Near-field properties of a shell nanocylinder pair with gain materials*

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We study the near-field response of a shell nanocylinder pair, with its core filled by gain materials, using a two-dimensional finite-difference time-domain method. It is shown that the gain materials in the core of the cylinder can compensate for the intrinsic absorption of the metal shell, leading to local-field enhancement in the gap of the active pair. A linear dependence is found between the field enhancement and the gain coefficient at resonance. The detailed physics is studied by calculating the electrical-field distribution of the shell pair filled with different gain materials. The influence of the gap width and the shell thickness on the interaction of two adjacent active shell cylinders is also investigated.

Keywords: shell nanocylinder pair, gain material, local-field enhancement

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1. Introduction

The plasmonic properties of a noble metal nanostructure have been intensively explored for various applications, such as the surface enhanced Raman scattering (SERS),[1,2] with the excitation of surface plasmons (SPs) of coupling electromagnetic (EM) waves with electron collective oscillations.[3−5] The plasmons-induced intense EM field at metal surfaces or junctions of coupled nanoparticles, termed "hot spots", can significantly increase the Raman enhancement factor G scaled as the fourth power of the electric field. This enhancement is crucial for the SERS. Since the plasmonic properties of a nanostructure depend particularly on its size and shape, to maximize electromagnetic field enhancement at a specific frequency, we need to geometrically optimize the SERS substrate.

Two directly adjacent nanoparticles, known as a "nanoparticle dimer", can give rise to intensive field enhancement at their junctions, which make them highly attractive for the SERS substrate design. Therefore, a number of studies with different dimer geometries, such as sphere dimer,[6,7] triangular dimer,[8] nanoshell dimer,[9] and nanowire dimer,[8,10] were carried out experimentally and theoretically. Particularly a strong local intensity enhancement in the cavity between coated metallic nanoparticles was found with an increase of 14 orders for the SERS.[7] The intensive local field enhancement was also reported between metallic particles such as Ag particles, in the SERS applications in biological and chemical fields.[11,12] A beneficial nanoparticle structure for the SERS application is the nanoshell, usually containing a dielectric core and an ultrathin coated layer of a certain noble metal such as gold and silver.[7,13] By varying the relative dimensions of the core and shell of the particle, the plasmonic resonant peak moves from visible to near-infrared regimes.[7,14] This tunable feature offers an opportunity of changing the plasmonic peak at a desired frequency for a particular SERS application.

Such nanosystems, however, suffer from absorption damping of metallic materials, especially at optical and near-infrared frequencies. In order to overcome this disadvantage, we introduce gain materials into the core region of the shell nanowire dimer for loss compensation. The gain materials introduced can be organic dye molecules,[15−17] nanocrystal quantum dots (NQDs),[18−20] or rare-earth ions doped to a host material.[21,22] The plasmonic effects and near-field properties of the shell nanocylinder pair with gain ma-

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terials are investigated using a two-dimensional finite-difference time-domain (FDTD) method.[23] In the structure, each metal shell forms a resonant cavity analogous to that for conventional lasers,[24] while the specific physical process is different. The gain coefficient of the dielectric core plays an important role in the enhanced local field confined in the junction of the shell cylinders. By changing the inter-cylinder distance, we compare the interaction of the active shell cylinders with that of the passive ones. The influence of the shell thickness on field enhancement with the same gain parameter is also discussed.

This paper is organized as follows. We describe the model applied in Section 2. In the sections followed, we analyze and discuss the properties of the shell cylinder pair with different gain coefficients. Finally, we end up with the conclusion.

2. Model

The near-field properties of a silver shell nanocylinder pair interacting with a linearly-polarized wave in visible and near-infrared regimes are investigated. Each nanocylinder comprises of a metal shell and a dielectric core. As shown in Fig. 1, the geometry of this silver shell nanocylinder pair is defined by the inner and the outer radii, r_1 and r_2, of the cylinder, and the inter-cylinder distance d. The metal and gain materials are assumed to be homogeneous, isotropic, and non-magnetic. In other words, magnetic permeability $\mu_i = 1$ with i = c, m, d for the core, metal shell, and surrounding medium regions, respectively. Hence, the corresponding wave numbers in each region are given by $k_i = \omega\sqrt{\varepsilon_i\mu_i} = \omega\sqrt{\varepsilon_i}$, where ε_i is the complex dielectric constant of corresponding regions.

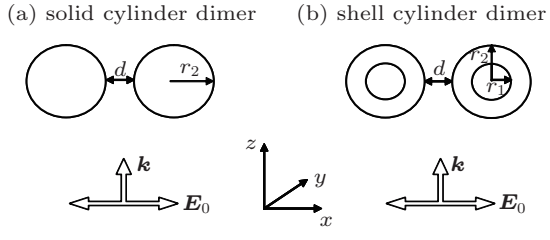


Fig. 1. Schematic diagrams of (a) a solid cylinder pair and (b) a shell cylinder pair. An electromagnetic plane wave with the wave vector $\boldsymbol{k}$ and the electric field $\boldsymbol{E}_0$ is projected on the pair.

The frequency dependence of the complex dielectric constant of the shell metal (sliver in our analysis) is described by the Drude model as

$$\varepsilon_{\rm m}(\omega) = \varepsilon_{\rm b} - \frac{\omega_{\rm p}^2}{\omega^2 + {\rm i}\gamma\omega}, \tag{1}$$

where ω is the incident frequency, $\omega_{\rm p}$ is the bulk plasma frequency, γ is the collision rate, and $\varepsilon_{\rm b}$ represents infinite-frequency relative permittivity. In this paper, we set these parameters as $\omega_{\rm p} = 9.5$ eV, $\gamma = 0.015$ eV, and $\varepsilon_{\rm b} = 5$. When the thickness of the silver shell is much less than the mean free path of the conductive electrons, the size effect on the collision rate should be considered by making use of

$$\gamma = \gamma_\infty + AV_{\rm F}/R, \tag{2}$$

where γ_∞ is the bulk collision rate, $V_{\rm F}$ is the Fermi velocity,[25] R is the effective mean free path for the collision with boundary, and the constant A, usually a unity, depends on the structure shape and the theory applied.[26]

To realize an active shell cylinder pair, we introduce a gain material into the core region. The properties of the gain material can be described in terms of the real part of the refractive index, n_0, and the imaginary part of the refractive, k, as

$$n = n_0 + {\rm i}k, \tag{3}$$

where k, also called "extinction coefficient", determines the nature of the core medium. It is lossless and passive for $k = 0$, lossy and passive for $k > 0$. For optical gain, the imaginary part of the refractive index k is negative, i.e., optical gain occurs as $k < 0$. In this paper, we consider rare-earth doped silica as the gain material, due to its most compatible properties among existing fabrication techniques in nanoshell synthesization. The real part of the refractive index in the core region is then $n_0 = 1.43$ and the gain coefficient k varies with the extent of the amplification.

When the nanocylinder size is much smaller than the incident wavelength, the electron oscillation under a linearly-polarized mode can be considered as an ideal dipole. If two shell cylinders are brought to each other, the electric field $\boldsymbol{E}$ felt by each cylinder is the sum of the incident light field $\boldsymbol{E}_0$ and the near-field $\boldsymbol{E}_{\rm nf}$ of the neighbouring cylinder[27]

$$\boldsymbol{E} = \boldsymbol{E}_0 + \boldsymbol{E}_{\rm nf}. \tag{4}$$

3. Results and analysis

The inner and outer radii of a shell nanocylinder in the pair are fixed to be $r_1 = 30$ nm and $r_2 = 36$ nm. For comparison, we also study the solid cylinder pair

with the radius of $r_2 = 36$ nm. The inter-cylinder separation d of 10 nm is introduced for both the solid and shell cylinder pairs, and the testing point is set in the center of the interaction gap. In the nanosystem, the plasmon mode on one cylinder couples with the other,[8,28] so the most strongly enhanced EM energy is localized at the junction. As shown in Fig. 2(a), the plasmonic resonance of a solid cylinder pair is 439 nm, while the highest field intensity occurs at 725 nm for the shell cylinder pair, indicating a lower energy required to drive the coupled plasmon oscillation modes in the shell cylinder pair than that in the solid one. When the gain material is introduced, the local-field enhancement depends on the coefficient k of the core medium. It is shown that the lower the gain coefficient k is, the higher the electric-field intensity is in the center of the gap. Besides, as the parameter k decreases, the resonance wavelength shifts slightly from 725 nm to 714 nm, suggesting an enhanced coupling between plasmon oscillations of the two active shell cylinders. In Fig. 2(b), it is shown that the field enhancement at the resonance decreases linearly as the gain coefficient increases. It should be pointed out that for the gain coefficient lower than -0.08, the simulation is unstable. The simulation results show that the maximal field enhancement occurs at a resonance wavelength of $\lambda_{\rm res} = 714$ nm with the gain k approaching -0.08. Thus, the simulated maximal amplification coefficient of light intensity is then derived from $g = 4\pi k/\lambda_{\rm res} \sim -1.41 \times 10^4$ cm^{-1}. This value can be achieved by doping rare-earth ions into a dielectric host, such as Pr^{3+}, Ho^{3+}, Er^{3+}, Nd^{3+}, and Tm^{3+}.[22] In addition, the amplification coefficient as high as $|g| \sim 10^5$ cm^{-1} has also been found in a quantum dot system.[29] In general, the amplification coefficient g is proportional to the gain dosage concentration N and its emission cross section $\sigma_{\rm e}$. Therefore, different values of k in our simulation can be realized with different dosage concentrations N experimentally.

The active shell nanocylinder pair is a strongly coupling system between light, atom states, and collective electron oscillations. Thus the optical response is extremely sensitive to the gain coefficient k as well as the exciting frequency and geometry parameters. To investigate the interaction between the metal absorption and gain amplification under a plane wave, the electric field distribution of the shell cylinder pair versus the different gain coefficient along the x axis in a range from -30 nm to 30 nm is shown in Fig. 3. It can be found that the smaller the gain parameter k is, the higher level the electric-field intensity reaches in the gap region. In other words, more energy is transferred from the active core to the plasmon excitation in the silver shell for the smaller gain parameter k, leading to a stronger plasmonic coupling between the two active cylinders. Thus, the higher field intensity is found in the gap region.

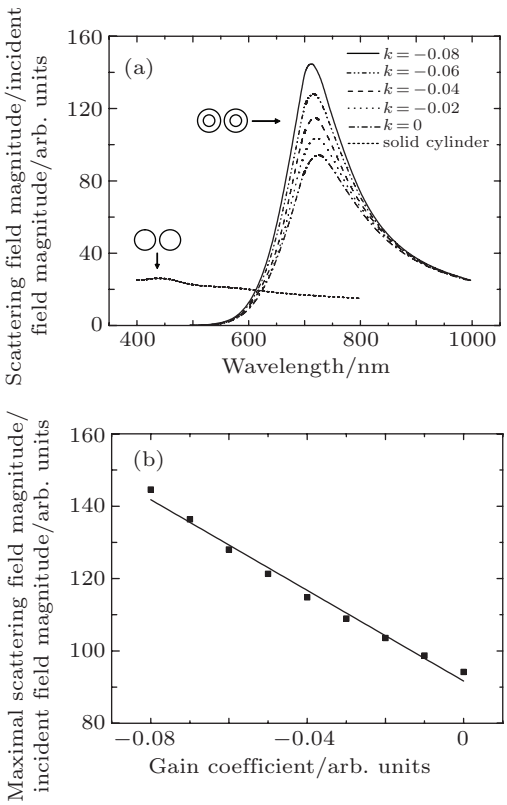


Fig. 2. (a) Field enhancement for the shell cylinder pair with $k = 0$, -0.02, -0.04, -0.06, and -0.08 (bottom to top). For comparison, the result for a passive solid cylinder pair is also presented. (b) Calculated data (discrete points) and linear fit (line) of the field enhancement as a function of the gain coefficient k at the resonance.

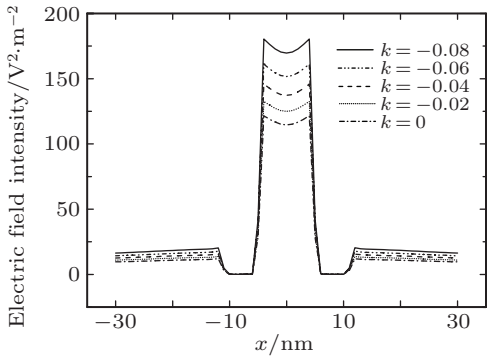


Fig. 3. Scanned electric-field distribution versus different gain coefficients at resonance along the x axis in the range of -30 nm to 30 nm, for $k = 0$, -0.02, -0.04, -0.06, and -0.08 (bottom to top). The incident wavelength is 725, 721, 718, 716, and 714 nm, respectively.

The detailed process can be explained as follows. Erbium ions are good gain materials and behave as quasithree-level systems.[30] When the external source is injected to the shell nanocylinder pair, energy is absorbed by the gain material, stimulating Er^{3+} to rise to a highly excited state. Through resonance coupled transitions, the excited Er^{3+} is then relaxed to the ground level, and energy is transferred to the plasmon excitation of the metal shell. Consequently, energy dissipation of metal, such as electron collisions and electron-surface scattering, is compensated.

It is obvious that high field enhancement occurs at the junction of the cylinder pair when the incident light is polarized along the x axis. The polarization-excited surface plasmon mode in one cylinder couples with the other. As a result, energy is localized in the gap of the shell cylinder pair effectively. Though the distance effect on the field intensity has already been investigated, there is no further research on the interaction between two adjacent active cylinders. To give an intuitionistic explanation, we investigate the field enhancement of an active shell cylinder pair as a function of interaction separation for various gain coefficients k at resonance. As a comparison, we also calculated the passive shell cylinder pair as a function of d ranging from 4 nm to 20 nm with a numerical step of 2 nm.

It is shown in Fig. 4 that the local field intensity in the gap of the two interacting active shell nanocylinders falls drastically with the same trend of passive cylinders as the interaction distance increases. Therefore, for a polarized plane wave, the plasmon coupling in active shell cylinder pair can also be treated approximately as one type of dipole–dipole interaction. The electric field generated by a dipole of distance d is given by[31]

$$\boldsymbol{E} = \frac{2\chi \boldsymbol{E}_0}{4\pi\varepsilon_0 d^3}, \tag{5}$$

where χ is the dipole tensor. Accordingly, dipole–dipole coupling strength decays cubically with the inter-cylinder distance d. Therefore, the local field intensity falls with the same trend. Note that the gap of the pair below 3 nm is not considered here due to the quantum mechanical effect, for instance, the electron tunnelling across the junction in such a small distance. While for larger separations, the plasmon mode is well described by classical electromagnetic theory.

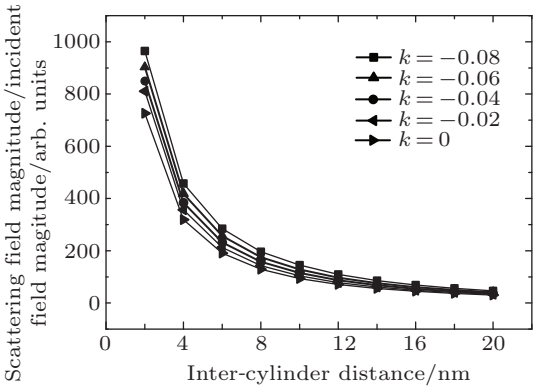


Fig. 4. Field enhancement versus the inter-cylinder distance d for $k = 0$, -0.02, -0.04, -0.06, and -0.08 (bottom to top). The discrete inter-cylinder distance d ranges from 4 nm to 20 nm with a step of 2 nm.

In order to understand how the gain material compensates the metal loss, the optical response of the shell nanocylinder pair for different shell thicknesses is also investigated. Figure 5(a) shows the field enhancement as a function of the wavelength for different shell thickness $r_2 - r_1$, varying from 4 nm to 20 nm, with a constant gain parameter k of -0.05. The inner

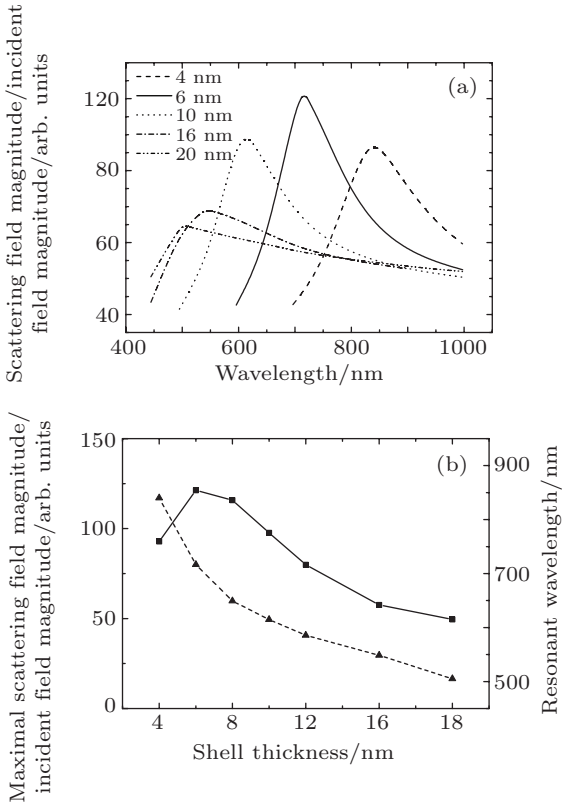


Fig. 5. (a) Near-field response of an active nanoshell cylinder pair of different shell thickness, varying from 4 nm to 20 nm (right to left), with a constant gain parameter $k = -0.05$. (b) Variation of the maximum field enhancement (solid line) and resonant wavelength (dashed line) with the shell thickness.

radius and the distance between the two shell cylinders are set to be 30 nm and 10 nm to minimize the influencing factors of gain core and gap size. The results show that the highest field intensity occurs when the shell thickness is 6 nm. A further increase of the shell thickness will decrease the field intensity at the monitored point, because that thicker shell will cripple the compensation effect of the active core. The explicit variation of the maximum intensity and resonance wavelength with the shell thickness are presented in Fig. 5(b). With the same gain material introduced, the resonant wavelength shifts to blue as the shell thickness increases. This trend is similar to that of a passive nanoshell with different shell thicknesses in water according to Ref. [32].

4. Conclusions

We have investigated the optical response of a nanoshell cylinder pair with various gain coefficients k by filling different gain materials into the core region. As the parameter k decreases, the local field intensity in the gap of the active shell cylinder pair grows up linearly. The enhancement can be understood by the fact that the amplification of the gain material in the core region compensates the intrinsic loss of the metal shell, resulting in an enhanced coupling of two active shell cylinders. The detailed distribution of the electric field is shown to support the explanation. In addition, the influence of the inter-particle distance on the field enhancement shows the feature of a dipole–dipole-type interaction approximately for the plasmonic coupling of two active cylinders. The spectral response of the active shell cylinder pair with different shell thicknesses reveals that a thicker shell will cripple the compensation effect of the gain core region, which suggests a design principle for nanoparticle synthesization in experiments.

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