Local Surface-Plasmons in Nonspherical Metal Nanoparticles *

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When a small metallic nanoparticle is irradiated by incident light, the oscillating electric field can cause the conduction electrons to oscillate coherently, which excites the local surface plasmons (LSPs). As is well known, excited LSPs can gather the energy of incident light to the surface of metallic nanoparticle. Recently, some nonspherical particles, e.g. tetrahedron, are suggested to obtain stronger localized electric field. We employ the discrete dipole approximation method to calculate the optical response of the tetrahedron nanoparticle, including the extinction and distribution of the electric field around the particle. The influences of some parameters, including the nanoparticle size, incident direction and polarization, are investigated to analyse the response modes and to obtain stronger localized electric field.

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Optical properties of metal particles have been of interest for a long time. In 1857, Faraday tried to obtain the optical properties through his examination of metal colloids. He has determined that metal particles scatter and absorb light strongly, although they are many times smaller than the wavelength of light.[1] At present the effect is understood by the theory of surface plasmon resonance (SPR), which represents the collective oscillation of conduction electrons within metal particles excited by light at particular frequencies. On smooth surface of bulk gold or silver, surface plasmons (SPs) can propagate in a long distance.[2,3] However, it cannot propagate in the structure of metallic particles, forming the localized surface plasmon resonance (LSPR).

The fundamental relationship between LSPs and incident light in particle structures are explored by many researchers, and more applications of SPR are developed. For instance, in an effort to reduce the detection limit of SPR biosensing to zeptomoles (10^{-21} moles per liter), Van Duyne and co-workers have focused on detecting adsorbate-induced changes in the light scattered from a single silver nanoparticle.[4] LSPR also creates intense electric field around a nanoparticle surface, which has great applications on near-field Raman scattering of adsorbed molecules.[5,6]

In this Letter, optical response of the tetrahedron nanoparticle is investigated in detail. It is shown that the structure with culminations and edges can excite more intense electric field around culminations and edges. Here we choose the tetrahedron structure because it is simple and easily fabricated.

The discrete dipole approximation method[7] is used to calculate the optical response of tetrahedron nanoparticle. We present the extinction spectrum (extinction = scattering + absorption) of a single tetrahedron silver particle and describe its near field distribution.[8]

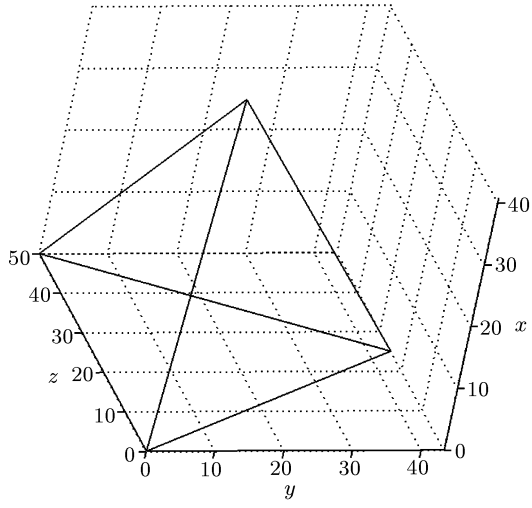

Fig. 1. Three-dimensional tetrahedron view.

Figure 1 shows the 3D view of a tetrahedron. One face is parallel to the yz plane, the opposite 'vertex' is in the $+x$ direction, and one edge is parallel to the z axis. In this work, each edge of the tetrahedron is discretized to equal 50 grids, so the whole tetrahedron concludes 14722 cubes. The size of the tetrahedron can be varied. To describe the size of the tetrahedron, we define $A_{\rm eff} = (3V/4\pi)^{1/3}$, where V is the volume of the tetrahedron. Here the material of particle is silver, and its dielectric constants are the same as the values reported in Ref. [9].

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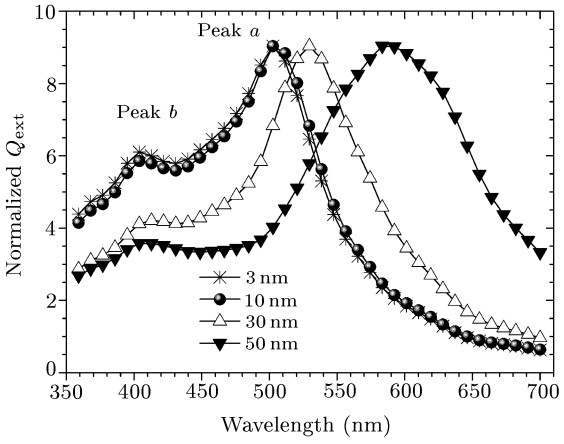

Fig. 2. Normalized extinction spectra of a tetrahedron with $A_{\text{eff}} = 3$, 10, 30 and 50 nm.

We first study the influence of particle size to optical response. Figure 2 shows the normalized extinction spectra of a tetrahedron with $A_{\text{eff}} = 3$, 10, 30 and 50 nm. The light is incident from the $-x$ direction with the polarization direction in the y axis. The incident wavelength varies from 350 nm to 700 nm. The extinction spectra with $A_{\text{eff}} = 3$, 10 nm have two clear peaks. The lower one appears at constant wavelength, the higher extinction peak exhibits red shifts when the A_{eff} increases. The spectra with $A_{\text{eff}} = 3$ nm and $A_{\text{eff}} = 10$ nm are almost the same, due to the fact that the wavelength of LSPR peak does not depend on size for the quasistatic approximation when particles becomes smaller.[10] For faster calculation, we only consider the situation with $A_{\text{eff}} = 3$ nm. In this situation, the edge of tetrahedron is about 10 nm.

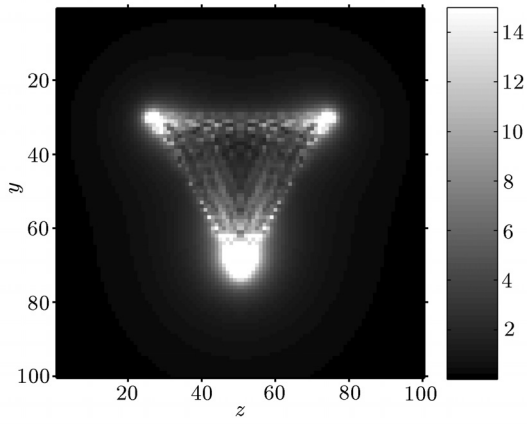

Fig. 3. Near-field electric field image at the yz plane when wavelength is 504.1 nm (peak a in Fig. 2) and the polarization direction along the y axis. The interaction of 3 poles appears.

In the spectrum with $A_{\text{eff}} = 3$ nm (Fig. 2), the main peak is at 504.1 nm (denoted as peak a), and the other one is at 402.0 nm (denoted as peak b). The near-field electric field images of peaks a and b are shown in Figs. 3 and 4, respectively. The amplitude of near-field electric field in the images is limited to unity and the limited level is at 15 times of incidence. The images are plotted on the yz plane, which is perpendicular to the incident direction. In Fig. 3, an interaction of 3 poles of tetrahedron is shown clearly. In Fig. 4, an interaction between a pole and an edge is presented. The different interactions in Figs. 3 and 4 may be caused by different distortions of a dipole in the y direction.

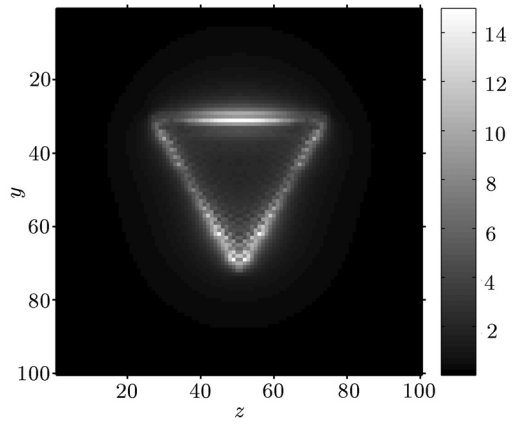

Fig. 4. Near-field electric field image at the yz plane when wavelength is 402.0 nm (peak b in Fig. 2) and the polarization direction along the y axis. An interaction between a pole and an edge appears.

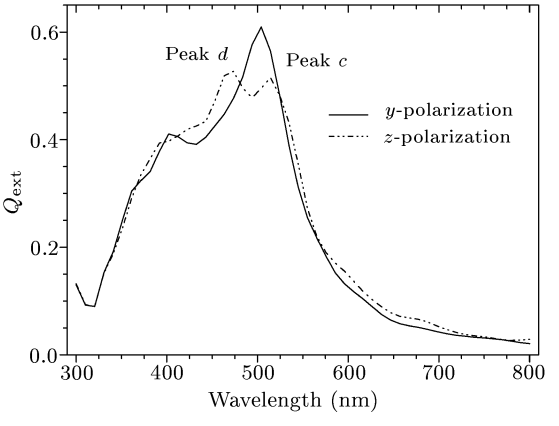

Fig. 5. Extinction spectra of a tetrahedron with the of the polarization directions along the y and z axes.

Then we rotate the polarization direction of the incident light to the z axis. Figure 5 shows the extinction spectra of a tetrahedron with the polarizations in the y and z directions. The incidence wavelength varies from 300 nm to 800 nm. It can be observed that the main peak in the y-polarization divides to two peaks in the z-polarization, one is at the wavelength 514.3 nm (denoted as peak c), and the other is at the wavelength 473.5 nm (denoted as peak d). Figures 6 and 7 show the near-field electric field image of the two peaks with the z-polarization. Figure 6 displays the distribution when the incidence wavelength

is 514.3 nm (peak c). It is shown that an interaction between 2 poles, just like a dipole lying at an edge of the tetrahedron. Figure 7 presents an image similar to Fig. 6, but the incidence wavelength is 473.5 nm (peak d). The different interactions in Figs. 6 and 7 may be caused by different distortions of a dipole in the z direction. It is easy to find that the situation with the z-polarization show great difference to the situations with the y-polarization.

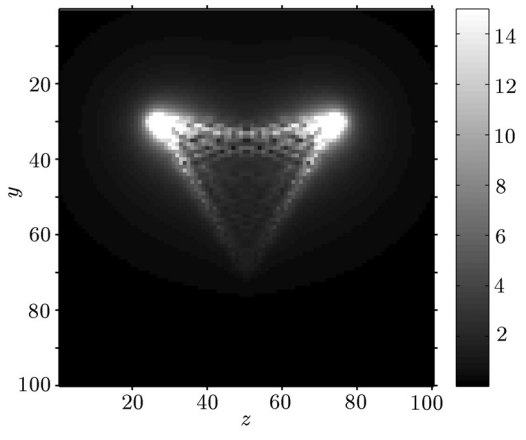

Fig. 6. Near-field electric field image on the yz plane at wavelength 514.3 nm (peak c in Fig. 5) with the z-polarization. An interaction of two poles appears.

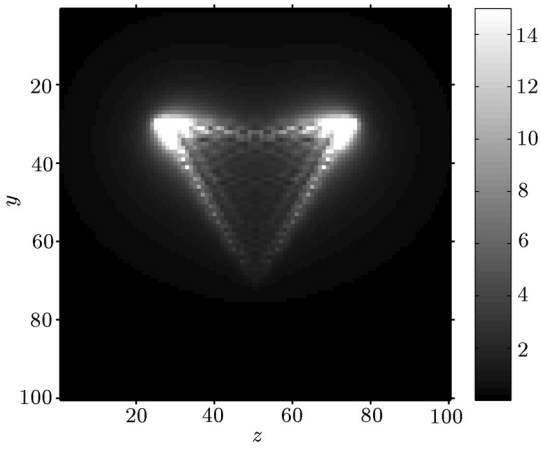

Fig. 7. Near-field electric field image on the yz plane at wavelength 473.5 nm (peak d in Fig. 5) with the z-polarization. An interaction of two poles also appears.

In Figs. 3, 4, 6 and 7, the electric field out of the image plane is weak. In our calculation, all the polarizations are located in the yz plane, so most energy of incident light is gathered at the face of tetrahedron parallel to the yz plane. Thus we only present the electric field in the yz plane. The result fixes the properties of LSPs, localized on surface.

A tetrahedron has four faces, the incidence direction can be decompounded by the directions perpendicular to faces, and two orthogonal polarizations are considered. Therefore, we may predict the extinction spectrum in other incidence situation based on these four peaks mentioned above. Figure 8 shows the extinction spectra with the incidence direction rotated by an angle θ in the xy plane. No new extinction peak is found.

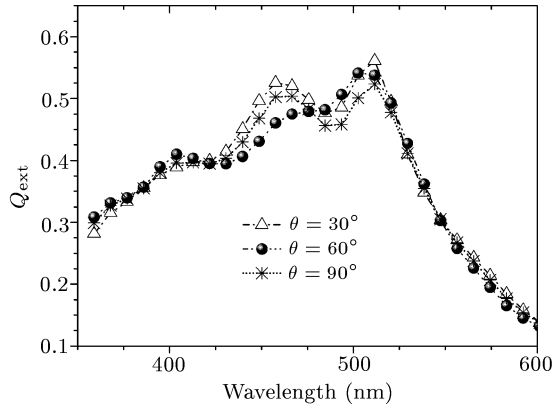

Fig. 8. Extinction spectra with the incidence direction rotated by an angle θ in the xy plane with $\theta = 30°$, $60°$ and $90°$.

In these four peaks, the amplitude of near-field electric field is much higher than that around a common sphere nanoparticle (no more than 10 times of incidence).[10] In the weak mode of tetrahedron (Fig. 4), the amplitude can reach more than 14 times of incidence. In the other mode (shown in Fig. 6), the amplitude in some 'hot point' can be more than 50 times, as shown in Fig. 9.

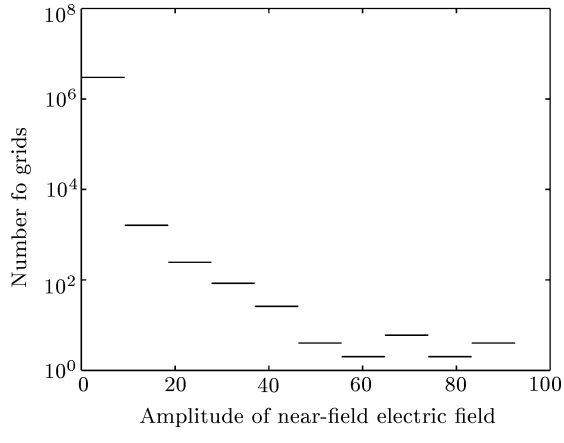

Fig. 9. Histogram of the amplitude of near-field electric field at grids in Fig. 6. Several 'hot points' enhanced more than 50 times are found.

In conclusion, we have found four LSPs peaks of a metallic tetrahedron nanoparticle using the discrete dipole approximation method and have attempted to explain some extinction spectra of a metallic tetrahedron nanoparticle. These LSPRs can cause much higher amplitude of local-field electric field than that around a common sphere nanoparticle. With the above analysis, we can control the wavelength of the LSPR peak by selecting suitable size of nanoparticles,

the incident direction and the polarization. Compared to general sphere nanoparticles, much more enhanced surface electric field will be excited in the suitable wavelength, which is very useful in surface-enhanced Raman spectroscopy, single molecule detective, near-field optical probe, etc.

References

[1] Faraday M 1857 *Philos. Trans. R. Soc.* London **147** 145
[2] Otto A 1968 *Z. Physik.* **216** 398
[3] Kretschmann E 1971 *Z. Physik.* **248** 313
[4] McFarland A D and Van Duyne R P 2003 *Nano Lett.* **3** 1057
[5] Jeanmaire D L and Van Duyne R P 1977 *J. Electroanal. Chem.* **84** 1
[6] Haynes C L, McFarland A D and Van Duyne R P 2005 *Anal. Chem.* A **77** 338
[7] Draine B T and Flatau P J 1994 *J. Opt. Soc. Am.* A **11** 1491
[8] Wiley B J, Im S H, Li Z Y, McLellan J, Siekkinen A and Xia Y 2006 *J. Phys. Chem.* B **110** 15666
[9] Palik E D 1985 *Handbook of Optical Constants of Solids* (New York: Academic)
[10] Kelly K L, Coronado E, Zhao L L and Schatz G C 2003 *J. Phys. Chem.* B **107** 668