FDTD Simulations on Plasmonic Properties of End-to-End and Side-by-Side Assembled Au Nanorods

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(Received 4 April 2014; revised 8 May 2014; accepted 20 May 2014)

Abstract: The surface plasmon resonance (SPR) of gold (Au) nanorod can be tuned in a large visible-near infrared (Vis-NIR) region by changing the aspect ratio of nanorod. Compared with the SPR of isolated Au nanorod, assembly of Au nanorods exhibits strong coupling effect in the nanogap and wealthy changes in the optical spectra. The SPR coupling effects and localized electronic fields for end-to-end (E-E) and side-by-side (S-S) assembled Au nanorods dimers are studied through finite-difference time-domain (FDTD) simulation. With decreasing the gap spacing, the longitudinal SPR (SPR_L) red-shifts for the E-E orients Au nanorods dimer and blue-shifts for S-S orientes Au nanorods dimer. The transverse SPR (SPR_T) has slight red-shifting for S-S assembly and no shifting for the E-E assembly. Moreover, a new coupling SPR appears for the E-E assembly in a long wavelength in the NIR region, blue-shifting and enhancing with decreasing the gap spacing. Based on the spring oscillator model and the polarization of nanoparticles with incident electric field, the SPR shifting and the appearance of new coupling SPR of assembled Au nanorods are proposed.

Key words: gold nanorods; assembly; finite-difference time-domain (FDTD); coupling effect

CLC number: O469 **Document code**: A **Article ID**: 1005-1120(2014)03-0248-07

1 Introduction

Noble metal nanostructures have been of an important research subject not only due to their unique and improved chemical and physical properties[1-4], but also motivated by their potential applications in fields of catalytic[5-7], optoelectronic[8,9], molecular diagnostics[10,11], and data storage[12,13]. From ancient time, gold (Au) colloid has been used to stain glass of wine red, mauve, blue and other colors. These effects are the result of changes in the surface plasmon resonance (SPR) absorption, at which the frequency of free electrons of metals oscillats in response to the alternating electric field of incident electromagnetic radiation[14].

The optical properties of small metal particles have inspired many researchers in the past century. The interaction between the incident electromagnetic wave and a nonspherical metal nanoparticle can be described by the radiation of a lossy dipole induced at the center of the particle. Assuming the scattering and higher order polarization terms are negligible. The first theoretical framework to fully explain this peculiar interaction between light and matter (for the case of spherical particles) was published by Mie in 1908[15]. Then the theory was developed, for example, Gans functions, to calculate the optical resonance of ellipsoids and rod[16]. With the development of colloidal chemistry, noble nanostructures of various morphologies can be obtained in experiment. More and more investigations show that the optical property of metal

Foundation items: Supported by the National Natural Science Foundation of China (11274173, 11374159); the Fundamental Research Funds for the Central Universities (NZ2013304, NJ20140005); Qing Lan Project of Jiangsu Province.

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nanocrystals depends highly on the morphology of nanostructures. For example, two distinctive plasma resonances usually appear for Au nanorod: a strong longitudinal surface plasmon resonance (SPR_L) shifting in the visible-near infrared (Vis-NIR) region with increasing aspect-ratio of Au nanorod and a weak transverse surface plasmon resonance (SPR_T) located at about 520 nm[17-19]. Pd nanocubes and nanorods exhibit resonant peaks in the region of 330—870 nm in the absorption spectra, whereas the spherical Pd nanoparticles have no resonance in the Vis-NIR region[20].

In the synthesis of nanomaterials through chemical methods, nanoparticles can usually be organized into well-defined assembly due to the adsorption of polar group, static electricity, soft template, and changes of surface tension in the solution. Moreover, with the development of nanotechnology, nanoparticle monomer is required to assembly into functional unit. For instance, in the excitation of electronic field, compared with the surface-enhanced Raman effection of isolated Au nanoparticle, the assembled Au nanoparticles dimmer and multimer will lead to redistribution of surface charge and strong near field coupling effect in the nanogap[21,22]. However, for the measured optical absorption spectra, the SPR properties are an average effect of various nanostructures. Therefore, one needs to make clear the SPR property of a certain assembly under different excitations of electronic field. Near-field optical technology provides one expensive experimental method, and another method is simulation based on electromagnetic field theory.

In the theoretical simulations, Gans function can not accurately reflect the optical properties of the non-rod or assembled system. In recent years, study on the optical properties of different shaped nanostructure has made great achievements by solving Maxwell equations depending on computer and kinds of numerical methods, including finite-difference time-domain(FDTD). FDTD method supplies a simple, convenient, systematic approach for calculating the optical response of nanostructures and their assembly with arbitrary symmetry and geometry by solving Maxwell's equations on discrete grids.

Herein, we describ the SPR coupling effect and local field distribution induced by Au nanorods dimer under different incident electronic field. Optical constant of dielectric permittivity with the wavelength adapts Johnson and Christy database attached with the FDTD. The background refractive index is 1.33, and perfect match layer boundary condition is implemented. Corresponding to the experimental results, the obtained Au nanorods with qusi-semispheres capped at two ending surfaces are calculated. As is shown in Fig. 1, there are transverse and longitudinal polarizations to the rod axis. And two distinctive plasma resonances can be achieved when the metallic nanorods are irradiated by incident light.

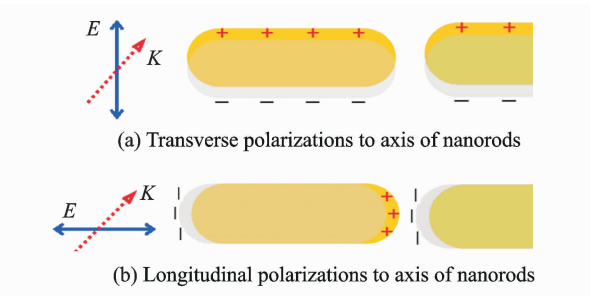


Fig. 1 Two polarizations of metallic nanorod under electric field

2 FDTD Simulated Results

The extinction spectra usually involve absorption and scattering. For the small sized Au nanorods used in our calculation (15 nm in diameter), the scattering intensity is very weak compared with that of the absorption, as shown in Fig. 2(a). And only SPR absorption is considered in the FDTD simulation. For the optical absorption spectra of Au nanorods with different aspect ratios (see Fig. 2(b)), in addition to a weak SPR_T peak localized at about 520 nm, as inserted in Fig. 2(b)), there is a strong and tunable SPR_L peak shifting in the NIR range of 600—1 300 nm. The simulated spectra agree well with the experimental results, as previously reported[23,24].

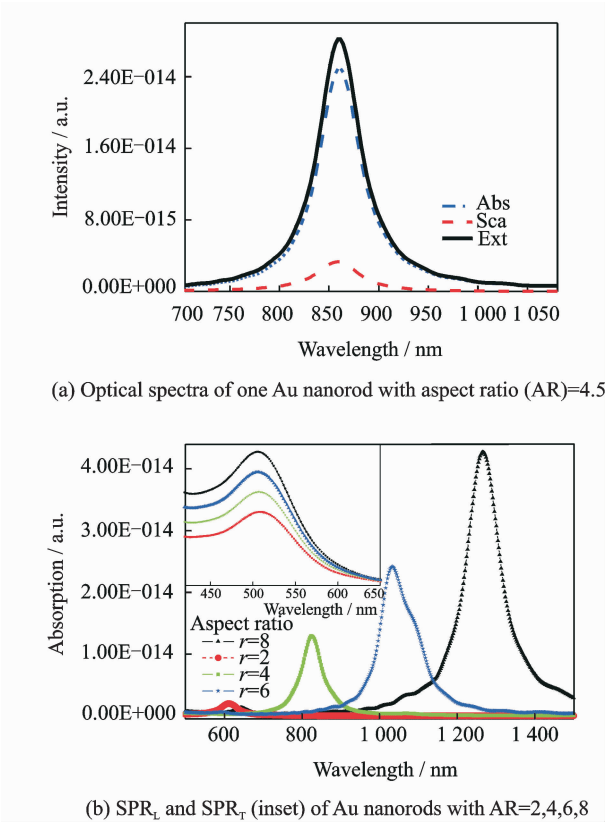


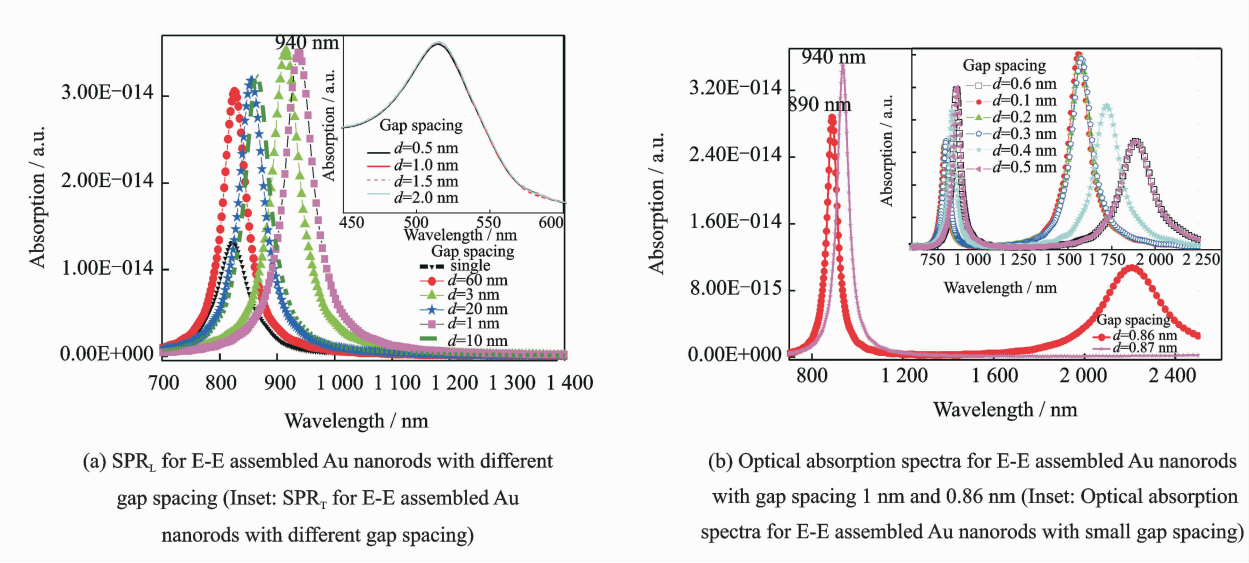
Fig. 2 FDTD simulated optical spectra of Au nanorod monomer

In the following simulation of Au nanorods assembly, the aspect ratio (AR) of nanorod is 4. Fig. 3 shows the optical spectra of end-to-end(E-E) oriented Au nanorods dimmer. The results indicate that the SPR$_L$ red-shifts obviously with decreasing the gap spacing (see Fig. 3(a)), and it is different from the SPR$_L$ of one nanorod monomer with doubled aspect ratio (for Au nanorod with AR=8, the SPR$_L$ is 1 288 nm, as shown in Fig. 2(b)). While the SPR$_T$ of E-E oriented Au nanorods has no shifting (see inset of Fig. 3(a)). When the gap spacing is 1 nm, a new and weak coupling SPR absorption appear at about 3 800 nm (the weak SPR is not shown here). When the gap spacing is 0.866 nm, this new SPR of Au nanorods assembly is located about 2 200 nm. With further decreasing the gap size, the location of coupling SPR blue-shifts and the intensity enhances. Simultaneously, the SPR$_L$ of E-E Au nanorods assembly blue-shifts from about 940 nm to about 780 nm, as shown in inset of Fig. 3(b).

For the SPR shifting of E-E Au nanorods assembly, it can be explained according to the spring oscillator model[25]. When the polarized light is applied perpendicular to the assembly direction, the interaction of two Au nanorods polarized charge does not affect the vibration of the nanorods along this perpendicular direction, which is responsible for the fixed SPR$_T$, as inserted in Fig. 3(a). When the polarized light is applied parallel to the direction of assembly, the attraction from the neighbouring Au nanorod decreases the restoring force of vibration with decreasing the gap spacing, which in turn reduces the SPR frequency of the Au nanorod. As a result, the SPR$_L$ of the E-E assemldy red-shifts in the spectra. When the gap spacing is less than 1 nm, the anticipated SPR$_L$ blue-shifting and the appearance of new coupling SPR of Au nanorods assemblies in a longer wavelength possibly depend on the strong coupling effect and tunneling effect of surface electrons.

Corresponding to the optical spectra, the localized electronic field of the E-E assembled Au NRs dimmer is obtained under the irradiation of corresponding SPR wavelength, as shown in Fig. 4. When the gap is 60 nm, electronic fields of two Au nanorods have no obvious coupling effect and the position of SPR$_L$ is near the same position of one Au nanorod. With decreasing the gap size to 10 nm, coupling effect occurs in the gap. When the gap size is 1 nm, the gap field is divided into two parts, which should be responsible for the appearance of new SPR in the longer wavelength. With further decreasing the gap size, the electronic fields are enhanced in the gap and regions around the Au nanorods, which possibly accounts for the enhancement and blue-shifting of the new coupling resonance of E-E oriented Au nanorods.

Fig. 5 is the FDTD simulated absorption spectra for S-S oriented Au nanorods dimer. Compared with SPR$_L$ for Au nanorod monomer, the SPR$_L$ peak position of S-S orients Au nanorods dimer blue-shifts obviously, as shown in Fig. 5(a) (SPR$_L$ and SPR$_T$ of Au nanorod monomer with AR=4 are located at about 815 nm and 510 nm, see Fig. 2(b)). It is quite clear that



(a) SPR_L for E-E assembled Au nanorods with different gap spacing (Inset: SPR_T for E-E assembled Au nanorods with different gap spacing)

(b) Optical absorption spectra for E-E assembled Au nanorods with gap spacing 1 nm and 0.86 nm (Inset: Optical absorption spectra for E-E assembled Au nanorods with small gap spacing)

Fig. 3 Calculated SPR absorption spectra for E-E assembled with gap spacing

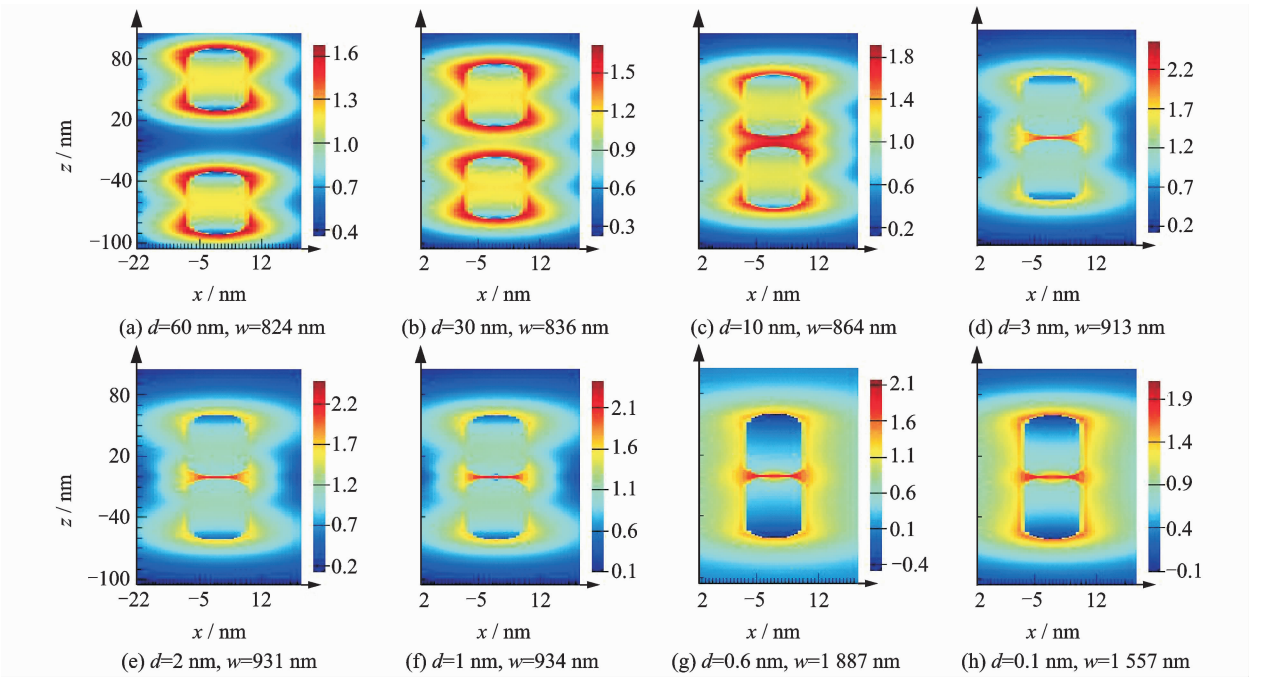
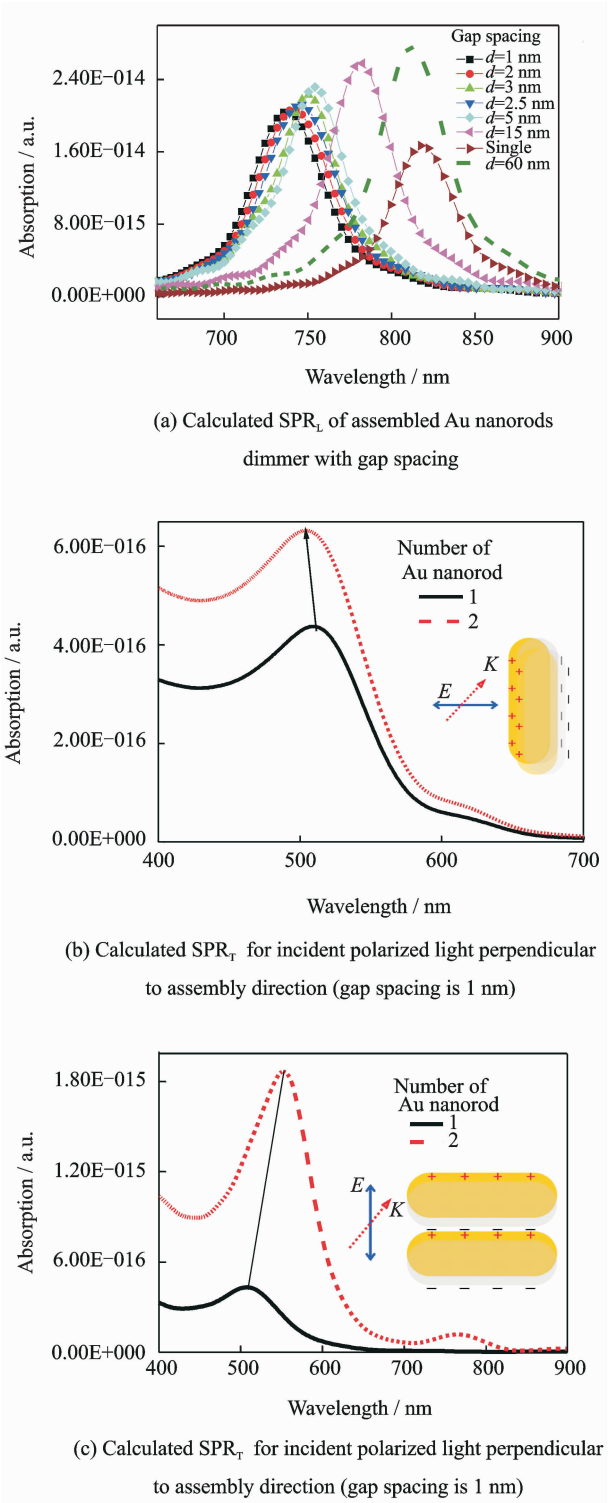


Fig. 4 Electric field distribution of E-E oriented Au nanorods dimmer with decreasing gap spacing (d=60, 30, 10, 3, 2, 1, 0.6, 0.1 nm)

there are two SPR_T polarizations for S-S oriented Au nanorods dimmer. When the polarized light is applied perpendicular to the assembly direction (as inserted in Fig. 5(b)), the SPR_T blue-shifts slightly from about 510 nm to about 505 nm for the S-S orients Au nanorods dimer with gap 1 nm, as shown in Fig. 5(b). When the polarized light is applied parallel to the assembly direction (as inserted in Fig. 5(c)), the SPR_T red-shifts obviously from about 510 nm to about 535 nm, as shown by Fig. 5(c).

Under the longitudinal polarization, the same polarization charge from Au nanorod heads does not affect the longitudinal resonance frequency. However, one end with negative charge will be affected by the positively charged end of another nanorod. Longitudinal vibration frequency of the S-S oriented Au nanorods dimer increases compared with that of single Au nanorod. As a result, the SPR_L for S-S oriented Au nanorods



(a) Calculated SPR_L of assembled Au nanorods dimmer with gap spacing

(b) Calculated SPR_T for incident polarized light perpendicular to assembly direction (gap spacing is 1 nm)

(c) Calculated SPR_T for incident polarized light perpendicular to assembly direction (gap spacing is 1 nm)

Fig. 5 FDTD simulated absorption spectra for S-S oriented Au nanorods

blue-shifts with decreasing the gap spacing. When the incident light perpendicular to the assembly, two transverse resonances appear for the S-S oriented Au nanorods. (1) The polarized light is applied perpendicular to the oriented direction of Au nanorods dimer, the SPR_T blue-shifts very slightly with decreasing the gap spacing. (2) The polarized light is applied parallel to the oriented direction, the SPR_T peak red-shifts obviously with decreasing the gap spacing (or increasing the number) of nanorods, which is similar to the SPR_L red-shifting of nanoparticle chain[21].

Corresponding to the optical spectra, the localized electronic field of the S-S orient Au nanorods dimer is also obtained under three different polarizations, as shown in Fig. 6. Fig. 6(a) is the localized electronic field for the S-S assembled Au nanorods dimer under longitudinal polarization. When the gap is 60 nm, electronic fields of two Au nanorods have no obvious coupling effect and the position of SPR_L is near the same position of one Au nanorod. With decreasing the gap size, coupling effect occurs in the ending gap and SPR_L blue-shifts, which is similar to that of "dog-bone". When the polarized light is applied perpendicular to the assembly direction (as shown by the inset of Fig. 5(b)), no obvious coupling effect occurs in the nanogap of Au nanorods dimmer with decreasing the gap size. When the polarized light is applied parallel to the oriented direction (as shown by the inset of Fig. 5(c)), strong coupling effect occurs in the nanogap, leading to the enhancements of electronic field and red-shifting SPR_T intensity with decreasing the gap size.

Compared with the experimental results of Au nanorods assembles, the measured SPR evolutions agree well with that of FDTD simulation. In the simulation process, the aspect ratio of Au nanorod is 4, and the S-S and E-E assembled Au nanorods are symmetrical in morphology. While the SPR properties obtained in experiment are an average effect of different polarizations on various Au nanorods dimmer, multimer and even monomer, as shown Fig. 7. Moreover, the obvious coupling effect of electron field occurs when the gap is about 1 nm. It is not possible for experimental realization due to the chain length (1.5—2 nm) of applied linking molecular (as inserted in Fig. 7). As a result, the new coupling SPR in the longer wavelength, as predicted in simulation,

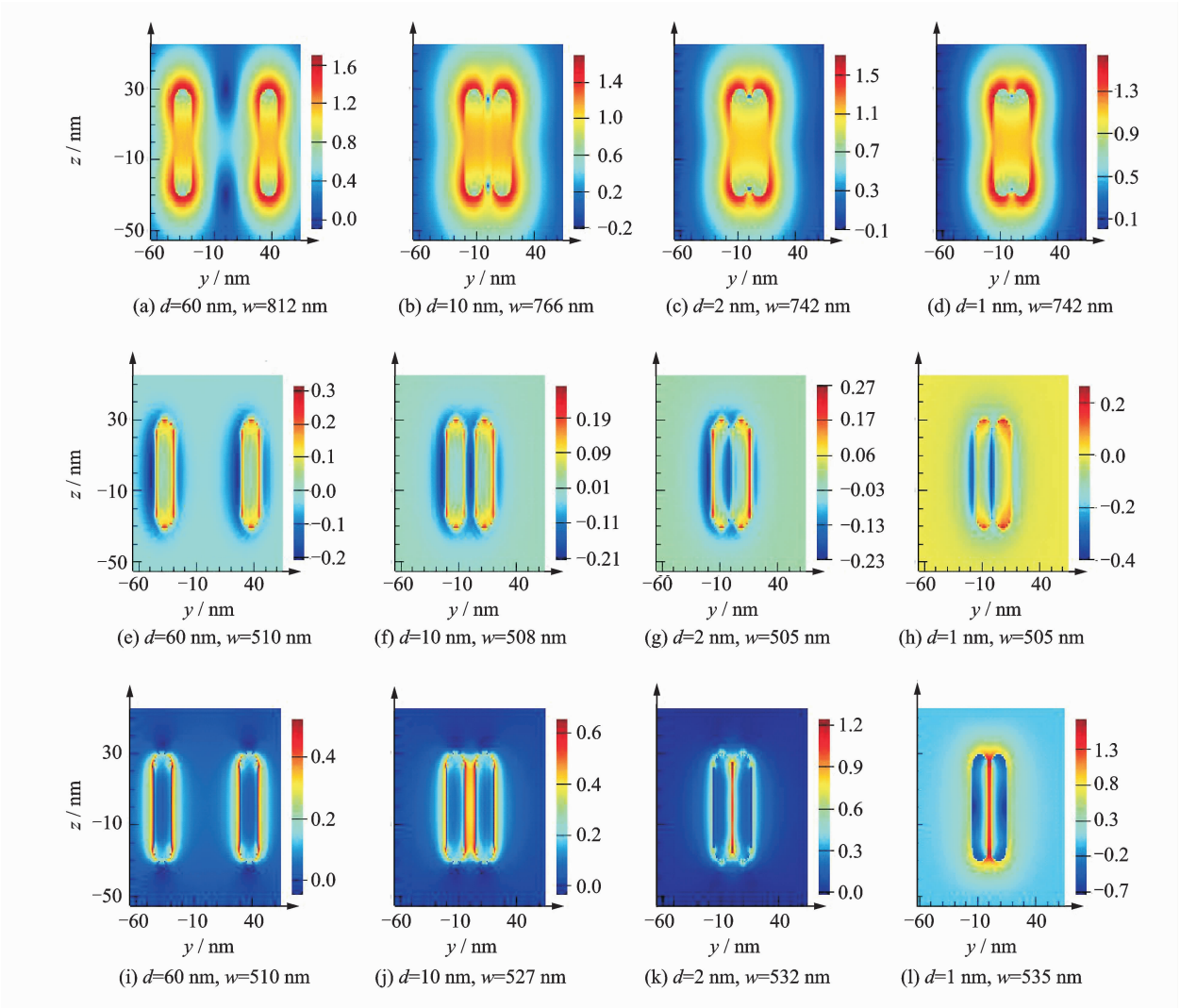
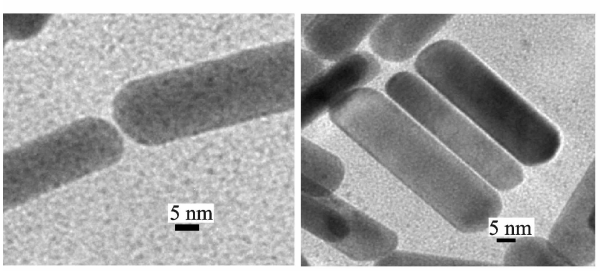


Fig. 6 Electronic field distribution of S-S oriented Au nanorods with decreasing gap spacing



(a) TEM image of E-E oriented assembles (b) TEM image of S-S oriented assembles

Fig. 7 TEM images of linked Au nanorods with 1—2 nm spacing

can not be detected in experiments at present.

3 Conclusions

We introduce the FDTD simulation on the SPR properties and localize electronic field of E-E and S-S oriented Au nanorods dimer. It is found that SPR_L red-shifts for the E-E orients Au nanorods dimer and blue-shifts for S-S orients Au nanorods dimmer with decreasing the gap spacing. Moreover, a new coupling SPR appears for the E-E assembly in a longer wavelength region, blue-shifting and enhancing with further decreasing the gap spacing. For the SPR_T property, there are two different transverse polarizations for the S-S oriented Au nanorods dimmer. The SPR shifting and the appearance of new coupling SPR of assembled Au nanorods dimer are explained by means of spring oscillator model and the polarized charge distribution on nanoparticles.

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(Executive editor: Xu Chengting)