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# Analysis of surface plasmon resonance in the composite core(Au)/interlayer/shell(Ag) nanoparticles

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ABSTRACT

Using the discrete dipole approximation, we analyze surface plasmon resonance (SPR) in the core(Au)/interlayer/shell(Ag) nanoparticles. Here, the role of the Au core is typically central. We focus on the effect of the interlayer properties on SPR. If the interlayer is metallic, the contribution of the Au core to SPR is found to be suppressed, while the semiconductor interlayer can enhance this contribution. The porous Si interlayer exhibits the combined features inherent to a cavity and amorphous Si. These conclusions are illustrated by showing the distribution of electric field in and near nanoparticles.



## 1. Introduction

Noble metal nanostructures have been widely applied in the areas of optics, biosensor, and medical diagnostics, solar cells, surface enhanced Raman spectroscopy, etc. [1–3]. Most of the applications are closely related with the properties of the surface plasmon resonance (SPR), which results from the collective motions of the conduction electrons with the restoring force provided by the induced surface charges [4]. Au and Ag nanostructures have attracted considerable attention recently due to their tunable surface plasmon resonance from visible to near IR, which is highly dependent on their structural characteristics such as their size, shape, composition, and deposited substrate as well as their external dielectric environment. It has been shown that the SPR band of Au nanoshells supported on dielectric cores could be readily tunable from 500 nm to 1200 nm by varying their diameters, shell thickness, or both. Various kinds of nanostructures based on Au and Ag, such as core/shell structures [2–5], nanoalloys [6,7], dimmers [8–10] and their combinations [11,12], have been designed and produced many novel optical properties.

Recently, core/shell nanostructures based on Au and Ag have been found especially versatile to adjust their properties by combining with such materials as other metals [13,14], semiconductors [15–19], magnetic materials, [10,20], etc. Many novel phenomena appear due to the property difference and interaction between the core and shell. For example, in Au/CdS core/shell system, a pronounced photoinduced charge separation at the interface of Au and CdS was found, which can enhance photoelectric conversion efficiency [16], while a light-induced phase transition from magnetite to hematite was observed in the Au/iron oxide core/shell system, where the gold cores act as plasmonic nanoheaters [20]. Xu et al. [2] have discussed the SPR properties of separate core/shell nanostructures, whose core and shell are separated by vacuum cavity, and found a cavity resonance enhancement effect and new absorption bands due to more interfaces and the consequent plasmon coupling. Mott et al. [21] synthesized nanoparticles similar to Ag/Cavity/Au core/shell structure and found the amount of gold added in the coating procedure has a large impact on the structure of the nanoparticles and the resulting optical properties. The cavity provides the separate core/shell system with the opportunity to cooperate with the other functional materials, which may endow the system with remarkable properties. Currently, the core/shell system with dielectric $SiO_2$ spacer has been studied by a few researchers. In this system, the SPR properties have been proved quite different from that of the core and shell due to the coupling or hybridization between the core plasmon and the shell plasmon [22–24]. To the authors' knowledge, the SPR properties of the core/shell system separated by other materials, such as semiconductors, magnetic materials, etc., have been rarely researched before.

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In the present work, the DDA code is utilized to study theoretically the SPR properties of core(Au)/interlayer/shell(Ag) nanoparticles. We mainly focus on the effect of different kinds of interlayer, including insulant vacuum cavity, coinage metal Cu, semiconductors AlGaAs and amorphous Si, magnetic material Ni and porous material porous Si, on the SPR properties of the nanoparticles. The results show that the interlayer materials have great influence on the SPR properties of these systems. The metal interlayers (Cu and Ni) tend to cause a "short-cut" effect, which depresses the contribution of the inner Au core to SPR and leads to only one peak that Ag shell dominates existing in the extinction spectra. However, semiconductor interlayers (AlGaAs or a-Si) can enhance this contribution and cause new absorption bands. In addition, the SPR of Au/p-Si/Ag system exhibits the characteristics of both Au/Cavity/Ag and Au/a-Si/Ag systems because it integrates these two structures. Our work shows that the tunable SPR properties can be achieved through controlling the kind of interlayer material in the separate Au/Ag systems.

## 2. Model and methods

In addition to UV–visible extinction spectroscopy, many computational methods such as discrete dipole approximation (DDA), finite difference in the time domain method (FDTD) and the boundary element method (BEM) have also been used to reveal the optical properties of noble metal nanoparticles. Among all of these methods, the DDA, which is also known as the coupled dipole approximation, is most frequently used for calculating of the scattering and absorption by targets of arbitrary geometry [2].

The DDA [25,26] starts by dividing the target into a cubic array of N-point dipoles, whose positions and polarizabilities are denoted as $r_i$ and $\alpha_i$ ($i = 1, 2, \ldots$), respectively. $\alpha_i$ can be achieved by

$$\alpha_i = \frac{3d^3}{4\pi}\frac{\varepsilon_i - 1}{\varepsilon_i + 1} \tag{1}$$

where $d$ is the interdipole spacing and $\varepsilon_i$ is the complex dielectric function at location $r_i$.

The polarization induced in each dipole as a result of interaction with a local electric field $E_{\mathrm{loc},i}$ can be described as follows

$$P_i = \alpha_i \cdot E_{loc,i} \tag{2}$$

For each isolated particle, $E_{\mathrm{loc},i}$ is the sum of an incident field and a contribution from all other dipoles in the same particle. That is

$$E_{loc,i} = E_{inc,i} + E_{self,i} = E_0 \exp(iK \cdot r_i) - \sum_{j \neq i} A_{ij} \cdot P_j \tag{3}$$

$E_0$ and $K$ are the amplitude and wave vector of the incident wave, respectively, and the interaction matrix $A$ has the following form:

$$A_{ij} \cdot P_j = \frac{\exp(ikr_{ij})}{r_{ij}^3}\left\{k^2 r_{ij} \times (r_{ij} \times P_j) + \frac{(1 - ikr_{ij})}{r_{ij}^2} \times [r_{ij}^2 P_j - 3r_{ij}(r_{ij} \cdot P_j)]\right\} \tag{4}$$

where $k = \omega/c$. By defining $A_{jj} = {\alpha_j}^{-1}$, the above equations can be reduced as:

$$\sum_{k=1}^{N} A_{jk} \cdot P_k = E_{inc,j} \tag{5}$$

Then the scattering problem of such systems can be reduced by finding the polarizations $P_j$ that satisfy a system of 3 N complex linear equations. Once the lattice site $r_i$ and the dielectric constant at this site are determined, the polarizations $P_j$ can be solved from Eq. (5). And then, the absorption cross section $C_{\mathrm{ext}}$ and absorption efficiency $Q_{\mathrm{ext}}$ can be obtained from Eq. (6) and Eq. (7) [4].

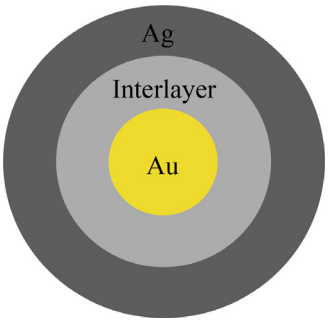


**Figure 1.** The model of the core(Au)/interlayer/shell(Ag) system.

$$C_{\mathrm{ext}} = \frac{4\pi k}{|E_0|^2}\sum_{j=1}^{N} Im(E_{inc,j}^{*} \cdot P_j) \tag{6}$$

$$Q_{\mathrm{ext}} = \frac{C_{\mathrm{ext}}}{\pi R^2} \tag{7}$$

The model of the core(Au)/interlayer/shell(Ag) system used in this article is shown in Figure 1. The Au core and Ag shell are separated by different kinds of interlayers, including vacuum cavity, Cu, Ni, AlGaAs, porous Si (p-Si), and amorphous Si (a-Si). The dielectric function of the metal nanoparticles, which is close related to their optical properties, will be size dependent when the characteristic size of the particle becomes smaller than the mean free path of the conduction electrons [27–29]. The work done in the reference [30] suggests that morphological differences are much important below a certain size threshold about 5 nm, while above this size, the size-corrected effect of dielectric constant is ignorable. In this simulation, the radius of the Au core and the thickness of the interlayer and the Ag shell are fixed as 20 nm, 10 nm, and 10 nm, respectively. The dielectric function of the materials related in this work has been chosen from Palik's handbook [31] and SOPRA N&K Database [32]. All the systems are simulated in vacuum with the refractive index of the surrounding medium fixed at unity.

## 3. Results and discussion

### 3.1. The extinction spectrum simulation

Figure 2(a) shows the absorption spectra of the bare Au core with radius 10 nm, the empty Ag shell with thickness 10 nm and inner radius 20 nm, and the Au/Cavity/Ag system, where the Au core radius, cavity and Ag shell thickness are all fixed at 10 nm. As shown in Figure 2(a), the wavelength of the SPR for the bare Au core and the empty Ag shell is located at 515 and 423 nm, respectively. The extinction spectrum of the bare Au core is quite close to the exiting results in similar conditions received from experiments [23,33] and simulations [23,34]. This, to some extent, identifies the validity of our calculations. In the absorption spectrum of the Au/Cavity/Ag system, a striking absorption peak is located at 436 nm, which is so strong that only very carefully can we note the peak at 331 nm. Recently, Xu et al. [2] have also found that two or more obvious resonance absorption peaks, depending on the structure parameters, appear at the absorption spectra of the Au/Cavity/Ag(Au) systems. This can be explained by the plasmon hybridization theory, which is a mesoscale electromagnetic analog of the molecular-orbital theory. The plasmon hybridization theory separates complex nanoparticle geometries into simpler constituent parts and then calculates how the plasmon resonances of the elementary parts interact with each other to generate