculation of the spectra. Due to anisotropy the plasmon resonance bands show substantial redshift from the actual position [1]. In this model the anisotropy in the particles is represented by a parameter β we call it as shape anisotropy or shape parameter [1] because it actually determines the shape of the particles. The similar studies have also been carried out theoretically by R. Gans for small ellipsoidal particles [6]. The shift of SPR peak with shape of the particles is due to the dependence of dielectric function (DF) on the surface geometry or change in curvature of the particle surface [4]. The reason of this unique feature is due to change of the

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polarizability for the change of shape of the particles. This change in polarizability in turn changes the restoring force constant which determines the plasmon oscillations frequency or more precisely the SPR frequency [4]. The SPR peak positions were then determined from the absorption spectra and plotted with β. The plot gives an exponential decay type variation. On the other hand a similar variation of the spectral peak shift for spherical particles has been observed when interparticle interaction is taken into account and varied. In case of interacting NPs, coupling of the electric fields of the two adjacent particles take place which decreases the SPR frequency and hence enhance the resonance wavelength [8]. Consequently, SPR peak get redshifted [8]. To observe this phenomenon, we have varied the values of interaction parameter K from 10 to 80 for the particles of radius 2 and 5 nm. Here SPR peak position as determined from the spectra is plotted with the inverse of the interaction parameter K. The theoretical plot is then fitted and we get such an exponential equation. Due to similar nature of the two equations we compared their exponents and get a correlation between the parameters β and K. This correlation gives the equivalent spectral shift by two ways i.e. either by varying the anisotropy (β) or by changing the values of interaction K. The correlation between the interaction parameter K and the interparticle distance has already been established in our earlier work on the noble metals which shows a universal scaling behavior [8]. This correlation is very much helpful for different applications of the Au and AgNPs in field of plasmonics, surface enhanced Raman scattering, photonics, optoelectronics and others.

2. Calculation Method

The OA property of metal nanoparticles is usually studied by using Mie theory [9] which gives the scattering and extinction of light in a dilute medium having particle size < 20 nm. In a very dilute medium and smaller particle (< 20 nm) size the higher order multipoles do not have significant contribution in scattering and hence extinction can be used to calculate absorption. This is known as so called "quasi-static limit". When the medium is relatively denser, "quasi-static limit" breaks down and one has to use effective medium theory [10] where an inhomogeneous matrix-cluster medium by a homogeneous one with an effective dielectric function having the same optical response. For such medium Garcia *et al.*[11] have further modified the MG effective medium model to calculate the absorption. Here, the optical absorption spectra of embedded Au and Ag NPs are calculated using the above model. The details description of the model is not given here which can be found in our earlier article [5]. In the calculation of absorption using above model, the parameters R, K, β, ε_m, and f are used. Where, the parameter R is the radius of the NPs, K represents the interaction between the NPs, β represents the shape or anisotropy of the particles and other two parameters such as f and ε_m represents the volume fraction and dielectric function (DF) of the surrounding medium, respectively. Since, the dielectric constant (DC) of metal NPs depends on size, the bulk values DCs has to be corrected for size. The bulk values of DC of Au was taken from the experimental data table of Jonson and Christy [12] and then corrected for the NP size [13].

The similar studies on the above phenomena had also been carried out for Au and Ag NPs synthesized in silica as embedding medium using sol-gel [11] and ion implantation [14], [15], [16] techniques, respectively. In this article the effects of anisotropy and interaction on the OA spectra for Au and Ag NPs have been studied. In the study we have first taken the values of β as 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.20, 0.50, 0.75 and 1.00 while the other parameters such as R, ε_m, f and K are kept fixed. However, whenever required the values of R have been varied. Then to study the effect of variation of interaction between the particles we have varied the values of K from 10 to 80, keeping the other parameters fixed. The value of ε_m and f are 2.26 and 0.1 used for calculation.

3. Results and discussion

In Fig. 1(a)-(b) we have shown the theoretical OA spectra of non interacting Ag NPs of radii 2 nm and 5 nm as a function of wavelength and for different values of β embedded in silica. The spectra exhibit broad absorption bands corresponding to plasmon resonances of Ag NPs. The existence of such absorption bands (commonly known as SPR bands) at various wavelength position for different values of β arises due to the absorption of electromagnetic excitation by the conduction electrons oscillations on the surface of NPs embedded in silica [2, 5]. Here it is to be pointed out that the intensities of the SPR absorption decreases towards lower wavelength side due to decreasing density of free electrons in the surface of the metal NPs [1].

In the Fig. 2(a)-(b) the similar spectra for Au NPs have been shown for r = 2 nm and 5 nm respectively. In Fig. 2 (a)-(b) the similar absorption spectra for Au NPs of radius 2 and 5 nm have been found and represented. The effects of the variation of the shape parameter (β) on the OA spectra corresponding to the longitudinal oscillations of Au and Ag NPs embedded in silica for the radius 2 nm and 5 nm is depicted in the Fig 2(c)-(d) respectively. It is seen that decreasing the value of β from 1 leads to substantial redshift of the SP absorption peak position i.e. the shift of SPR peak towards higher wavelength side. Similar shifts of SPR peak position has also been seen in

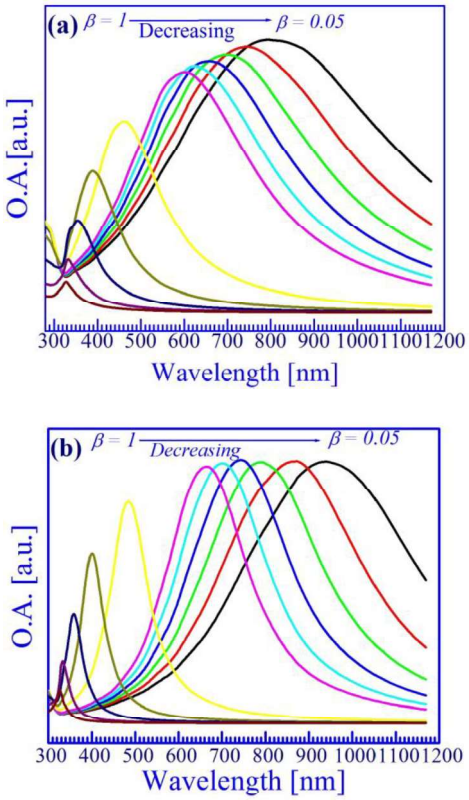

Fig. 1 (a) The OA spectra of non-interacting (K = 0) Ag NPs of radii *(a)* r = 2 nm (b) r = 5 nm as a function of wavelength for various values of β.

case SPR peak position has also been seen in case of nanorods or prolate spheroids particles [1]. This has a consequence that lowering the values of β produce anisotropic or elongated NPs similar to nanorods. Therefore, we have considered only smaller values of β than 1. Although, it has been seen that anisotropic MNPs exhibit two plasmon resonances, due to the transverse and longitudinal oscillation of the conduction electrons [1, 4]. The transverse oscillation has not been considered here because it does not change with aspect ratio or shape parameter β [1] but the longitudinal SPR depends largely on β through the aspect ratio [1]. Here, we only calculated the longitudinal absorption spectrum of anisotropic Au and Ag NPs of radii 2 and 5 nm as shown in Fig. 2(a)-(b). Our theoretically spectra correspond to that calculated by *Eustis et al.* [3]. A shift of plasmon resonance peak towards the longer wavelength side (redshift) with decrease in the value of β has been observed along with the increased intensity of the absorption peaks. This happens due to the fact that with the decreased value of β produces the larger degree of anisotropy and surface curvature of the particle which also affect the DF through change in polarizability. Then, from the spectra we have determined the exact SPR peak position and then plotted with the parameter β in both the cases. The theoretical data points so obtained are then fitted

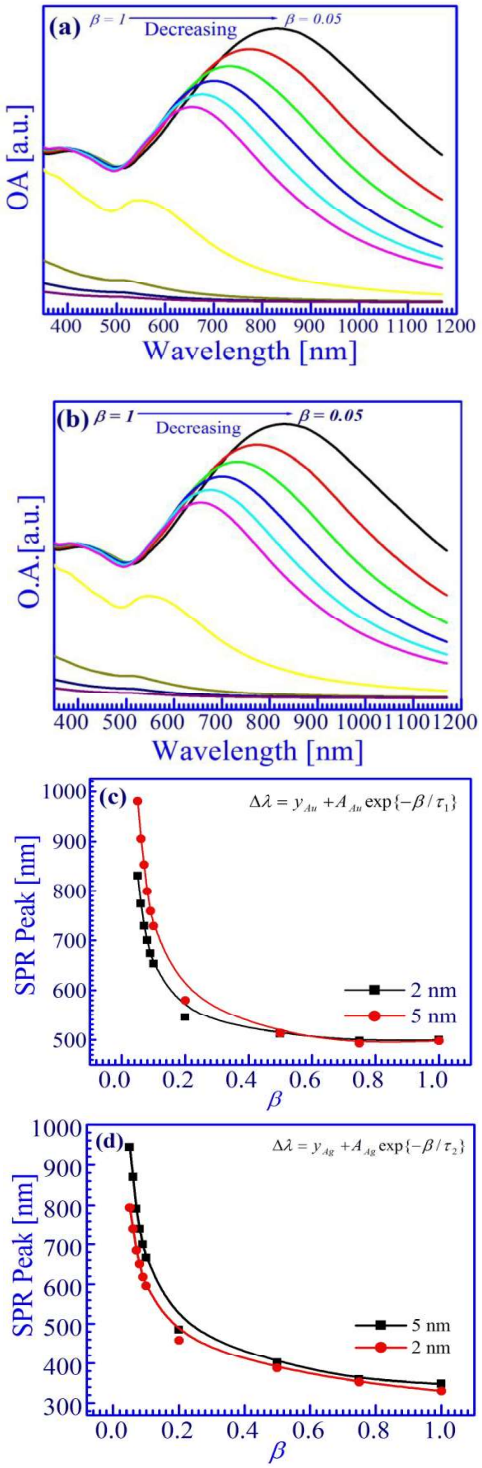

Fig.2.(a) The OA spectra at various wavelengths of Au NPs of radius r = 2 nm and (b) r = 5 nm for different values of β. (c) - (d) Variation of the SPR peak position of Au and Ag NPs with β.

using exponential type decay curve as shown in the Fig. 2 (c)-(d). The exponential fits of the SPR wavelength shift as obtained from theoretical data is given by the following equation

$$\Delta\lambda = y_0 + A_1 \exp\{-\beta/\tau_1\} \quad (1)$$

where, y_0, A_1, τ_1 are constant for particular MNP. Since the constants y_0 does not effect on the nature of variation and hence can be neglected. Therefore, the above equation can be written as

$$\Delta\lambda \approx A_1 \exp\{-\beta/\tau_1\} \quad (2)$$

where, Δλ is the shift of the SPR peak position.

Now let us consider the spectra of interacting Ag NPs of radii 2 and 5 nm as shown in Fig. 3(a)-(b) and for Au NPs of radius 5 nm in Fig.(c) in the same wavelength range. In this case the interaction is characterized by a parameter *K* whose values are taken as 20, 30, 40, 50, 60, 70 and 80. We see that in each of the cases the spectra show plasmon resonance peak in the visible range shifting continuously towards red end. The plot of Fig. 3(d) shows that variation of the SPR absorption peak shifts with 1/*K*. The similar nature of variation of SPR peak shift for other size and type of NPs can also be found (which is not shown here). The reason for this is that as one increases the value of *K* the interaction of the electric field of two particles get enhances resulting the coupled plasmon oscillations [8, 17] whose frequency is found smaller than the frequency of individual oscillations leading to such redshift. The amount of peak shift and the intensity depend on strength of the coupling [8, 17] and the distance between the particle and radius. This interaction or mechanism of coupling can be explained in details using the dipolar coupling model [17]. In this model the NPs are considered to be polarized with an effective dipole moment which interacts with one another. This interaction is attractive in nature for parallel polarization. This interaction reduces the plasmon resonance frequency resulting in large redshift of the absorption peak [8].

The theoretical data points on fitting gives us an exponential decay curve as shown in Fig 3(d). This curve can be represented at the best by the equation

$$\Delta\lambda \approx y_{0Ag} + A_{0Ag} \exp\{-1/K\tau_2\} \quad (3)$$

where, y_{0Ag}, A_{oAg}, τ_2 are the constants for Ag NPs. Again neglecting y_{0Ag} we get,

$$\Delta\lambda \approx A_{0Ag} \exp\{-1/K\tau_2\} \quad (4)$$

It is seen that the equations (2) and (4) are almost similar. Therefore, the exponents of both the equations can be equated and we get

$$\frac{\beta}{\tau_1} = \frac{1}{K\tau_2} \Rightarrow \beta = \left(\frac{\tau_1}{\tau_2}\right)\frac{1}{K} \Rightarrow \beta = D\left(\frac{1}{K}\right) \quad (5)$$

where, $D = \left(\frac{\tau_1}{\tau_2}\right)$ is constant depends on the type

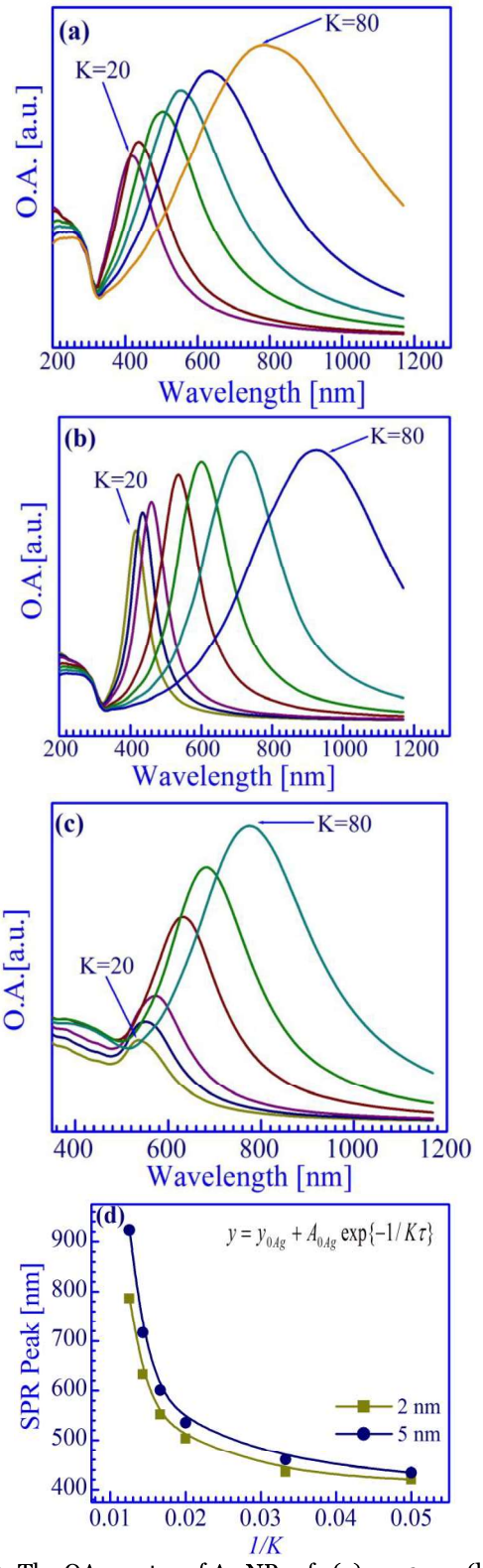

Fig.3. The OA spectra of Ag NPs of (a) *r* = 2 nm (b) *r* = 5 nm for different values of *K*. (c) The OA of Au NPs of *r* = 5 nm.(d) Variation of SPR Peak position as function of 1/*K* for Ag NPs.

of metal NPs. In the table 1 gives the list of values of the above constants for Au and Ag NPs of radii 2 and 5 nm.

Table 1. The values of the different constants of Ag and Au NPs

Type of metal	Particle Size r (nm)	Value of τ_1	Value of τ_2	Value of D
Ag	2	0.09846	0.00394	25
Ag	5	0.09153	0.00392	23
Au	2	0.06346	0.00368	17
Au	5	0.07455	0.00407	18

The constants A_1 and A_{OAg} also do not affect the nature of the decay. Therefore, the interaction and anisotropy have been correlated through the eq. (5) which provide us two alternative or means for tuning of the spectra of Ag and Au NPs. For isolated or non interacting NPs or particles in a dilute medium one can use the shape tuning. But in case of NPs arrays or clusters, we can use both of the above parameters for spectral tuning. The eq. (5) mathematically acts as a ruler equation for estimating anisotropy from the interaction or interaction from the anisotropy. The similar ruler equation for distance dependent plasmon coupling relating interparticle distance with ineraction parameter has also been observed [8]. Therefore, the study opens up for the possible applications of the Au and Ag NPs in field of plasmonics, photonic, optoelectronic devices, SERS and others.

4. Conclusion

The theoretical OA spectra of Ag and Au NPs have been studied systematically and separately considering anisotropy and interaction between the particles. A systematic shift of plasmon resonance peak with the parameter β and K in wide range of wavelength is seen. The exponential decay of such SPR peak with β and $1/K$ has been found. This observation, gives a mathematical correlation between the parameter β and K. It is also found that the correlation is independent of the metal type. In practical applications point of view this is very much important.

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