Surface plasmon resonance of dumbbell nanostructure

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Received 30 October 2013, revised 5 May 2014
Accepted for publication 23 May 2014
Published 24 June 2014

Abstract
We present an intuitive theoretical description of the optical properties of a complex metal nanostructure, consisting of two nanoshells connected by a nanorod giving a dumbbell-like appearance. The simulations were done using the finite element method. The effects of the length and radius of the nanorods and of the dimensions of the nanoshells on the plasmon properties of the system were analyzed. The peak position and intensities in the absorption spectra were found to have a strong dependence on the geometrical parameters of the dumbbell. This study provides evidence that the localized surface plasmon modes play a key role in the broadband light harvesting capabilities of these nanostructures, and this is promising for a wide range of practical applications, for example in surface-enhanced spectroscopies.

Keywords: surface plasmons, simulation, optical properties

1. Introduction

Surface plasmons are electromagnetic surface waves originating due to the collective oscillation of the conduction electrons near the metal surface [1, 2]. Light coupling with surface plasmons results in enhancement of the local electromagnetic field and strong resonance in the extinction profile of conductive nanoparticles, leading to the optical phenomenon known as localized surface plasmon resonance (LSPR) [3, 4]. This interaction produces coherent localized plasmon oscillations with a resonant frequency that strongly depends on the shape and size of the nanoparticles, as well as on the surrounding dielectric media [5]. While the effect of the size and the influence of the dielectric media have been studied quite extensively, both experimentally [6] and theoretically [7], this has not been the case when it comes to experimentally studying the effect of complicated shapes. Most of the nanoparticles usually obtained are spherical in nature or are rod-like with circular cross-section. Theoretically, both shapes are interesting due to their symmetry. While the positioning of the SPR peaks obtained from spherical grains is controllable by controlling the sphere radius, the nanorods present two variables: rod length and radius of cross-section. Thus, one expects a higher degree of control with metal clusters of more complex shapes. One rarely comes across metal clusters with complex shapes experimentally; thus making inroads along these lines is difficult. However, with the maturing of the methods used to theoretically simulate the optical properties of metal nanoclusters [8], exotic shapes have been reported—for example, nanorods with triangular cross-section [9, 10], pyramid-shaped grains [11], etc.

While nanoparticles embedded in dielectric media with fairly constant dielectric constant over the frequency ranges of interest are well studied, the case where the dielectric constant of the surrounding media varies with the frequency has not attracted much attention. However, situations in which a nanoparticle having another nanoparticle in its vicinity whose dielectric constant varies with the frequency can lead to interesting LSPR features [12]. For example the two nanoparticles would interact electromagnetically with each other, showing high field enhancement in the gap. Recently, a bow-tie nanoparticle, formed from nanoparticles with equilateral triangle shape, excited at its LSPR wavelength, has been reported to generate extremely large fields within the gap [4, 13]. This has been exploited to study Raman spectra for samples which would usually give weak signals in surface-enhanced Raman spectroscopy (SERS). This clearly shows that the study of exotic structures can also lead to applications of importance.

Hence, in this work we undertake to further our understanding of optical properties of dumbbell-shaped
nanoparticles that were experimentally reported recently. Wang et al [14] and Kuldeep et al [15] have reported experimental evidence of SPRs in dumbbell-shaped clusters formed from spherical nanoparticles. While the clusters of Wang et al were of gold, Kuldeep et al reported two core–shell (the core of cesium bromide and the shell of metal cesium) structures in which the connection was via nanorod bridges of cesium. Though Kuldeep et al did not have control over the size of the dumbbells (in contrast to Wang et al), their results were interesting, as the exotic shape allowed for four possible control parameters, namely, the length \( l \) of the nanorod bridge separating the two parts of the spherical core–shell structure, the cross-sectional radius \( r \) of the nanorod, the radius of the dielectric spherical core \( R_i \) and the radius of the core–shell structure \( R_o \); see figure 1. The shell thickness is given by \( R_o - R_i \).

In this paper, the localized surface plasmon resonance of a dumbbell structure is investigated using the finite element method. The dependences of the plasmon resonance on various geometrical parameters are discussed. For field polarization orthogonal and parallel to the interparticle symmetry axis, the spectral properties of the structure are usually different. In this paper, the behavior of the dumbbell structure in the presence of an unpolarized incident electromagnetic radiation is studied for experimental conditions analogous to those reported by Kuldeep et al [15]. However, results with polarized light are included here whenever required. The next section explains the simulation model used in the calculations. The ‘Results and discussion’ section provides a detailed analysis of the behavior of the surface plasmon resonance with various geometrical parameters.

### 2. Simulations

The simulations were done using the commercially available finite element method (FEM) package COMSOL Multiphysics 4.2 (with the RF module) along with Matlab (R2010a). The three-dimensional simulation domain was composed of four spherical volumes: a core, a shell, an embedding medium, and a perfectly matched layer (PML), in addition to a cylinder connecting the shells as shown in figure 1. The nanoparticle core was taken to be CsBr, enclosed in a Cs shell modeled using the empirically
determined bulk dielectric constants provided by Palik [16] with linear interpolation. The medium surrounding the nanosystem was considered to be air. A plane wave was used for excitation of the nanostructure and was inserted on the inside of PMLs surrounding the embedding medium. The dimensions of the embedding volume and the PML were chosen such that reflecting waves from the computational domain walls would not affect the simulation results. Discretization of the simulation domain was performed using the built-in meshing algorithm in COMSOL, which partitioned the simulation space into a collection of tetrahedral finite elements. Large field enhancements, possibly due to plasmon resonances, required the application of mesh parameters to ensure convergence of the simulation in the required frequency regime.

3. Results and discussion

In the following paragraphs we discuss the study of the absorption spectra of a single dumbbell-shaped CsBr–Cs cluster. Since the absorption spectra of the structure depend on four variables, namely $l$, $r$, $R_i$ and $R_o$, we have simulated the spectra keeping three parameters fixed and varying one at a time.

3.1. The effect of nanorods on the absorption

Before proceeding to the dumbbell structure, it is worthwhile to investigate the surface plasmon resonance peak due to the nanorod. Under usual circumstances the length of the nanorod is far greater than its radius, $l \gg r$; then due to the anisotropy in its shape, we expect it to have two modes of oscillation, namely the transverse mode along the short axis and the longitudinal mode along the long axis. More explicitly, when light is incident along the $y$-axis, as in our case (figure 1), the linearly polarized light with the electric field along the $x$-axis ($E_x$) gives the longitudinal mode excitation, while that along the $z$-axis ($E_z$) results in transverse mode excitation. Such polarization dependence has been reported [17, 18]. However, the simulation for a cesium nanorod having $r$ and $l$ as 10 nm and 40 nm respectively shows just one broad peak around 570 nm, with no evidence of peaks in the UV or IR region. To investigate why we get a broad peak, we have simulated the SPR due to the transverse mode and longitudinal mode separately and obtained peaks at 500 nm and 600 nm due to the two modes respectively. The two peaks are close to each other because of the small dimensions of the nanorod [19]. Also, the longitudinal LSPR is much stronger compared to the transverse mode due to the larger polarizability of the nanorod along the longitudinal direction. Hence, the aggregation of the two peaks gives a single broad peak around 570 nm, i.e. closer to the peak position of the longitudinal mode.

To achieve further understanding of the contribution from the nanorod, we have investigated the influence of its size. An interesting observation made was that a redshift occurs in the SPR peak for increasing aspect ratio for the longitudinal mode, while the peak blueshifts for the transverse mode excitation. For the unpolarized wave, the peak followed the trend shown by the longitudinal mode of excitation (figure 2(b)). As the transmission electron microscope (TEM)
images of Kuldeep et al [15] suggest, their nanorods were parallel to the substrate (xz-plane) and the absorption spectra were obtained in the transmission mode, implying that for unpolarized light both transverse and longitudinal modes exist. The main result of their work was that as the aspect ratio increases, the SPR peaks shift to lower wavelengths. This implies that the transverse mode played a dominant role there.

We now proceed to investigate the role of nanorod bridges in the dumbbell structure. For this, we have maintained the outer radius of the shells at 50 nm and the inner radius at 20 nm, while varying the length and radius of the nanorod. The curves of figure 3 are distinctly different from those shown for a nanorod without shells on its two sides (figure 2(a)). Not only has an additional peak appeared in the UV region, but also the contributions from the two structures (shells and nanorod) seem to interact constructively, giving resonant absorption peaks whose intensities have increased (comparison shows a ×50 increase). Such intensity/field enhancements have been reported [20], with Nie et al showing ×14 enhancements due to constructive coupling of SPRs [22]. For completeness, we have also simulated spectra for two nanoshells kept in close proximity without a nanorod connecting them. Only one spectrum is given in figure 3 for brevity. As can be seen from figure 3, the peak in the visible region nearly disappears.

Figure 4 shows the field patterns corresponding to the peaks in the UV (figure 4(a)) and visible (figure 4(b)) ranges of the spectra for the transverse modes. As explained in the above paragraphs, the visible peak is due to the plasmon resonance along the nanorod, which is enhanced by the two Cs–CsBr spherical shells; however, it should be noted that the fields are not concentrated just on the cylinder. In fact a coupling of the localized plasmons of the shells along the cylinder is also observed, possibly leading to an enhancement in the absorption (figure 4(b)). Figure 4(a) shows that the UV peak is essentially concentrated on the CsBr–Cs interface. The role of the shell’s thickness in the SPR spectra and further details will be discussed in the next section.

Combining the results, we have shown the variation of the absorption peak intensity and position for both the UV and the visible peaks with the aspect ratio of the nanorod. As
The previous section clearly showed that the shells act as amplifiers, increasing the plasmon oscillations and hence the resonant absorption in the visible region caused by the nanorods. The shell also contributes a peak in the UV region whose absorption intensity is influenced by the aspect ratio of the nanorod. This section will look into the effect of varying the shell size on the absorption patterns. The simulations in this section were done keeping the nanorod dimensions fixed at $l = r = 10$ nm and varying $R_0$ and $R_r$, the core–shell dimensions. Figure 7 shows some of the simulated absorption spectra, where we have varied the outer radius of the shells ($R_o$), keeping the radius of the core ($R_r$) constant (20 nm). Also, the combination of our simulations reveals a variation of the peak position with the shell thickness. It can be seen that $\lambda_{\text{max}}$ for the visible peak exhibits no shift with change in the shell thickness. This shows that the SPR peak position in the visible region depends solely on the variation of the dimension of the nanorods. However, the UV peaks show a linear relation with $R_o - R_r$, with the slope reflecting a redshift with increasing $R_o - R_r$.

Figure 8 shows that there is a linear relation between the absorption intensity of the peak in the UV range and the thickness of the metallic cesium shell ($R_o - R_r$). As explained above, an accumulation of opposite charges takes place on either side of the conductive nanorod due to the longitudinal mode of excitation. Thicker shells for a given nanorod length mean larger accumulations of charges and hence more absorption, as is evident from the increased absorption peak intensities. Interestingly, as the shell size increases (beyond 50 nm), an SPR peak appears in the IR region. Oldenburg et al [26] have done extensive work on metal shells and have shown that each surface gives its own plasmon mode. The two modes couple across the shell thickness with the coupling strength based on the dipole model following the $(R_o - R_r)^{-3}$ trend. Hence, with increase in the shell thickness the couplings between the two surfaces, i.e. CsBr–Cs and Cs–air coupling, would diminish. We believe that such diminished coupling gives rise to the IR peak. We have tried to investigate which surface contributes to the IR peak using the field pattern. The field pattern for the peak in the IR region is shown in figure 8 for different shell thicknesses. It can be seen that the IR peaks corresponding to the plasmon resonance occur at the outer surface of the shell. It has been observed expected, the peak position ($\lambda_{\text{max}}$) of the SPR visible peak shows a linear relation with the aspect ratio (figure 5). Such size dependent shifts (redshift with increasing grain size) have been well documented [21]. However, since the shell dimensions were kept fixed in these simulations, we do not observe any variation in the UV peak maxima positions. Figure 6 shows that there is a linear relationship between the absorption intensity of the two peaks and the aspect ratio. The intensity depends on the amount of oscillating electrons present and hence is related to the metal present in the cluster. As the aspect ratio of the nanorod increases, the metal content increases and hence an increase in the absorption intensity is observed. Interestingly, these simulations were done for fixed shell dimensions and yet the contribution of UV absorption by these spheres increases with increasing aspect ratio of the nanorods. However, one has to remember that the metallic nanorod provides a conductive path. The existence of a conductive path allows for charge transfer plasmons (CTPs) [23] for the charges distributed on the nanoshells. These charges appear due to charge accumulation from the longitudinal excitation mode. The large accumulation of charges of opposite signs on either side of the nanorod gives an enhancement of the local fields (figure 4(b)) [24, 25]. Also, a CTP is sensitive to the number of oppositely signed charges present on either side of the nanorod and hence on the nanorod’s conductivity. Increase in length of the nanorod decreases the conductive path, leading to charge accumulation and hence enhanced absorption intensity.

3.2. The effect of the core–shell system

Figure 7. The simulated absorption spectra for increasing cesium shell thickness, keeping the aspect ratio/length of the nanorod constant. Combining the results for the UV and visible peak positions ($\lambda_{\text{max}}$) of the simulated spectra reveals no variation in visible peak position, while the UV peak position shows a steady redshift.
previously that the plasmon resonance peak of the Cs sphere occurs in the far IR range [27]. The above analysis shows that dumbbell metal nanostructures are highly tunable and suitable for use by the experimentalist who might require controllable geometrical parameters in developing light harvesting sensors, etc.

4. Conclusion

We have investigated the localized surface plasmon resonance of a dumbbell structure consisting of two CsBr–Cs core–shell structures connected with a Cs nanorod. As a primary step, the plasmon resonance of a Cs nanorod is studied and it is found that the plasmon absorption peak resides in the visible region. The study of the dumbbell structure revealed that the two nanoshells enhance the absorption in the visible region in addition to contributing a peak in the UV range. As the shell thickness of the dumbbell structure is increased, another peak appears in the IR region. Tunability of these resonance conditions with various geometrical parameters was observed.

Acknowledgments

We would like to acknowledge our gratitude to the University Grants Commission (UGC, Delhi) for financial assistance (F. No. 39-531/2010 SR) for carrying out this work. Also, the financial travel grant given by the University of Delhi (Innovation Projects, SGTB-101) is gratefully acknowledged.

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