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Particle plasmons resonant characteristics in arrays of strongly coupled gold nanoparticles

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ABSTRACT

Using the finite difference time domain (FDTD) method, we investigated the optical properties of a periodic array of strongly coupled gold nanoparticles (MNPs). We show the two kinds properties of transmission spectra with both different interparticle spaces and different radii of the particles. It is found that some distinct extra resonant peaks appear in the forbidden band gap and the resonant frequency depends strongly on the space between the particles and the radius of the particles. Based on the localized nature of the field distribution, we also show clearly the presence of local plasmons resonant modes that originate from quadrupole plasmon polaritons.

1. Introduction

The optical properties of metallic nanoparticles and their arrays have been a subject of continuous attention [1,2]. Along with the fast progress of modern lithographic technique [3], the MNPs and their arrays have a wide variety of applications of nanoscale devices in chemistry [4], biology [5] and applied physics [6]. One of the most important features of metallic nanoparticles array is the strong enhancement of an incident field [7] at the plasmon resonance frequency on or near the particle surface, when the light frequency matches the frequency of collective oscillations of the conduction electrons in the particle. The enhancement of an incident field at special frequency is commonly explained by resonant excitation of surface plasmon [7–10].

Surface plasmons have been intensively studied since a number of decades already. They are surface charge density waves, with an associated electromagnetic field, propagating along the interface between a dielectric and a metal. Surface plasmons can be categorized into two types: localized plasmon resonances, in which incident light is absorbed or scattered by the oscillating electric dipoles or quadrupoles within a metal nanoparticle; and surface plasmon polaritons, which propagate along metal surfaces in a waveguide-like fashion until released at some distance from their point of origin. The former are important for generating local field factors, which enhance linear and nonlinear optical effects near the metal surface. However, metal nanostructures often support both types of plasmons simultaneously. Particle surface plasmons can be excited in nanoparticles of free-electron like metals, such as Au and Ag, resonant peaks are observed at particular frequencies. In particular, the resonant frequency of the particle plasmon depends mainly on the dielectric functions of the metal, for example, silver clusters generally have higher particle plasmon energies than gold clusters. The spectrum line position also depends on the size of the metal array, the experiment proves that there is a spectral red-shift with increasing cluster size due to electromagnetic retardation [2], with the condition of that the size of the metal is greater than approximately 10 nm. In addition, particle plasmons also depend on the shape of the particle, surrounding medium and relative arrangement [11]. MNPs with different shapes exhibit different plasmon resonances, Particles of spherical shape also have a subject of intensive research [2,12,13].

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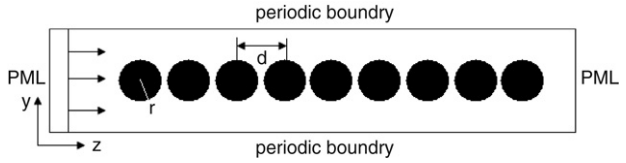

Fig. 1. The structure of the globose metallic nanoparticles array, Periodic boundary conditions are imposed on the four surfaces along x and y directions, while perfect matched layers are imposed at the left and right surfaces along z direction. The input light wave is polarized along the y direction and propagates along the z direction.

In this paper, we discuss in detail how plasmon modes strongly shift with the distance between metallic nanoparticles and the radius of the nanoparticles varied. For nanoparticles pairs or arrays, there is a spectral shift as a function of separate distance and surface plasmon frequencies split. These phenomena can be explained by "collective particle plasmon" quadrupole resonances which results from electromagnetic coupling between neighboring particles in linear array. Interparticle coupling plays a major role in the properties of particle plasmons [14].

2. Strongly coupled gold nanoparticles arrays

The rapid development of computer techniques and information technologies in recent decades has fueled the need for efficient tools for electromagnetic modeling. A number of computational techniques are currently used for electromagnetic modeling, including the method of moments, the FDTD method, and the finite element method (FEM). Among these, the FDTD, introduced by K.S. Yee in 1966, appears to be one of the most widely used methods for many engineering applications. Electromagnetic filed is governed by time-dependent Maxwell equations. The FDTD method is a direct method for the solution of the Maxwell equations. The most used FDTD formulations are based on the Yee grid. In the discretized formulation of the partial differential Maxwell equations, the time derivations of the electric and magnetic field on a grid node can be approximated with the central difference equations. In this method, the new value of electric field (or magnetic field) is calculated from the previous value of it and the adjacent nodes values of magnetic field (or electric field). Applying this time updating scheme from the Maxwell equations, the local material parameters have to be known. Once the dielectric tensor relative to the director distribution of any structure at every grid point is defined, we can obtain the sequences of light propagation.

In our work, we simulated the scattering spectrum and the distribution of the field intensity of the globose metallic nanoparticles array, as depicted schematically in Fig. 1, by the FDTD method.

The frequency-dependent optical properties of the metallic nanospheres are approximated by the Drude model, which defines the dispersive permittivity as:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \mathrm{i}\omega\gamma_p}. \tag{1}$$

In our simulation, the nanoparticles arrays consist of metal that is modeled with a bulk plasmon frequency $\omega_p = 1.37 \times 10^{16}\ \mathrm{s}^{-1}$, $\varepsilon_\infty = 1$, and an electron relaxation time $1/\gamma_p = 245$ fs.

The globose metallic nanoparticles are arrayed in the air. Perfectly matched absorbing boundary conditions are applied at the left and right surfaces of the computational space along z direction whereas periodic boundary conditions are applied on other boundaries along x and y directions. By placing nine unit cells of the periodic metallic nanoparticles in the computational space along z direction, we can simulate the temporal transmission of plane wave that normally incidents on the metallic nanoparticles

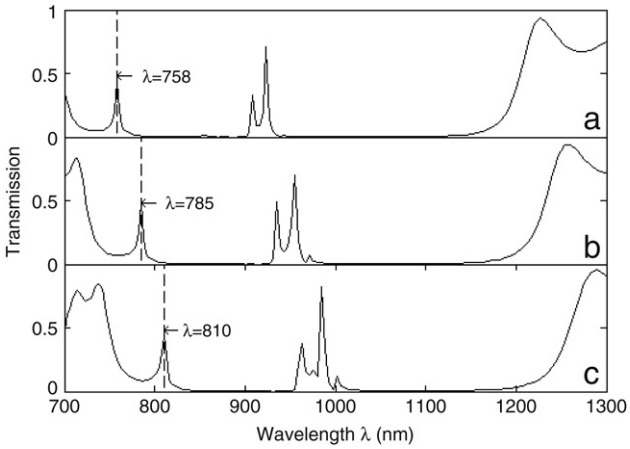

Fig. 2. The transmission spectra of the metallic nanoparticles arrays as a function of wavelength for different interparticle distances (a) $d = 477$ nm, (b) $d = 495$ nm, and (c) $d = 513$ nm. The radii of the particles in all three structures are $r = 180$ nm.

array which extends infinitely in the x and y directions. We simulated the structure with an FDTD cube of size $L_x \times L_y \times L_z = 900\ \mathrm{nm} \times 900\ \mathrm{nm} \times 9000\ \mathrm{nm}$ (When we consider the influence of the spacing between the particles, the size of the FDTD cube has a little change, it is introduced in detail in the explanation of Fig. 2). In order to partition the FDTD scheme onto a parallel grid, we divide the simulation cube into 100 slices along the x axis, y axis and 1000 slices along the z axis. We excite the particles by an ultrashort, linearly polarized pulse. The input light wave polarized along the y axis and irradiated the spheral metallic nanoparticles array along the z direction in our work. The duration of the pulse needs be very short, so this pulse can span the range of frequencies properly. In our work, the width of the pulse's spectral response is 4×10^{14} Hz that from 0.667×10^{14} Hz to 4.667×10^{14} Hz. Distribution of the field intensity can be used to discriminate between spectral features which correspond to the collective quadrupole excitation or other physical resonances.

3. Results and discussion

For the multi-particles system that is simulated in our work, the metallic particles periodically modulated the incident plane wave, so there are surface plasmons excited on the air-metal interface. The surface plasmon can couple with the incident plane wave at the frequencies that satisfy:

$$\vec{k}_{sp} = \vec{k}_0 \sin\theta_0 \pm p_1\vec{a}_1 \pm p_2\vec{a}_2 \tag{2}$$

where $\vec{k}_{sp}$ is the wave vector of the surface plasmon. $\vec{k}_0$ is the wave vector of the incident light in free space, θ_0 is the angle of incidence, $\vec{a}_1$ and $\vec{a}_2$ are the reciprocal lattice vectors of the periodic metallic particle, and p_1 and p_2 are integers.

The nanoparticles metallic array shows a strong absorption photonic band in the portion of the spectrum. When the frequency of the light locates at the forbidden photonic band gap, the light cannot transmit through the photonic crystal. And the collective excitation of the conduction electrons leads to a characteristic oscillation frequency that is associated with what is called plasmon excitation. Plasmon resonances correspond to peaks of the spectrum. Because of the electrons in metal particle are now driving at a resonant frequency with a relatively large oscillation amplitude, correspondingly a large amount of energy is dissipated by the damping mechanism. Meanwhile enhanced electromagnetic fields due to particle plasmon resonances with oscillating electric quadrupoles may radiate a substantial amount of energy to infinity in the form of scattering.

In the case of the nanoparticles metallic array with particle radius $r = 180$ nm, Fig. 2 show the transmission spectra of the nanoparticles array with different interparticle distances $d = 477$ nm, 495 nm and 513 nm, respectively. When the interparticle distance d is varied, we also proportionally change the lattice constants of the x and y directions. For Fig. 2, the lattice constants of the x and y directions are (a) 867 nm, (b) 900 nm, and (c) 933 nm. The three nanoparticles metal arrays structures all have a wide forbidden band gap, and there are some extra modes appearing in the forbidden band gap. These extra resonance modes are strongly related to the incident light polarization [15]. Along with the spacing increasing, the peaks of the plasmon resonances have a slight redshift. When the spacing is increased to $d = 513$ nm from $d = 477$ nm, the resonance wavelength near the lower photonic band edge (shown with dotted line in Fig. 2) is shifted to 810 nm from 758 nm. When the spacing is increased, the energy that required driving the resonant oscillation reduced [16], this phenomenon results in a spectral redshift. From Fig. 2, we also know that along with the spacing between the nanoparticles increasing, more syntonic modes appear in the forbidding band gap. For interparticle distance $d = 477$ nm, near the wavelength of 950 nm, only few resonant excitation modes of surface plasmons appear. Along with the interparticle distance increasing, the amount of resonant excitation modes near the wavelength of 950 nm increases, the intensities of the syntonic modes strengthen, and spectrum red-shifts. This means that the resonant excitation modes of surface plasmons become steadier. So, the space between the nanoparticles strongly influences the characters of the nanoparticles arrays, this results from that the spacing between the nanoparticles affects the interactions of the particles.

The radius of the particles also plays an important role in determining the plasmon resonance wavelength of a metallic nanoparticles array. Fig. 3 show the transmission spectra of the nanoparticles arrays as a function of wavelength for spherical particles arrays that have different radii $r = 150$ nm, 180 nm and 200 nm, while the distances between the center of the particles in all three structures are $d = 495$ nm. For large particle ($r = 200$ nm), one can see that the amount and the peak value of the harmonic oscillation modes are much less. The high frequency mode has a slight shift and becomes narrow as the radius increasing, this occurs because of the finite size of the particle relative to the wavelength of light, with the decreased width arising because of radiative damping and the increased wavelength due to dynamic depolarization. For a spherical particle, the plasmon frequency depends on the density of conduction electrons, and therefore on the chemical identity of the elements. Along with the radius decreasing, the low frequency modes are manifold. From Figs. 2 and 3, we know that there are many syntonic modes existing in the forbidding bang gap. These modes maybe mean many different oscillations, and we know more information about the resonant modes through describing the electric field distribution.

In Fig. 4, we draw the spatial images of the peaks instantaneous electric field component Ez at steady state for the nanoparticles array. Data are shown for three different resonance wavelengths (a) 955 nm, (b) 934 nm, and (c) 785 nm with the particle radius $r = 180$ nm and the interparticle spacing $d = 495$ nm. Different syntonic modes mean different surface charge distributions and different oscillations. Once the spectrum was outlined, on-resonance excitation was used to excite individual modes to examine the corresponding spatial distribution of the field intensity. Such distributions can be used to discriminate between spectral features which correspond to the collective quadrupole excitation and other physical resonances or, in some cases, unphysical artifacts of the simulation or frequency

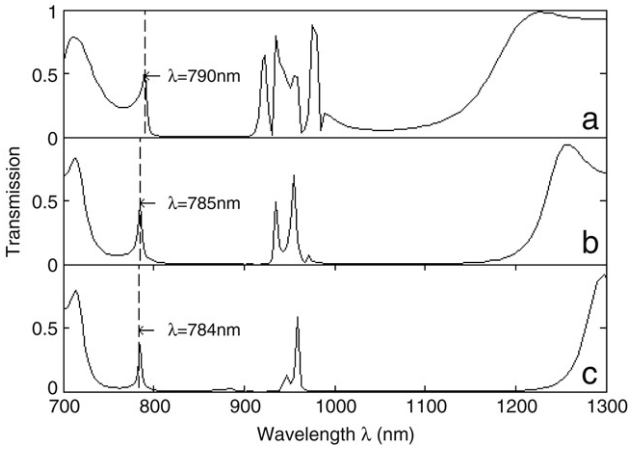

Fig. 3. The transmission spectra of the nanoparticles arrays as a function of wavelength for different radii of the particles (a) $r = 150$ nm (b) $r = 180$ nm and (c) $r = 200$ nm, respectively. The interparticle spaces in all three structures are 495 nm.

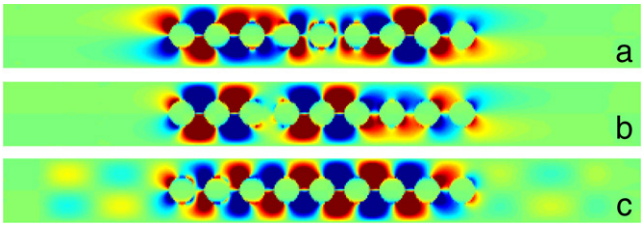

Fig. 4. The instantaneous electric field component Ez distributions at different resonance wavelengths (a) 955 nm, (b) 934 nm, and (c) 785 nm. The radius of the particles is $r = 180$ nm, The interparticle spacing is $d = 495$ nm.

domain transform which can be eliminated once identified. In Fig. 4, areas colored red have positive field amplitude, while areas colored blue have negative field amplitude. For the radius of the particles is $r = 180$ nm and the interparticle spacing is $d = 495$ nm, the distribution of the electric field component Ez at the wavelength of 785 nm is regular. Positive–negative field alternately appears in the gap of the nanoparticles. For the many-particles system, interactions between particles allow a greater degree freedom for plasmon resonances to occur. There is a quadrupole field distribution for the plasmon mode in the array of the nanoparticles. This indicates an alternating surface charge distribution in which each individual particle is polarized but electrically neutral. The existance of a dielectric gap means that the interparticle interaction is highly capacitive in nature, and therefore a big magnitude of opposing surface charge builds up on particles. The resonance peak located at the wavelength of 934 nm also exhibits a quadrupole like oscillation behavior. Field intensity has a great change at the gap between the third particle and the forth particle and it is very feeble in this area.

Fig. 5 show the instantaneous electric field component Ez distributions at the peaks near the lower photonic band edge (shown with dotted line in Fig. 2) in the nanoparticles arrays with 180 nm radius and different interparticle spaces. The distances between the center of global metallic nanoparticles are $d = 477$ nm, 495 nm, and 513 nm, respectively. The interparticle spacing d strongly influences the interaction between the nanoparticles. For short-distance interparticle spacing array ($d = 477$ nm), due to strongly interparticle coupling and interaction between the particles and the input light, the peak near the lower photonic band edge that locates at 758 nm exhibits a quadrupole oscillation like oscillation, But the electric field becomes weak at the back three particles. When the interparticle spacing is increased above $d = 495$ nm or 513 nm, the coupling between