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Optical properties of plasmonic dimer, trimer, tetramer and pentamer assemblies of gold nanoboxes

Yanpin Gao [a], Ruifeng Zhang [a], Jui-Ching Cheng [b], Jiunn-Woei Liaw [c,d,*], Cuiman Ma [a]

[a] School of Electronic Information Engineering, Tianjin University, 92 Weijin Rd., Nankai District, Tianjin, China
[b] Department of Electronic Engineering, Chang Gung University, 259 Wen-Hwa 1st Rd., Kwei-Shan, Tao-Yuan 333, Taiwan
[c] Department of Mechanical Engineering, Chang Gung University, 259 Wen-Hwa 1st Rd., Kwei-Shan, Tao-Yuan 333, Taiwan
[d] Center for Biomedical Engineering, Chang Gung University, 259 Wen-Hwa 1st Rd., Kwei-Shan, Tao-Yuan 333, Taiwan

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ABSTRACT

The scattering and absorption properties of the monomer (single), dimer (double), trimer (triple), tetramer (quadruple), and pentamer (quintupling) assemblies with gold nanoboxes as building blocks are studied theoretically. Using the finite element method, the far-field and near-field optical responses of 1-D and 2-D assemblies are analyzed numerically to identify the plasmon modes. Our results illustrate that the longitudinal plasmon modes of 1-D array are red-shifted and more higher-order modes appear as the number of nanoboxes increases. Moreover, the 2-D assemblies show their versatile multiple modes. For example, five configurations of the tetramer (tetris structure) exhibit different plasmon modes as illuminated by different-polarized plane waves. Due to the symmetry breaking of the 2-D assemblies, the Fano resonances and dips are observed. These phenomena demonstrate that the plasmon modes of a nanobox-cluster assembly are tunable to manipulate light on demand by tailoring the configuration.

1. Introduction

The synthesis methods of Au or Ag nanocubes, nanoboxes, nanocages and nanoframes have been developed in the past decade [1–11]. Recently, the techniques of using nanocubes as building blocks to assemble nanostructures (e.g. dimers or chains) have been developed using polymer [5,6] or DNA [11–13] binding. The surface plasmon resonance (SPR) and photothermal properties of nanocubes [14–17] and the biomedical application for theronostic [10] have been studied. Moreover, the surface enhanced fluorescence (SEF) using Ag nanocubes [18], and the surface enhanced Raman scattering (SERS) of nanocube dimers have been investigated [19–21]. The potential applications of the assemblies are for the SEF and SERS biomedical chip. In contrast to the top-down method of using lithagraphy method to produce a nanoscale pattern, the self-assembly of nanoparticles is a bottom-up method [5]. The advantage of the nanocube or nanobox is that the cubic shape makes the assembly more orderly [4,5], compared to the other shaped nanoparticles [22]. Therefore the plasmonic superlattices can be fabricated more accurately using the assembly of the cubic nanoparticles. Due to the coupled SPR, the optical properties, including the scattering and absorption, of one-dimensional (1-D) and two-dimensional (2-D) plasmonic assemblies are more complicated than those of a single nanoparticle (monomer). These properties strongly depend on the pattern of a plasmonic assembly, even though the overall size of the assembly is smaller than

* Corresponding author at: Department of Mechanical Engineering, Chang Gung University, 259 Wen-Hwa 1st Rd., Kwei-Shan, Tao-Yuan 333, Taiwan. Tel.: +886 32118800x5339; fax: +886 3 2118050.
E-mail address: markliaw@mail.cgu.edu.tw (J.-W. Liaw).

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the wavelength of the illuminating light. Because of that, we can design the optical properties of a 1-D or 2-D assembly on demand by tailoring a specific pattern. The disadvantage of Au nanocubes is that the SPR of a single nanocube is close to the interband transition of Au, about 530 nm, which causes a severe ohmic loss. In contrast, the plasmon modes of a hollow nanoparticle, e.g. nanobox, nanocage, or nanoframe, are red-shifted from the interband transition, which is tunable by adjusting the thickness of the metal shell. To simulate and analyze the optical properties of plasmonic nanostructures, numerous numerical methods have been developed and applied, including the finite element method (FEM) [17,23], discrete dipole approximation [19], finite difference time domain method [24], boundary element method [25,26], multiple multipole method [27–29], surface integral equation methods [30,31] and so on.

The purpose of this paper is to study the optical properties of 1-D and 2-D assemblies of hollow Au nanoboxes. In particular, the optical properties of the tetramer, which is analogous to "tetris", will be studied systematically. The 2-D assemblies possess the combination of face-face and edge-edge elements [5], so that their versatile multiple plasmon modes will be more interesting than those of 1-D ones. In this paper, the FEM will be adopted for the simulation due to its flexibility and versatility in handling complicated cluster-structures. The scattering cross section (SCS) and absorption cross section (ACS) properties of the 1-D and 2-D bottom-up assemblies with Au nanoboxes will be analyzed numerically.

2. Method

The classical electromagnetic theory is used to study the optical responses of 1-D and 2-D assemblies of Au nanoboxes illuminated by a plane wave. For example, there are five configurations of the tetramer assemblies (tetris structures), as shown in Fig. 1. The outer edge length and thickness of wall of each identical nanobox are denoted by a and t, and the interparticle gap is d. Throughout the paper, the time factor $\exp(i\omega t)$ will be omitted. The permittivity of Au is a complex function of wavelength, which is denoted by $\varepsilon_{Au}=\varepsilon'-i\varepsilon''$, where $\varepsilon''>0$. The frequency-dependent permittivity of Au is referred to Ref. [32]. A commercial FEM code (HFSS, ANSOFT) is used to simulate the electromagnetic field induced by a plane wave normally incident on a 1-D or 2-D assembly of nanoboxes. The surrounding medium is assumed to be lossless, say water. The total electromagnetic fields in the medium can be expressed as the sum of the incident field and scattered field; $\mathbf{E}^t=\mathbf{E}^i+\mathbf{E}^s$, $\mathbf{H}^t=\mathbf{H}^i+\mathbf{H}^s$, where the superscripts "i", "s", and "t" denote the incident, scattered and total parts, respectively. The scattered and absorption powers of light by the structure, in terms of the Poynting vector, are defined as

$$P_s=\frac{1}{2}\mathrm{Re}\left\{\int_S(\mathbf{E}^s\times\overline{\mathbf{H}}^s)d\mathbf{a}\right\}, \tag{1}$$

$$P_a=\frac{-1}{2}\mathrm{Re}\left\{\int_S(\mathbf{E}^t\times\overline{\mathbf{H}}^t)d\mathbf{a}\right\}, \tag{2}$$

where the surface S can be any closed surface enclosing the whole assembled structure. Here $\overline{\mathbf{H}}$ is the conjugate of the magnetic field, and Re stands for the real part. Alternatively, the absorption power can be expressed by

$$P_a=\int_V\rho_v dv \tag{3}$$

where V is the total volume of the assembly (multi scatterers), and ρ_v is the volume loss density in these dissipative objects, which are the metallic nanoparticles.

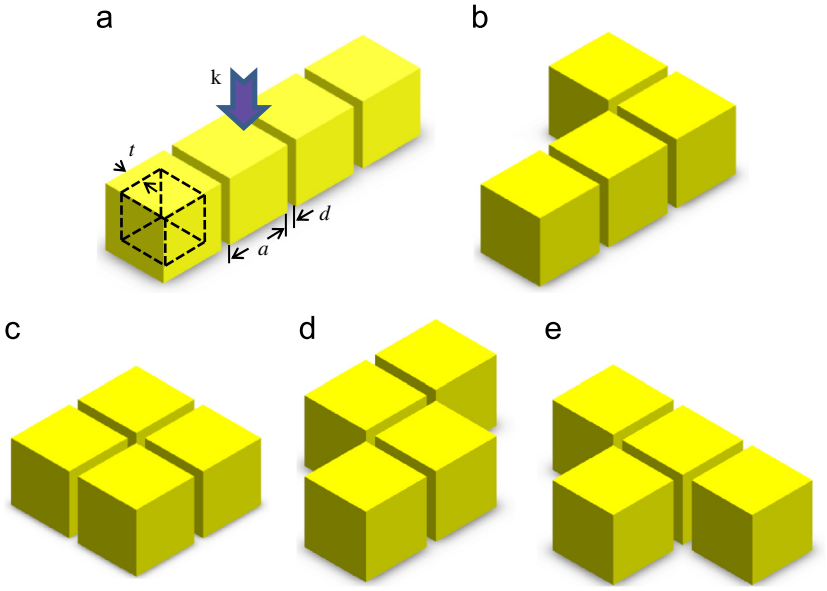

Fig. 1. Five configurations of tetramer (tetris structure) with four identical Au nanoboxes: (a) I (b) L (c) O (d) Z (e) T shapes. The edge length and wall thickness of a hollow nanobox are denoted by a and t, the wavevector is $\mathbf{k}$, and the gap is d.