Solid State Communications 149 (2009) 239–242

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Particle plasmons resonant characteristics in arrays of strongly coupled gold nanoparticles

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ARTICLE INFO

Article history:
Received 15 July 2008
Received in revised form
18 October 2008
Accepted 11 November 2008 by P. Sheng
Available online 24 November 2008

PACS:
42.25.Bs
73.20.Mf
73.63.-b

Keywords:
A. Nanoparticle
D. Plasmon
D. Transmission spectrum
D. Field distribution

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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doi:10.1016/j.ssc.2008.11.017

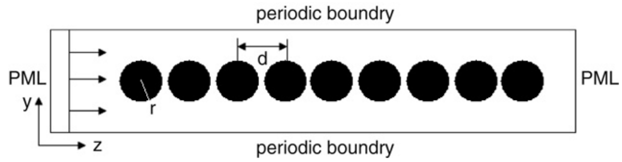

Fig. 1. The structure of the globose metallic nanoparticles array, Periodic boundary conditions are imposed on the four surfaces along x and y directions, while perfect matched layers are imposed at the left and right surfaces along z direction. The input light wave is polarized along the y direction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

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

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 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.

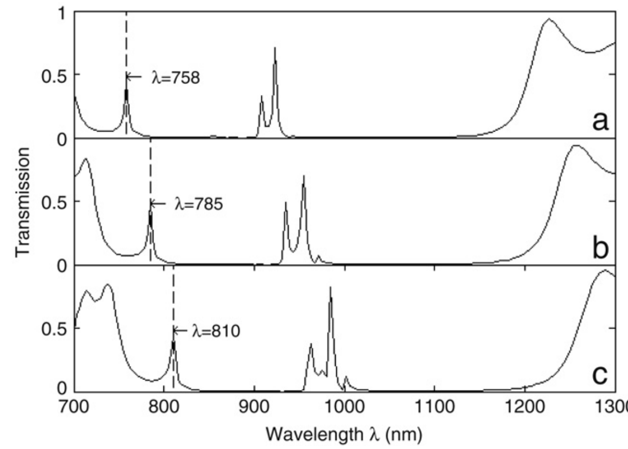

Fig. 2. The transmission spectra of the metallic nanoparticles arrays as a function of wavelength for different interparticle distances (a) $d = 477$ nm, (b) $d = 495$ nm, and (c) $d = 513$ nm. The radii of the particles in all three structures are $r = 180$ nm.

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:

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

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.