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Tailoring the localized surface plasmons in Au and Ag nanoparticles through interparticle interaction and dielectric function of the surrounding medium

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The plasmonic properties of noble metal nanoparticles (NPs) nowadays, play an important role in different practical applications due to 'strong absorption of incident light' by the metal NPs commonly known as localized surface plasmon resonance (LSPR). The LSPR position can be changed by changing interaction of their electric fields via the separation between the NPs and with the change in dielectric constants (DCs) of surrounding medium. Such changes lead to a large redshift of LSPR peak of metal NPs. Here, the LSPR of interacting Au and Ag NPs of radius 10 nm embedded in SiO_2 have been studied theoretically using a modified Maxwell-Garnett (MG) model. In the model, a parameter, K is taken to represent the interaction between the NPs. For the study, we have taken the values of K as 10 to 80 and the values of DC from 0.5 to 5.0. Such K and DC values results in large redshift of the LSPR of the two metals. The observed redshift with K is explained by considering the coupling between the electric fields of two adjacent particles. Further, the DC of the surrounding medium alters the geometry of the electric field at the surface of the NPs leading to a large spectral shift which gives us two means of tailoring the plasmon resonance which is very much important for studying the plasmonic properties of noble metal NPs and their practical applications.

Keywords: Surface plasmon resonance, nanoparticle, interparticle interaction, redshift.

Introduction

In last two decades, there has been a growing interest in the studies of embedded metal nanoparticles (NPs) due to their outstanding optical absorption (OA) properties. In case of noble metals, surface plasmon resonance (SPR) is the main optical property[1]. In contrary to bulk, noble metal nanostructures exhibit unique and strongly enhanced OA properties due to the above phenomenon in the visible region of the electromagnetic spectrum. Further in noble metal NPs, the plasmon resonance get localized and is commonly known as localized surface plasmon resonance abbreviated as LSPR[2] which is the oscillation executed collectively by the free or conduction electrons of the surface of the NPs when excited by an incident electromagnetic radiation[1,3]. The LSPR in colloidal solution of noble metal exhibits characteristic color which attracts a considerable attention to researchers[4]. Recently, the plasmonic properties of embedded noble metal NPs find a lot of interest rather than the isolated NPs. The plasmonic properties of embedded NPs can additionally be tailored through changing the dielectric properties of the medium. It is well known that the dielectric properties of the medium as well as the metals are frequency dependent, so it can be changed by changing the frequency in a controlled manner. Thus the embedded NPs open up an additional possibility of tuning the LSPR properties of noble metals (Au and Ag) and find many practical applications in nonlinear optics, optoelectronic devices, surface enhanced Raman scattering (SERS) and waveguides[1–3] . The study also finds great interest in fundamental scientific research in nanophysics, photochemistry and molecular biology. In the present study we focused only on the SPR of embedded Au and Ag NPs which modifies the local field greatly near the NP surface than the incident one. As a result the incident field strongly scatters around the resonance frequency. The enhancement of the local field and strong scattering were found to be of very much unique for bio-molecular manipulation, labeling, and detection[5]. From the applications point of view, the single or isolated of metal NPs is of little impor-

tance, rather, a recent trend has been seen to focus on the NPs assembly or array[6]. The strong dependence of the plasmonic properties on the interactions between the particles has been revealed by the studies of assemblies of nanoparticles[7]. The surface plasmons of two neighboring NPs coupled together via this interaction leading to shifts and confinement of energy between the particles. The effects of confinement have been found to play a major role in 'surface enhanced Raman scattering' (SERS) experiments[8]. This interaction also creates a strong optical force toward the interparticle space[9] which can be used in optical nano positioning of a molecule for applications of Au and Ag NPs in biosensors and others. Thus the coupling of the two plasmon oscillations lead to systematic shift of the SPR peak positions for certain geometry of nanostructures. Recent advancement in techniques enable the researchers to synthesize well-defined metal NPs assemblies which also enable to tune the OA properties systematically[10,11]. Therefore, it is possible to utilize such properties of surface plasmon coupling to measure nanoscale distances within the biological systems stated above.

'One of the fastest and effective ways to understand various plasmonic properties of the material is the computer simulation of the theoretical functions'. Recently, we have studied the effects of NP size, shape, and local environment on the OA of Au, Ag, and Cu NPs[1,3] using a modified MG theory as developed by Garcia *et al.*[12]. They have incorporated two parameters to account for geometrical and distribution homogeneity into the theory in a simple manner. Thus the SPR band becomes very sensitive to the shape of NPs as well as inter-particle separation. A correlation between shape parameter of the modified model and the aspect ratio has been established, recently[3].

In this article we have calculated the OA spectra of Au and Ag NPs embedded in silica using the above modified theory[12]. First we have calculated the OA spectra of Au and Ag NPs of radius 10 nm for different media having different values of the dielectric constants (DC) without considering interaction between the particles. A large redshift of the SPR peak position ranging from ~502 nm to ~608 nm for Au and from ~338 nm to ~503 nm for Ag NPs have been observed in the spectra. Then, we have considered the interaction between the particles to calculate the spectra. Here, also a large enhancement of the spectral shift (from ~535 nm to ~1040 nm for Au and ~498 nm to ~994 nm for Ag NPs almost covering the major part of the electromagnetic spectrum) has been observed. This work is thus open up a wide range of possible applications of plasmon resonances of Au and Ag NPs different fields mentioned earlier.

Calculation method

The study of OA properties of small metal NPs is usually done by Mie theory which gives us the extinction and scattering of light. When the particle sizes are smaller than wavelength of light, absorption due to higher order multipoles is reasonably small and hence can be neglected[13]. Under this circumstance, the extinction may be used to calculate absorption. But in a relatively denser medium this theory cannot be applied and one has to use MG theory[14]. We have calculated the OA spectra of Au and Ag NPs of radius 10 nm embedded in silica using the Garcia *et al.* modified model[12]. This model is sensitive to size, shape, interparticle interaction and the DC of the medium. Following this model the effective dielectric function (DF) of the metal is first calculated by incorporating radius of the NPs by employing the phenomenological formula[1] for DF of metal and taking the bulk values of DC from the experimental work of Jonson and Christy[15]. Using this formula the size corrected real and imaginary part of the DF of the NPs is calculated. After having obtained the corrected values of DF for metal, the OA spectra of Au and Ag NPs have been calculated for the different values of the DC of the medium without considering the interparticle interaction and then calculated by varying the interaction, keeping the value of the DC of the medium fixed. The following parameters such as particle radius R, interparticle interaction K, the shape parameter β, the medium DC ε_m, and volume fraction f are used for calculation. While tailoring the spectra by DC we have only varied the values of ε_m keeping the remaining parameters viz. R (=10 nm), β (=1/3, spherical NP), and f (= 0.1), K (= 0) are kept fixed. On the other hand while tailoring by interaction, the parameter K is only varied while all other parameters mentioned above are kept fixed. In either case SPR peak redshifts with wide range.

Results and discussion

The effects of DC of medium and interparticle interaction

on OA spectra of Au and Ag NPs have been discussed. The spectra show a wide redshift which provide ones the two ways of possibility of tailoring of SPR absorption peak as discussed below in the subsequent sections.

Tailoring SPR peak position by varying DC of surrounding medium:

The theoretical OA spectra of Au and Ag NPs with wavelength in the range 300 nm to 800 nm for different values of DC of the surrounding medium have been shown in the Fig. 1(a)-(b).

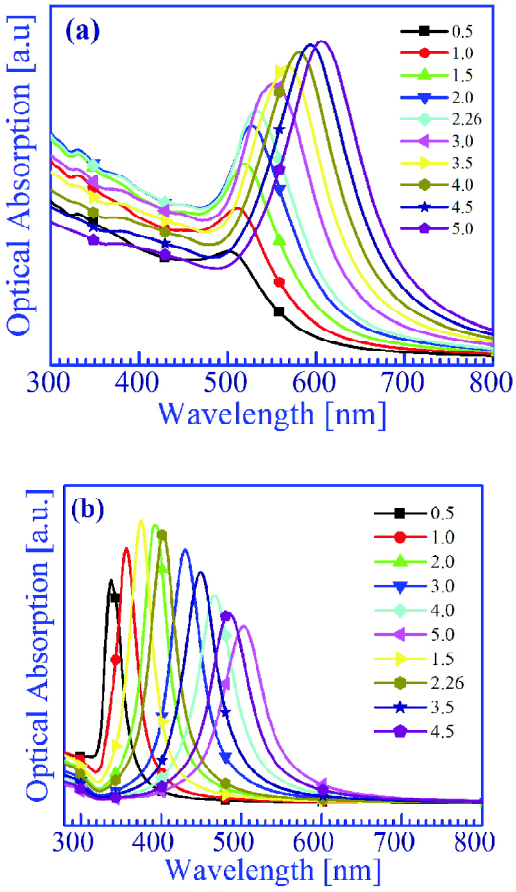

Fig. 1. The OA spectra of (a) Au and (b) Ag NPs for different values of DCs of the surrounding media.

Here the value of DC is varied from 0.5 to 5.0. In both the cases the SPR peak is seen to shift towards higher wavelength (from 502 nm to 608 nm for Au and 338 nm to 503 nm for Ag NPs) with the increase of DC. The intensity of SPR absorption is initially found to increase and then decreases with the DC. This change of the OA spectra can be explained with the help of the theory under consideration. According to the theory the DC of the surrounding medium plays an important role in the spectra. It has two important effects on the SPR processes namely it determines the light wavelength near the NP surface which changes the geometry of the electric field and another important phenomenon is the polarization of the embedding medium[16]. Due to this polarization the charge separation occurs at the interface between NP surface and the medium. As a result there is a charge accumulation at the boundary of the medium. This polarization charge partially compensates the charge accumulated due to conduction electron movement on the NP surface. Hence, there is a net reduction of charges at NP surface. The reduction will be larger for the larger value of DC of the medium. Consequently, there is a reduction of restoring force and the corresponding frequency of plasmon oscillation.

In the lower wavelength side, there are some small absorption peaks with considerable intensity is seen. These arise due to the fact that in the NP the energy levels are well separated and some transition between these inner levels take place which are known as interband transition (IB).

The SPR peak positions of both the spectra are then plotted with DCs as shown in the Fig. 2.

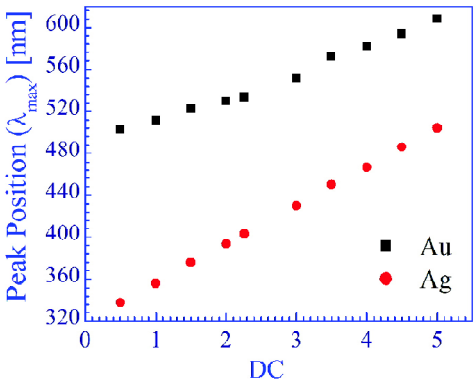

Fig. 2. The variation of the SPR peak position (λ_{max}) of Au and Ag NPs with DCs of the surrounding media.

The plot gives a systematic linear variation as expected. Thus our calculated spectra exhibit wide range of tunability with the DC of the surrounding medium. For practical applications, this enhancement and tuning the SPR peak with DC

of the surrounding media is very much important. The similar changes in the SPR spectra have also been observed experimentally[17–20].

Tailoring the SPR peak position by varying the interaction parameter:

The OA spectra of Au and Ag NPs with wavelength in the range 300 nm to 1200 nm for different K are shown in the Fig. 3(a)-(b).

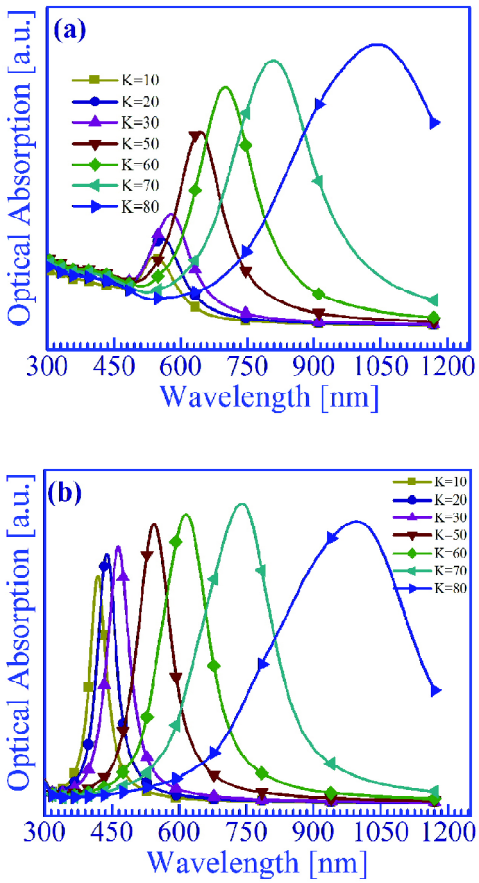

Fig. 3. The OA spectra of interacting (a) Au and (b) Ag NPs of radius 10 nm with different values of interaction K.

For both the system, the SPR peak positions redshift from ~535 nm to ~1040 nm for Au and ~498 nm to ~994 nm for Ag NPs with increase of K. Similar shift has also been seen for other sizes of NPs. The origin of this type of SPR peak shift can be explained by considering the dipolar coupling model. According to this model, the electric field between two nearby NPs increases as a result of the increased interaction and hence the SP oscillations get coupled together[10,17,21]. The frequency of the coupled oscillations is found to get shifted to the lower value than individual plasmon oscillations frequency. Therefore, the corresponding absorption wavelength at the SPR frequency is observed to be redshifted. The amount of this redshift depend on strength of the interaction[10] i.e. higher the value of interaction larger the amount of redshift.

The variations of the SPR peak position with K are shown in the Fig. 4 for Au and Ag NPs respectively.

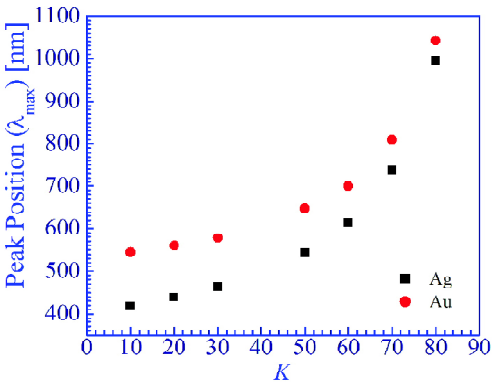

Fig. 4. The variation of the SPR peak position (λ_{max}) of Au and Ag NPs with the parameter (K) for particle radius 10 nm.

The plot shows an exponential type growth giving the larger SPR peak shift with the increase in the interparticle interaction. If we consider up to first order of approximation the variation becomes linear. Thus according to convenience and requirement one can tailor the position of the SPR peak by considering the exponential or linear variation by varying the values of interaction parameter. The similar variation and redshift of SPR peak positions with interparticle separation has been reported experimentally by Jain *et al.*[10] for Au NPs pair and Gunnarson *et al.* for the Ag nanodisc pairs[22]. Thus our study is very much helpful for practical applications of Au and Ag NPs in plasmonics, photonics, optoelectronics etc.

Conclusions

The effects of the DC of the surrounding medium and interparticle interaction on the OA spectra of Au and Ag NPs

have been studied theoretically using modified by García *et al.* theory. In either case we get a large redshift. Thus DC of the medium and the interparticle interaction parameter K has been used independently to tailor the SPR peak position in the wide range of wavelength. This opens up a huge possibility to use Au and Ag NPs as active plasmonic materials for the application in photonics, nonlinear optics, optoelectronics and others.

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