2D Simulation of Surface Plasmon Resonance

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Abstract

In the paper, interactions of an electromagnetic wave with a metallic nanoparticle in the optical range for a two-dimensional TM mode (p-polarization) are investigated by a set of new surface integral equations. A critical case of triangular silver is studied by the new integral equations to exhibit a strong local enhancement of the electric field at the sharp edges; the amplification of silver is around 300, which is much stronger than a dielectric nanoparticle. In addition, the surface plasmon resonance (SPR) in elliptical silver is demonstrated, and the results indicate the red shift of SPR can be caused by increasing the aspect ratio of the particle and the permittivity of the host.

Introduction

In the past few years, the noble metallic nanoparticles (e.g. Ag, Au) attract lots of attention, because of the so-called surface plasmon resonance (SPR), a collective oscillation of conductive electron in the overall metal. Due to the free electrons of metals, the permittivity exhibits frequency dependent (dispersive), and its real part usually is negative in certain range of UV to near-IR. When an illuminating light interacting with the metallic nanoparticles, SPR can be induced at a specific frequency. The unique feature leads to a near field enhancement in electric field and a strong scattering. In the last decade, chemists had successfully synthesized a variety of metallic nanoparticles with different shapes [1-5]. Recently using the dark-field single-object microscopy and spectroscopy, the SPR of a single metallic nanoparticle in spectrum can be characterized with the metallic nanoparticles, SPR can be induced at a specific frequency. The unique feature leads to a near field enhancement in electric field and a strong scattering. In the last decade, chemists had successfully synthesized a variety of metallic nanoparticles with different shapes [1-5]. Recently using the dark-field single-object microscopy and spectroscopy, the SPR of a single metallic nanoparticle in spectrum can be characterized by a white-light illumination [6-8]. A few of experiments indicate a high aspect-ratio nanorod exhibits a longer dephasing time than a spherical one, and induces a red shift of the peak position of SPR [5-7]. In addition, some measurements show the permittivity of the host material (e.g. air, water [1,2], oil [8], SiO2[9], ZrO2[10]) can also affect the red shift. Since there is no analytical solution for a nanoparticle with arbitrary shape, a number of numerical methods [11-13] were proposed to study the SPR problems quantitatively. These previous researches motivate us to study the red shift of SPR due to the effects of the aspect ratio and size of nanoparticle as well as the refraction index of the host material by a new set of surface integral equations with the aid of the boundary-element method (BEM). The advantage of BEM is to provide a flexibility of calculating arbitrary shape, especially a scatterer with large aspect ratio or sharp corners. The accuracy of the method has also been checked for the cases of circular metallic nanoparticles, and the results are in excellent agreement with the analytic solutions.

Theory

For the BEM, a set of surface integral equations was derived from Stratton-Chu formulation [14],

\[
H_z(x) = H_z^1(x) - \int_S H_z(x') n' \cdot \nabla' [G_1 - G_2] \, dl' - i\omega \int_S E_t(x') [\varepsilon_1 G_1 - \varepsilon_2 G_2] \, dl', \quad x \in S
\]

(1)

\[
D_n = D_n^1 - i\omega \int_S [\varepsilon_1 \mu_1 G_1 - \varepsilon_2 \mu_2 G_2] \, n \cdot dl' - \int_S D_n n \cdot \nabla' [G_1 - G_2] \, dl' - \int_S E_t n \cdot e_z \times \nabla' [\varepsilon_1 G_1 - \varepsilon_2 G_2] \, dl'
\]

(2)

\[
E_t = E_t^1 - i\omega \int_S [\mu_1 G_1 - \mu_2 G_2] \, t \cdot dl' - \int_S D_n t \cdot \nabla' \left[ \frac{G_1 - G_2}{\varepsilon_1 - \varepsilon_2} \right] \, dl' - \int_S E_t t \cdot e_z \times \nabla' [G_1 - G_2] \, dl'
\]

(3)

where \( G_j = \frac{i}{\lambda} H_0^{(1)}(k_j r), \, j=1, 2 \). \( H_0^{(1)} \) is the Hankel functions of the first kind of order zero for the Green functions \( G_j \), because of the time harmonic factor \( \exp(-i\omega t) \), and \( S \) is the boundary of the scatterer. The
wavenumbers, \( k_j, j=1,2 \), are of the surrounding medium and the metallic scatterer respectively. The total fields are the sum of the incident field and the scattering field; \( \mathbf{E} = \mathbf{E}^i + \mathbf{E}^s, \quad H_z = H_z^i + H_z^s \). In Eq. (1) to (3), the unknown are the surface total field (the tangential magnetic field \( H_z \), the normal displacement \( D_n \), and the tangential electrical field \( E_t \)), and the kernel functions are the combination of the Green’s functions of the metal and the surrounding dielectric material. After discretizing the problem, a matrix is constructed to calculate the surface components, the tangential magnetic field, the normal displacement field and the tangential electric field. Substituting these surface components into a set of integral representation, the whole interior and exterior field can be calculated, and the scattering cross section (SCS) at far field can be obtained too. For the MMP, two sets of multiple poles, at multi-centers for expansion with the coefficients as unknowns, are used to match the boundary conditions; one set is for the scatterer, and the other for the scattering part in the surrounding medium. After matching the boundary conditions at a number of collocation points, an over-determined matrix is established and solved by an algorithm of singular-value decomposition to obtain the strength (coefficients) of these multipoles, and then the whole interior and exterior field can be calculated in terms of these coefficients.

**Numerical Results and Discussion**

Consider a 2D TM problem; a \( p \)-polarization EM wave illuminating upon a silver nanoparticle embedded in a dielectric medium (host material). A critical case of a regular-triangle silver \(^3\) is considered to demonstrate the ability of the new integral equations, where the relative permittivity of the silver nanoparticle is \( \varepsilon_{2r}=(-4.422, 0.73) \) at \( \nu=3\text{eV} \) \(^1\), which is in a host medium of \( \varepsilon_{1r}=1 \), and the plane wave with an incident angle \( \theta_i = 0^\circ \). In the case, the equilateral triangle, with a side length \( 20\sqrt{3}\text{nm} \), is smoothed at the corners with a radius of 0.1 nm. In Fig. 1, two numerical results of BEM are plotted for comparison; one is divided by 900 collocation points (the circle) along the contour, and the other 1200 points (the solid line). The accordance shows the convergence of BEM. A strong local enhancement of the electric field is exhibited in the vicinities of the three vertices of the silver, where the maximum amplification reaches about 300 times of the incident field, as shown in Fig. 1. In contrast, the amplification is only about 10 for a dielectric scatterer \( (\varepsilon_{2r}=10) \) with the same configuration. Hence, the strong local field of metal is attributed not only to the edge effect but also to the plasmon effect. The near-field enhancement induced by the sharp edge of a metal is useful for the applications of surface enhanced Raman scattering. Normally, the number of collocation point is more for metal than dielectric by BEM to have a reasonable accuracy, because of the negative real part of the permittivity.

![Figure 1](image1.png)

**Figure 1:** (a) the normalized amplitude of the normal displacement field along the contour of an equilateral triangle calculated by BEM, (b) the tangential electric field. Three vertices are at \((0, 20\text{nm}), (-17.32\text{nm}, -10\text{nm}), (17.32\text{nm}, -10\text{nm})\). The solid line: silver (collocated by 1200 points), the circle: silver (by 900 points), and the dashed line: a dielectric material of \( \varepsilon_{2r}=10 \) (by 1200 points).

Another typical case, which is near SPR, is presented: a nanometer-sized elliptical silver \((a=10\text{nm}, b=40\text{nm})\) with \( \varepsilon_{2r}=(-10.546, 0.8385) \) \(^1\), in a host medium \( \varepsilon_{1r}=2 \), at \( \nu=2.3\text{eV}, \theta_i = 0^\circ \). The corresponding near field distribution of the electric and magnetic field are depicted in Fig. 2(a) and (b). Inside the metallic nanoparticle, the strength of the electric field is nearly uniform (an overall collective oscillation of free electrons), while the outside electric fields near the two tips of the elongated nanoparticle exhibit a strong amplification; the maximum value reaches about 15 times of the incident field. The scattering cross section (SCS) of the far field is plotted in Fig. 2(c), which shows a dipole behavior. To manifest the effect of shape on SPR, the SCS versus frequency of four nanoparticles with different aspect ratio \((b/a=1, 2, 4, \text{ and } 8)\) are calculated with a fixed area of \( 400\pi \text{nm}^2 \), as shown in Figure 3. Figures 3(a), 3(b), and 3(c) show the results of an individual nanoparticle in a host.
material, \(\varepsilon_{1r}=1\), \(\varepsilon_{1r}=2\), and \(\varepsilon_{1r}=4\), respectively.

Figure 2: (a) the total field of the electric field, (b) the magnetic field, (c) SCS at far

Figure 3: SCS vs. eV for an individual nanoparticle with various aspect ratio (b/a) in different host, (a) 1r =1, (b)1r =2, (c)1r =4, with i =0. ■: b/a=1, △: b/a=2, ●: b/a=4, and □: b/a=8.

The numerical results of 2D TM mode illustrate the larger the aspect ratio is, the peak position of SPR is shifted to the longer wavelength, i.e. the red shift. Furthermore, the larger the permittivity of the host is, the more the red shift becomes by comparing figures 3(a) to 3(c). In addition, the magnitude of the peak of SCS at resonance becomes larger and the linewidth becomes narrower for a higher aspect-ratio nanoparticle. According to Ref [6], the dephasing time is defined as, \(2\hbar/\Gamma\), where \(\Gamma\) is the FWHM of the linewidth. Therefore, we can infer that an elongated nanoparticle has a longer dephasing time than a circular one. As to the size effect, we vary the area (100\(\pi\), 400\(\pi\), 1600\(\pi\) nm\(^2\)) of an elliptical nanoparticle embedded in a host material (\(\varepsilon_{1r}=2\)) but with a fixed aspect ratio (b/a=4) to calculate the SCS, as shown in Figure . Comparing the three curves, we found that increasing the size results in the red shift of the SPR and the increase of the SCS, but the broadening of the linewidth for a fixed b/a. The effect of orientation is also considered, as depicted in Figure , by varying the incident angle (\(\theta_i=0^\circ\), 45\(^\circ\), 90\(^\circ\)) of the illuminating light to interact with a fixed elliptical nanoparticle (a=10nm, b=40nm) embedded in host, \(\varepsilon_{1r}=2\). The results indicate that when the maximum principal axis is parallel to the polarization of the incident electric field, a largest SCS is caused.

Figure 4: SCS vs. eV for an Ag nanoparticle with different area (\(\Delta : 100\pi\), ● : 400\(\pi\), □ : 1600\(\pi\) nm\(^2\)) but with fixed b/a=4 in a host (\(\varepsilon_{1r}=2\)) for \(\theta_i=0^\circ\)

Figure 5: SCS vs. eV for an illuminating light with various incident angle (● : \(\theta_i=0^\circ\), □ : \(\theta_i=45^\circ\), ▲ : \(\theta_i=90^\circ\)) on an Ag nanoparticle (a=10nm, b=40nm) in host, \(\varepsilon_{1r}=2\).
**Conclusion**

SPR of Ag nanoparticles were studied by the new surface integral equations. The numerical results demonstrate that the collective electron motion in the metallic nanoparticle can induce a strong near field enhancement and large dipole behavior at far field. Through a systematical study, the SPR is shown to be sensitive to four factors; 1. the shape (aspect ratio) of nanoparticle, 2. the permittivity of surrounding medium, 3. the orientation, 4. the size. Normally, the higher the aspect ratio is, the more the red shift induces. In addition, the red shift of SPR becomes more, if the same nanoparticle is embedded in a host with higher permittivity. A significant red shift of the peak of SPR can be induced by raising the aspect ratio of the particle or the permittivity of host; e.g. SPR occurs at 3.4eV for $b/a=1$, while 1.72eV for $b/a=8$, if $\varepsilon_r=2$.

**REFERENCES**