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Simulated localized surface plasmon spectra of single gold and silver nanobars

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ABSTRACT

Gold and silver nanoparticles can exhibit localized surface plasmon resonance phenomena resulting from the interaction with light, and it is always characterized by the extinction spectrum. In this paper, the extinction spectra for single gold and silver nanobars are investigated by using discrete dipole approximation method. We present a systematic study of the effects of the orientation, the length, and the refractive index of ambient medium on the extinction spectrum and resonance wavelength of single nanobars. The results show that the nanobar can excite both the longitudinal mode and transverse mode in visible and near-infrared regions at specific conditions.

1. Introduction

Gold (Au) and silver (Ag) nanoparticles can strongly scatter and absorb light at a certain wavelength in the visible and near-infrared regions. The attractive optical properties of metal nanoparticles are connected to their localized surface plasmon resonance (LSPR). LSPR is a coherent, collective spatial oscillation of the free electrons in a metallic nanoparticle, which can be directly excited by light. As a result of the LSPR, the absorption and scattering of light by nanoparticles, as well as the local electric field around the nanoparticles, will be strongly enhanced. The wavelength of light which can excite the LSPR (i.e. the resonance wavelength) is strongly dependent on the material, size, shape and the ambient medium [1–5]. In addition, the LSPR properties are also dependent on the spacing between the nanoparticles (i.e. the coupling between the plasmon resonances) and the polarization of the incident light [6–9]. These special optical properties of metal nanoparticles make them have tremendous potential applications in many fields, including optical imaging and photothermal therapy [10,11], chemical and biological sensing [12,13], surface enhanced Raman scattering (SERS) [14,15] and photovoltaic devices [16,17]. Tuning the optical properties of metal nanoparticles of different size and shape is a desired aim for applications. Simulate the optical properties of metal nanoparticles is considered as the first step to achieve this goal.

Many theoretical methods have developed to model the optical properties of nanoparticles, such as Mie theory [18], *T*-matrix method [19], finite difference time domain (FDTD) [20], and discrete dipole approximation (DDA) [21]. Among these, DDA is a frequently used numerical method for modeling the absorption and scattering of light by nanoparticles of arbitrary shape and composition. Schatz and co-workers [22,23] proved that the DDA is suited for modeling the optical properties of metal nanoparticles with different geometries and environments through the extensive studies on the extinction spectrum and the local electric field distribution in metal nanoparticles. Many research groups used DDA to simulate the optical properties of metal nanoparticles of different shapes and sizes [24–27]. Sosa et al. [24] used the DDA to study the main optical features of the extinction, absorption, and scattering efficiencies of gold and silver nanoparticles with different sizes and shapes (sphere, cube, spheroid, cylinder, and tetrahedron). Lee et al. [25,26] used the DDA to investigate the absorption and scattering properties of gold and silver nanorods. Recently, it is possible to produce size and shape controlled metal nanoparticles with the developments of synthesis techniques [28–30]. Advanced synthesis techniques are indeed able to produce nanobars of different size [31]. Thus, it is a great interest to model the optical properties of nanobars theoretically in detail.

In this paper, we investigate systematically the extinction spectrum and resonance wavelength of single nanobars of different sizes and compositions by using DDA method. This paper is organized as follows. In Section 2, we introduce the DDA method and the dielectric function used in this study. In Section 3, we give

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some numerical results and discussion for single nanobars of different sizes and compositions. Finally, a summary will be given in Section 4.

2. Theory

2.1. Discrete dipole approximation

The discrete dipole approximation (DDA) is a flexible and powerful technique for computing scattering and absorption by targets of arbitrary geometry. The DDA is an approximation of the continuum target by a finite array of polarizable points which acquire dipole moments in response to the local electric field. The DDA was apparently first proposed by Purcell and Pennypacker [21]. DDA method was developed further by Draine [32], Draine and Goodman [33], reviewed by Draine and Flatau [34], and extended to periodic structures by Draine and Flatau [35]. The freely available open-source Fortran-90 software package (DDSCAT 7.2) developed by Draine and Flatau [36] is used in this paper.

In the DDA approach, one represents the object of interest as a cubic lattice of N polarizable points. There is no restriction as to which of the cubic lattice sites is occupied, which means that DDA can represent an object or multiple objects of arbitrary shape. Let us assume an array of N polarizable point dipoles located at $\{\mathbf{r}_i, i = 1, 2, \ldots, N\}$, each one characterized by a polarizability α_i. The dipole moment induced in each dipole as a result of interaction with a local electric field $\mathbf{E}_{\mathrm{loc},i}$ is:

$$\mathbf{P}_i = \alpha_i \mathbf{E}_{\mathrm{loc},i} \tag{1}$$

where $\mathbf{E}_{\mathrm{loc},i}$ is the sum of the incident electric field and the contribution from all other dipoles

$$\mathbf{E}_{\mathrm{loc},i} = \mathbf{E}_{\mathrm{inc},i} + \mathbf{E}_{\mathrm{dipole},i} = \mathbf{E}_0 \exp(i\mathbf{k}\cdot\mathbf{r}_i - i\omega t) - \sum_{j\neq i} \mathbf{A}_{ij}\mathbf{P}_j \tag{2}$$

where $-\mathbf{A}_{ij}\mathbf{P}_j$ is the electric field at $\mathbf{r}_i$ that is due to the dipole moment $\mathbf{P}_j$ at location $\mathbf{r}_j$, including retardation effects. $\mathbf{A}_{ij}$ is a 3×3 matrix that represents the interaction between the dipole at $\mathbf{r}_i$ and $\mathbf{r}_j$, it is given as

$$\mathbf{A}_{ij} = \frac{\exp(ikr_{ij})}{r_{ij}}\left[k^2\left(\hat{r}_{ij}\hat{r}_{ij} - \mathbf{I}_3\right) + \frac{ikr_{ij}-1}{r_{ij}^2}\left(3\hat{r}_{ij}\hat{r}_{ij} - \mathbf{I}_3\right)\right], \quad i \neq j \tag{3}$$

where $k = \omega/c = 2\pi/\lambda$ is the wave number, $r_{ij} = \left|\mathbf{r}_i - \mathbf{r}_j\right|$ is the distance from points j to i, $\hat{r}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$ is the unit vector in the direction from points j to i, and $\mathbf{I}_3$ is the 3×3 identity matrix. Defining the diagonal matrix as $\mathbf{A}_{ii} = \alpha_i^{-1}$, and substituting into Eqs. (1) and (2) gives

$$\mathbf{A}_{ii}\mathbf{P}_i + \sum_{j\neq i}\mathbf{A}_{ij}\mathbf{P}_j = \mathbf{E}_{\mathrm{inc},i} \tag{4}$$

Thus, the problem is reduced to finding the dipole moments $\mathbf{P}_j$ that satisfy a system of $3N$ complex linear equations

$$\sum_{j=1}^{N}\mathbf{A}_{ij}\mathbf{P}_j = \mathbf{E}_{\mathrm{inc},i} \tag{5}$$

Once the above equation has been solved for the unknown dipole moments $\mathbf{P}_j$, the extinction, absorption, and scattering cross sections can be calculated by [32]:

$$C_{\mathrm{ext}} = \frac{4\pi k}{|\mathbf{E}_0|^2}\sum_{j=1}^{N} Im\left(\mathbf{E}_{\mathrm{inc},j}^{*}\cdot\mathbf{P}_j\right) \tag{6}$$

Table 1
Values of the plasma frequency $\hbar\omega_p$ [38] and the damping constant $\hbar\gamma$ [39].

Metal	$\hbar\omega_p$ [eV]	$\hbar\gamma$ [eV]
Au	9.03	0.0708
Ag	9.01	0.0212

$$C_{\mathrm{abs}} = \frac{4\pi k}{|\mathbf{E}_0|^2}\sum_{j=1}^{N}\left\{Im\left[\mathbf{P}_j\cdot\left(\alpha_j^{-1}\right)^{*}\mathbf{P}_j^{*}\right] - \frac{2}{3}k^3|\mathbf{P}_j|^2\right\} \tag{7}$$

$$C_{\mathrm{sca}} = C_{\mathrm{ext}} - C_{\mathrm{abs}} \tag{8}$$

2.2. Dielectric function

There are two sets of quantities that are often used to describe optical properties: the real and imaginary parts of the complex refractive index $\tilde{n} = n + ik$ and the real and imaginary parts of the complex dielectric function (or relative permittivity) $\varepsilon = \varepsilon_1 + i\varepsilon_2$. These two sets of quantities are not independent; either may be thought of as describing the intrinsic optical properties of matter. The relations between the two are

$$\tilde{n} = \sqrt{\varepsilon} \tag{9}$$

$$\varepsilon_1 = n^2 - k^2 \tag{10}$$

$$\varepsilon_2 = 2nk \tag{11}$$

$$n = \sqrt{\frac{\sqrt{\varepsilon_1^2+\varepsilon_2^2}+\varepsilon_1}{2}} \tag{12}$$

$$k = \sqrt{\frac{\sqrt{\varepsilon_1^2+\varepsilon_2^2}-\varepsilon_1}{2}} \tag{13}$$

where we have assumed that the material is nonmagnetic.

Metals contain significant numbers of free electrons. As the name implies, there are electrons that are not bound to any atoms, and therefore do not experience any restoring forces when they are displaced. The free electron model of metals is attributed to Paul Drude, so the model is generally called the Drude model. In this model, the dielectric function of a free electron metal is [37]

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \tag{14}$$

where ω is the angle frequency of incident light, γ is the damping constant which is related to electron scattering processes, ω_p is the plasma frequency, it can be written as

$$\omega_p = \sqrt{\frac{Ne^2}{m\varepsilon_0}} \tag{15}$$

where N is the free electron density, e is the electron charge, m is the effective mass of an electron, ε_0 is the vacuum permittivity. The plasma frequency and the damping constant for Au and Ag are given in Table 1.

Despite its applicability to metals such as aluminum, Drude model alone does not accurately describe the optical characteristics of many other metals. For the noble metals (Au and Ag), they also have substantial bound electron component, which appreciably alters the free electron optical properties. Especially for Au and Ag, the free electron Drude model is not adequate in the near-UV and visible wavelength range, shown as Fig. 1.

In Fig. 1, we compare the Drude model with experimental data taken from Johnson and Christy [39] for Au and Ag. We observe that the imaginary part of the dielectric function calculated using the Drude model deviate from the experimental data in the visible and near-ultraviolet region. For this reason, we use the experimental data taken from Johnson and Christy [39] in our simulation.