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Localized surface plasmon resonance of nanotriangle dimers at different relative positions

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ABSTRACT

The investigation of nanoparticle's optical properties is crucial for their biological and therapeutic applications. In the present work, a promising type of gold nanoparticle, the triangular prism which was reported to have multipolar surface plasmon peaks, was studied. The Plasmon ruler effect of nanotriangle dimers was observed and investigated for the first time. Well-defined trends of the extinction spectra maxima, which have a linear correlation with the triangle edge length, for lower order extinction corresponding to in-plane mode, were observed. On this basis, the optical property of nanotriangle dimers with different arrangements, including two nanotriangles aligned side-by-side, bottom-to-bottom, and in line, were studied. For the side-by-side arrangement, an additional peak was generated on the red shift side of the peak corresponding to dipole mode. When the distance between two prisms was scaled by the triangular side length, the relative plasmon shift can be approximated as an exponential function of the relative offset distance. Moreover, for dimers with nanotriangles arranged in line, there was a global blue shift of the extinction spectra with the approaching of two particles, including the higher order mode extinction. An interesting phenomenon was found for dimers with two nanotriangles aligned bottom-to-bottom. The resonance band split into two bands with the decreasing of the offset distance.

1. Introduction

With rapid growth of nanotechnology being applied in various fields, such as medicine/pharmacology [1-4], energy harvesting [5,6], and biology [7-9], researches that focus on the synthesis and evaluation of nanomaterial are attracting more and more attentions [9-12]. Due to the superior optical, biological, and chemical properties, noble metal nanoparticles with various morphologies, such as nanosphere, nanorod, nanoshell, nanocage, nanostar etc., are often employed as contrast agent [13,14] and drug carrier [15]. For example, the laser induced thermal therapy (LITT) usually takes advantage of the thermal response which is generated by the interaction between laser and injected nanoparticles, also known as surface plasmon resonance (SPR). The quantification of thermal effect is strongly dependent on the optical properties, i.e. absorption and scattering, of the nanoparticles. Furthermore, in the 'optical window' region, the tissue has a relative low absorption, which allows the light to propagate through a long distance and also weakens the local heating phenomenon for the healthy tissue [16]. The selective heat requires that the cancerous tissue has a relatively high absorption compared with surrounding healthy tissue. Therefore, the peak in the absorption spectra is an extremely important parameter that needs to be fully investigated. The optical properties of nanoparticle vary with the size, shape, composition, and properties of surrounding materials [17,18]. As mentioned above, though there are quite a few different shapes of nanoparticles being investigated, the optical properties of those nanoparticles and influence factors still need to be fully addressed.

Interesting optical properties of nanotriangles are illustrated owing to its high aspect ratio [19], which makes nanotriangle a promising candidate for nanomedicine and other related areas. The nanotriangle prisms have multipolar plasmon extinction effect, which is generated by localized surface plasmon and lighting rod effects [20]. These effects have been thoroughly studied numerically and experimentally for nanotriangles and other morphologis [20-24]. The single peak in visible region for small particles corresponds to the dipole mode. With the increasing of the particle radius, the peaks generated by higher order resonance become important [21]. Also, size, shape, and other geometric parameters has significant influence on thermal and optical performance of nanoparticles or nanostructures [25], which needs to be investigated thoroughly. Nanotriangle has a very broad SPR band in the near-infrared, which is an outstanding properties for photothermal therapy and other applications. The interaction between two nanoparticles are of great importance [26,27]. Therefore, in recent

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Nomenclature

$\mathbf{A}_{jk}$	interaction matrix of the jth and kth dipoles
C	cross section
$\mathbf{E}$	electric field
$\mathbf{E}_0$	amplitude of the electric field intensity
N	total number of dipoles
$\mathbf{P}$	polarization of dipoles
$\mathbf{r}$	position of dipoles
R	radius of nanoparticles
Greeks symbols	
α_j	polarizability of the jth dipole
Subscripts	
i, j, k	number of the dipoles
abs	absorption cross section
eff	effective radius
ext	extinction cross section
sca	scattering cross section
Superscript	
inc	Incident electric field

year, efforts have been made to investigate the plasmon coupling of nanotriangle dimers. The influence factors for optical properties of nanotriangle dimers with different types have been investigated, including the gap distance, coating thickness, nanotriangle thickness, and different coupling types [28-33]. It is found that there will be a redshift of the resonance wavelength when the thickness and gap width of bowtie nanotriangle decreases [28]. Furthermore, for the edge-to-edge nanotriangle dimer, two separated Plasmon modes are observed and can be tuned by changing the misalign distance [31]. However, previous studies mainly deal with the optical properties of nanotriangle dimers qualitatively. Herein, we present some quantitative results of exactly how the gap between different types of nanotriangle dimers influences their spectral characteristics, which are important to the precise control of optical response in their applications.

To calculate the absorption and scattering properties of particles, the Maxwell's equations need to be solved. The analytical solution can be obtained by Mie theory [34]. However, it is only suitable for homogeneous and isotropic spheres or spheroids. The discrete dipole approximation (DDA) method is one of the most versatile, important and widespread numerical methods to obtain the optical properties of small particles with arbitrary shapes and compositions, which also extended to the application of near-field recently [35,36]. The basic principle of DDA is to discretize a small particle into a cubic array of virtual N-point dipoles [37]. Then the scattering field of the whole particle can be approximated as the summation of all the dipoles. Theoretically speaking, DDA can be applied to calculate the optical properties of arbitrary shape target theoretically if it is properly discretized.

The interaction between two close nanoparticles will affect the localized SPR [26], which can be exploited in many applications, such as surface-enhanced Raman spectroscopy [38,39], universal plasmon ruler [40], nearfield image [41,42], and subwavelength optoelectronic devices [43,44]. It is worth to mention that the plasmon ruler effect has been applied to measure the distance between two metal nanoparticles in biological system [45,46] and optoelectronics [43,47], which usually concentrates on the usage of nanospheres. In 2009, Funston et al. studied the plasmon ruler effect of nanorod dimers [26]. However, the plasmon ruler effect of nanotriangles has not yet been observed and investigated. Therefore, in our present work, this effect is studied thoroughly, which is important to widen the application fields of plasmon ruler effect.

In the present work, the optical properties of gold nanotriangle dimers were studied. The size of nanotriangle can be changed to tune the absorption maximum to desired spectral region just like nanorod. Therefore, firstly, the influence of edge length was investigated. Afterwards, the optical properties for different types of nanotriangle dimers, including two nanotriangles aligned side-by-side, bottom-to-bottom, and in line, were studied. The influence of offset distance is found to have paramount influence on the performance of nanotriangle dimers. Also, multipolar surface plasmon peaks were observed duo to the interaction between two particles.

2. Theory and methods

The DDA method can be applied to calculate the optical properties of particles with arbitrary geometries and compositions. The DDA package, developed by Draine and Flatau [48], has been widely employed to calculate scattering and absorption of light by irregular particles. The basic principle of DDA is to discretize the target of interest into a cubic array of virtual N-point dipoles [37]. The polarization of the ith dipole is $\mathbf{P}_j = a_j\mathbf{E}_j$, where α_j is the polarizability of the jth dipole and $\mathbf{E}_j$ is the electric field in position $\mathbf{r}_j$, which can be expressed as:

$$\mathbf{E}_j = \mathbf{E}_j^{\mathrm{inc}} - \sum_{k\neq j}\mathbf{A}_{jk}\mathbf{P}_k \tag{1}$$

where $\mathbf{E}_j^{\mathrm{inc}}$ is the incident electric field, which is given by $\mathbf{E}_j^{\mathrm{inc}}=\mathbf{E}_0\exp(ik\cdot\mathbf{r}_j - i\omega t)$, where $\mathbf{E}_0$ is the amplitude of the electric field intensity and k can be expressed as ω/c. $\mathbf{A}_{jk}$ stands for the interaction matrix, where j and k is the number of dipoles. $\mathbf{A}_{jk}\mathbf{P}_k$ is the electric field at position $\mathbf{r}_j$, which is triggered by the dipole at position $\mathbf{r}_k$. It is given as [49]:

$$\mathbf{A}_{jk}\mathbf{P}_k = \frac{\exp\left(ik\mathbf{r}_{jk}\right)}{\mathbf{r}_{jk}^3}\left\{k^2\mathbf{r}_{jk}\times\left(\mathbf{r}_{jk}\times\mathbf{P}_k\right) + \frac{\left(1-ik\mathbf{r}_{jk}\right)}{\mathbf{r}_{jk}^2} \times\left[\mathbf{r}_{jk}^2\mathbf{P}_k - 3\mathbf{r}_{jk}\cdot\mathbf{P}_k\right]\right\},\quad j\neq k \tag{2}$$

If $\mathbf{A}_{jj}$ is defined as $\mathbf{A}_{jj} = -\alpha_j^{-1}$, then the scattering problem can be described as a set of linear equations as follows:

$$\sum_{k=1}^{N}\mathbf{A}_{jk}\mathbf{P}_k = \mathbf{E}_j^{\mathrm{inc}} \tag{3}$$

The extinction, absorption, and scattering cross section can be calculated by:

$$C_{\mathrm{ext}} = \frac{4\pi k}{|\mathbf{E}_0|^2}\sum_{j=1}^{N}\mathrm{Im}\left(\mathbf{E}_j^{\mathrm{inc},*}\cdot\mathbf{P}_j\right) \tag{4}$$

$$C_{\mathrm{abs}} = \frac{4\pi k}{|\mathbf{E}_0|^2}\sum_{j=1}^{N}\left[\mathrm{Im}\left(\mathbf{P}_j\cdot\alpha_j^{-1}\cdot\mathbf{P}_j^*\right) - \frac{2}{3}k^3\left|\mathbf{P}_j\right|^2\right] \tag{5}$$

$$C_{\mathrm{sca}} = C_{\mathrm{ext}} - C_{\mathrm{abs}} \tag{6}$$

where $\mathbf{P}^*$ is the polarization of each dipole. The corresponding extinction, absorption, and scattering efficiency is the ratio of cross section and πR_{eff}^2, where R_{eff} is the effective radius. R_{eff} is invariably utilized to characterize the size of an arbitrary shape small particle, which can be expressed as $R_{eff}=(3V/4p)^{1/3}$, where V is the volume of the particle.

The detailed description and mathematical formulation of DDA can be found elsewhere [48-50]. The results of DDA are compared with previous work [37,51], which is shown in Fig. 1. For the results of gold nanorod, the direction of electric field is parallel to the long axis. The dielectric constants of gold nanoparticles are