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Optical properties of U-shaped Ag nanostructures

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Abstract

The extinction spectra and E field distribution of a U-shaped nanostructure have been calculated using the discrete dipole approximation method, and compared to those of the parallel-nanorod structure. For a parallel-nanorod structure, when light propagates with its E field perpendicular to the nanorod axis only transverse plasmon modes are excited. Under the same condition for a U-shaped nanostructure, because the bottom nanorod builds a path for the electrons oscillations, longitudinal mode plasmon oscillations can also occur along the vertical nanorods. A U-shaped nanostructure has more hot spots than a parallel-nanorod structure; and at the longitudinal mode incidence, the E field enhancements are much larger than those of the parallel-nanorod structure. The longitudinal mode plasmon peaks red shift linearly with increase in the height, and decay exponentially with increasing nanorod radius. When the separation between two vertical nanorods increases, the longitudinal mode plasmon peaks first blue shift and then red shift linearly. These results could be used to engineer U-shaped nanostructures for specific plasmonic applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Silver nanostructures can exhibit localized surface plasmon resonance (LSPR), and at the plasmon resonance wavelength, λ_p, an enhanced local E field occurs at the surface, which is the major mechanism for surface enhanced Raman spectroscopy (SERS) [1]. The morphology of the nanostructure could affect the plasmon resonance dramatically [2]. Both experimental and theoretical studies have demonstrated that if the morphology of a nanostructure has more corners or recesses, there are more sites with high enhanced fields, which benefits SERS detection [2]. Most structures that have been investigated are solid structures such as spheres, spheroids, triangles, cubes, and cylinders. Hollow structures, such as the crescent moon Au structure, have a greater internal surface area, and could be used to generate a high E field as well [3]. Another type of structure is a U-shaped nanostructure. A U-shaped nanostructure will have more corners, more recesses, and a greater internal surface area compared to spherical particles, nanorods, triangular particles etc. Recently, Xu *et al* prepared a U-shaped Au nanostructure using the so-called nanoskiving method [4]. Because the U-shaped structure is anisotropic, the transmission spectra are dependent on the incident polarization. When light is incident with a polarization perpendicular to the direction of the two arms of the U, multi-current patterns are formed in the E field distribution [4]. However, the size of the U-shaped structure they studied was pretty large (diameter $\sim \mu$m), and the plasmon peak is located at the far infrared, which is far away from the traditional SERS excitation wavelength. Smaller U-shaped nanostructures would be preferred to serve as the SERS substrate.

Recently, aligned Ag nanorod arrays have been used to obtain a large SERS response for biological or chemical detection [5, 6]. The reproducible Ag nanorod structure was produced by the oblique angle deposition (OAD) technique. For this substrate, a base layer of 500 nm Ag film is first deposited onto glass slides, and then Ag nanorod arrays are coated on top of the Ag film. These nanorod arrays are randomly distributed on the surface and are composed of needle-shaped nanorods with a top diameter of ~99 nm and a length of ~868 nm. Driskell *et al* have investigated how the Ag base layer affects the Raman intensity [6]. The results show that the absolute Raman intensity of *trans*-1,2-bis(4-pyridyl)ethane (BPE) for silver nanorods on Ag film is three orders of magnitude stronger than that for silver nanorods on bare glass slides. This result demonstrates that when the

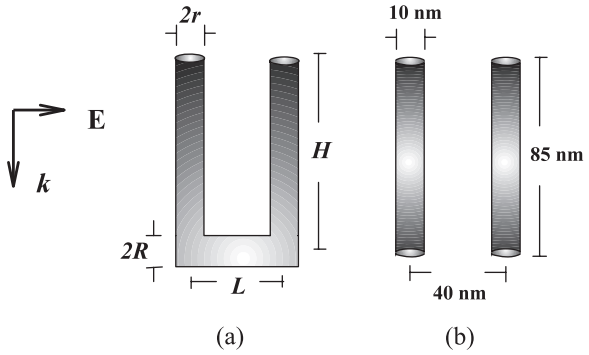


Figure 1. Schematics for the incident polarization and (a) the U-shaped nanostructure and (b) the parallel-nanorod structure.

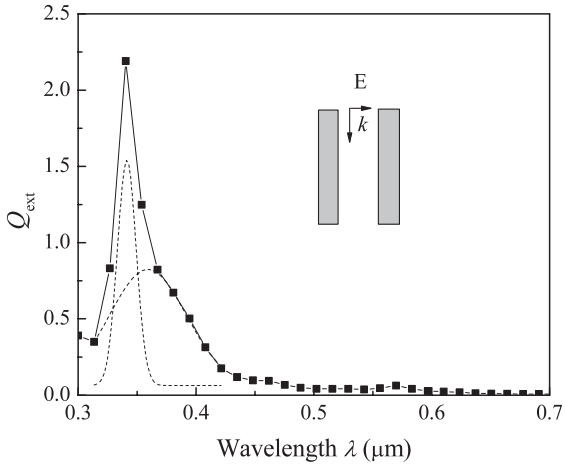


Figure 2. Calculated extinction spectra of the parallel-nanorod structure. The two dashed peaks are resolved from Gaussian peak fitting.

additional Ag base layer is added, there could be stronger E field coupling between the Ag film layer and the nanorods, and more SERS hot spots could be generated in between the Ag film and Ag nanorods. So far, theoretically, the effect of the underlying Ag film on the optical properties of the SERS substrate is not known. Structurally, the aligned nanorod arrays on a thin Ag film can be treated as a blanket structure and the simple unit in one dimension for such a structure is a U-shaped nanostructure. Once such U-shaped structures are arranged in a two-dimensional fashion, one obtains the Ag nanorod array substrate. Thus, the optical properties of U-shaped nanostructures could help us to understand the film effect and can be used as a crude model for the Ag nanorod SERS substrate (it is not a good approximation, since the connected U-shape will break the symmetry and change the electron conduction pathway). In this paper, the extinction spectra and near-field E field distributions of smaller U-shaped nanostructures are studied and compared to the parallel-nanorod structures. The results show that the U-shaped nanostructures can give higher E field enhancements, generate more plasmon modes, and create more hot spots than those of the parallel-nanorod structures.

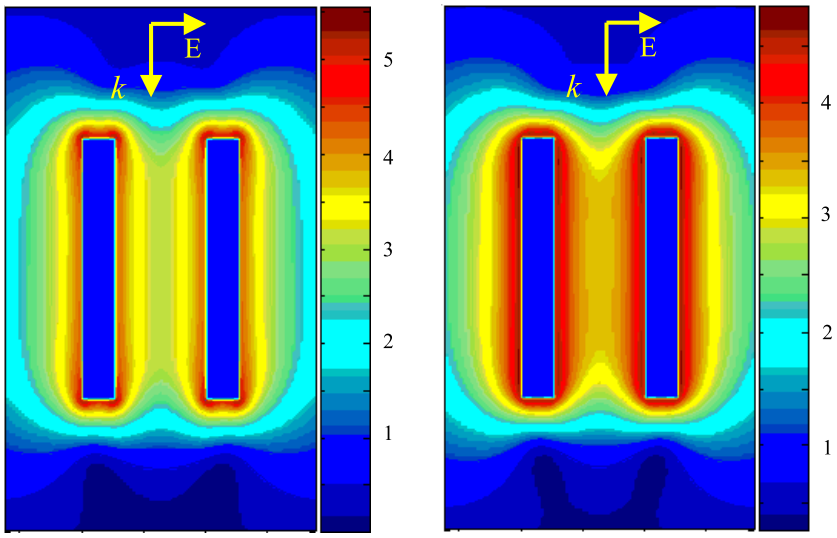
2. Discrete dipole approximation (DDA) calculation

The extinction efficiency Q_{ext} ($Q_{\text{ext}} = C_{\text{ext}}/\pi a_{\text{eff}}^2$, where a_{eff} is the effective radius of the nanoparticles and C_{ext} is the extinction cross section) and the E field enhancement distribution γ ($\gamma = |\vec{E}|^2/|\vec{E}|^2$, where $|\vec{E}_0|$ is the magnitude of the incident field and $|\vec{E}|$ is the magnitude of local electric field surround the nanostructure) of U-shaped nanostructures are calculated using the discrete dipole approximation (DDA) method [7, 8]. Figure 1 illustrates the topological structures of a U-shaped and a parallel-nanorod structure, and the polarization configuration of the incident light used in the calculations. The parallel-nanorod structure consists of two nanorods in the vertical direction with a radius r and a height H. The U-shaped nanostructure has an additional bottom cylinder in the horizontal direction with a radius R and a length L connecting the two vertical rods. In all the calculations, the excitation light propagates along the vertical direction with a horizontal polarization (figure 1). In order to further understand how different structural or topological parameters affect the extinction spectra, the topological parameters of the U-shaped nanostructure are changed systematically. When we systematically investigate how the structural parameters tune the plasmon peak, we change only one parameter and keep the others the same: the length L is changed from $L = 13$ to 80 nm; the height H is changed from $H = 40$ to 120 nm; the radius r is changed from $r = 4$ to 9 nm; and the radius R is changed from $R = 4$ to 10 nm. In all the DDA calculations, the lattice spacing is fixed at 1 nm, which meets the convergence requirement for DDA calculation [8]. The bulk dielectric constants of Ag used in the calculations are obtained from [9].

3. Results and discussions

Figure 2 plots the extinction spectrum of a parallel-nanorod structure with $r = 5$ nm, $H = 85$ nm, and $L = 40$ nm. The extinction spectrum has two peaks: the peak located at the longer wavelength ($\lambda_{\text{TDM}}^C = 0.359$ μm) is called the transverse dipole mode (TDM); and the peak located at the shorter wavelength ($\lambda_{\text{TQM}}^C = 0.341$ μm) is called the transverse quadrupole mode (TQM). When the incident light has a TDM wavelength, the maximum E field enhancement ($\gamma \sim 3.4 \times 10^5$) occurs around the side wall of each individual nanorod (figure 3(a)) and demonstrates a weak field coupling between the two nanorods. When the incident light has a TQM wavelength, the E fields are also coupled into the space between two nanorods (figure 3(b)). However, the maximum E field enhancement occurs not only at the tip of the nanorods but also around the contour of the parallel-nanorod surfaces. The maximum field enhancement γ is $\sim 6.8 \times 10^4$.

When a bottom nanorod is used to connect the two parallel nanorods, a U-shaped nanostructure is formed. Figure 4 plots the extinction spectrum of a U-shaped nanostructure with $R = 5$ nm, $H = 80$ nm, $L = 40$ nm, and $r = 5$ nm. Besides the plasmon peaks around $\lambda_{\text{TDM}}^C = 0.36$ μm and $\lambda_{\text{TQM}}^C = 0.34$ μm, which are observed in the parallel-nanorod structure, three more peaks appear at $\lambda_{\text{p}} = 0.82$ μm, 0.579 μm,



(a) $\lambda^{C}_{TDM} = 0.359$ (b) $\lambda^{C}_{TQM} = 0.341$

Figure 3. E field enhancement contours ($\log_{10}\gamma$) of the parallel-nanorod structure at different incident wavelengths: (a) $\lambda^{C}_{\mathrm{TDM}} = 0.359\ \mu$m and (b) $\lambda^{C}_{\mathrm{TQM}} = 0.341\ \mu$m.

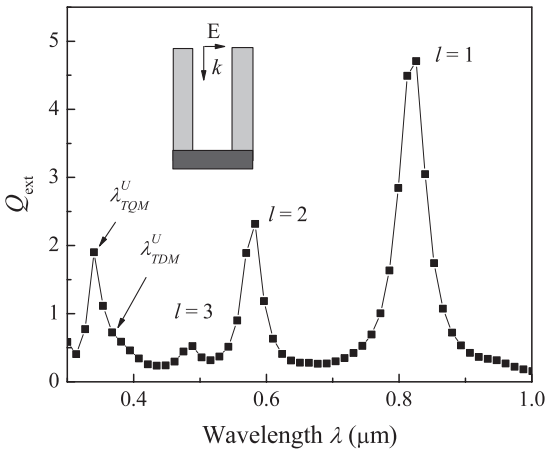
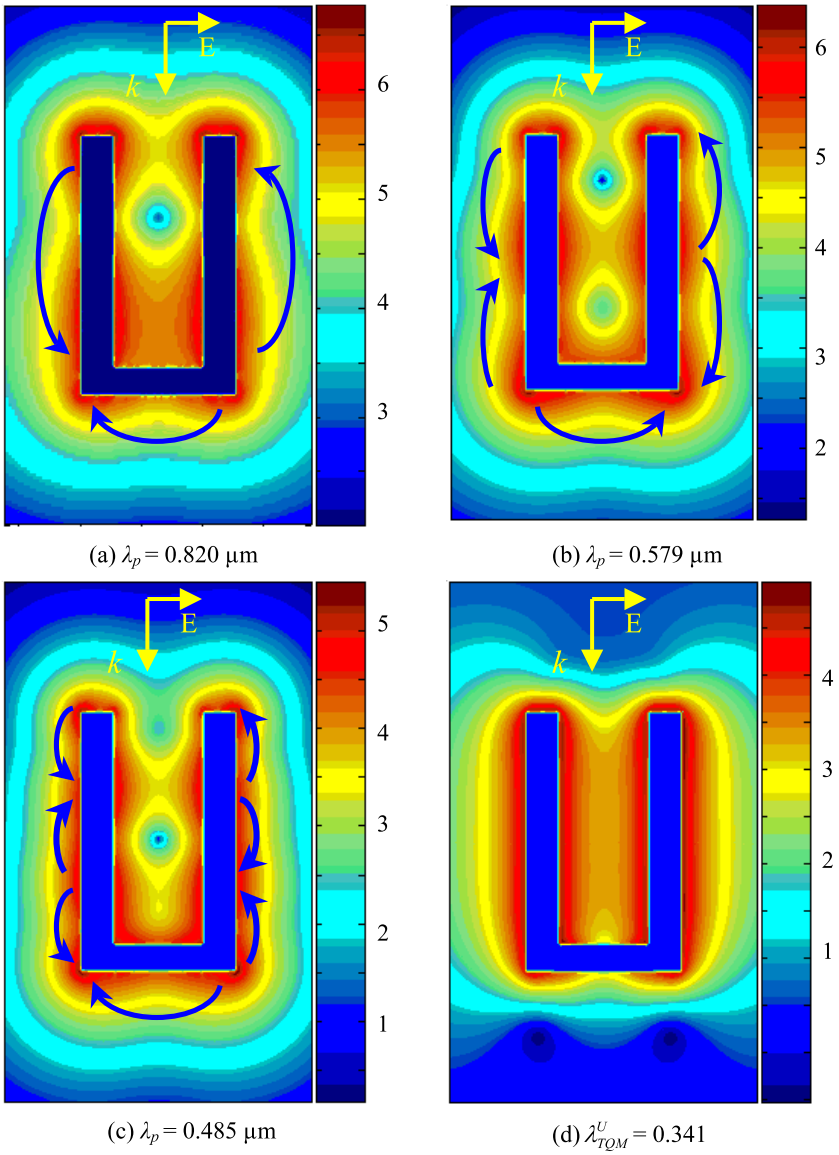


Figure 4. Calculated extinction spectra of the U-shaped nanostructure.

and 0.485 μm, respectively. The extinction efficiency at $\lambda_{\mathrm{p}} = 0.82\ \mu$m has the highest value, and the plasmon peak at $\lambda_{\mathrm{p}} = 0.485\ \mu$m has the smallest magnitude. The E field enhancement distributions are determined by the induced charge oscillation modes for each of the extinction peaks, as shown in figure 5.

In our calculation, the Ag bulk dielectric constants are taken from Palik's handbook [9]. When the size-dependent correction is taken into account [10], the motions of the free electrons in two vertical nanorods are limited by the boundary and their mean free path will be reduced. Therefore, the size-dependent dielectric constants are only used for two vertical nanorods, while the dielectric constants of the bottom nanorod correspond to the bulk. The calculated extinction spectrum of the U-shaped nanostructure with $R = 5$ nm, $H = 80$ nm, $L = 40$ nm, and $r = 5$ nm using the size-dependent dielectric constants has a similar shape as that shown in figure 4 and the plasmon peaks only blue or red shift by 1 nm. However, the extinction strengths at different peaks are different. Although the results calculated from two dielectric constants are quantitatively different, the locations of the plasmon peak are qualitatively the same. Thus, the results calculated from Palik's handbook could show the correct tendencies that would be expected in practical samples.

At $\lambda_{\mathrm{p}} = 0.82\ \mu$m, as shown in figure 5(a), E fields are coupled in the space between two vertical nanorods. A pin-like distribution occurs around the surface of each vertical nanorod. The maximum E field enhancement is $\sim 6.7 \times 10^6$, which is much larger than those at TM wavelengths for the parallel structure. Under this condition, one could envision that there are three dipole oscillations that have been excited along the U-shaped nanostructure: one dipole oscillation occurs along the long axis of the bottom nanorod and two dipole oscillations occur in the vertical nanorods, as indicated by the arrows in figure 5(a). There is strong E field coupling between the two vertical nanorods. This oscillation behavior is similar to the longitudinal plasmon mode (LM) of the vertical nanorods. In fact, for the parallel-nanorod structure with $r = 5$ nm, $H = 85$ nm, and $L = 40$ nm, its LM mode wavelength is $\lambda_{\mathrm{p}} = 1.043\ \mu$m. We use $l = 1$ to denote this resonance mode. At $\lambda_{\mathrm{p}} = 0.579\ \mu$m, as shown in figure 5(b), the E fields between the two vertical nanorods are coupled. The maximum E fields distribute around the top, the middle, and the bottom of the U-shaped nanostructure, and the magnitude is $\sim 1.5 \times 10^6$, which is also much larger than those of the parallel-nanorod structure. One could use five dipoles to simulate the field oscillations as illustrated by the arrows in figure 5(b). We use $l = 2$ to denote this plasmon resonance mode. At the plasmon peak of $l = 1$ and 2 for U-shaped nanostructures, the dipole oscillation distance is much larger than that of parallel-nanorods with TM mode incidence which could result in a larger E field enhancement. At $\lambda_{\mathrm{p}} = 0.485\ \mu$m, as shown



(a) $\lambda_p = 0.820$ μm (b) $\lambda_p = 0.579$ μm

(c) $\lambda_p = 0.485$ μm (d) $\lambda^U_{TQM} = 0.341$

Figure 5. E field enhancement contours ($\log_{10}\gamma$) of the U-shaped nanostructure at different incident wavelengths: (a) $\lambda_p = 0.82$ μm, (b) $\lambda_p = 0.579$ μm, (c) $\lambda_p = 0.485$ μm, and (d) $\lambda^U_{TQM} = 0.341$ μm.

in figure 5(c), the maximum E fields occur at the top, 1/4 of the way from the top, 3/4 of the way from the top, and at the bottom of the U-shaped nanostructure, with a magnitude of $\gamma \sim 2.2 \times 10^5$, which is one order of magnitude smaller than those at modes $l = 1$ and 2. When a single nanorod with a radius of 5 nm and height of 85 nm is irradiated under longitudinal mode wavelengths (the incident E field is parallel to the height), the quadrupole plasmon peak occurs at 0.488 μm and the maximum E fields also occurs around the two ends and 1/4 of the distance from two ends. The similarities between the plasmon peak and E field distribution demonstrate that this plasmon mode consists of quadrupole oscillations in two vertical nanorods and dipole oscillation in the bottom nanorods, as illustrated by the arrows in figure 5(c). We use $l = 3$ to denote this resonance mode. The peaks at $\lambda^U_{TQM} = 0.341$ μm and $\lambda^U_{TDM} = 0.36$ μm are due to the TM modes of the two vertical nanorods. Figure 5(d) shows the E field enhancement distribution of a U-shaped nanostructure at $\lambda^U_{TQM} = 0.341$ μm. The E field distribution is very similar to that of figure 3(b); in fact the field at the bottom looks like it is penetrating the bottom nanorod. Thus, the plasmon peak at $\lambda^U_{TQM} = 0.341$ μm is due to the TQM mode of the vertical nanorods. Similarly, the plasmon peak at $\lambda^U_{TDM} = 0.36$ μm is due to the TDM mode of the vertical nanorods. Comparison of the U-shaped and parallel-nanorod structure reveals that the addition of the bottom nanorod to bridge the two vertical nanorods can help to induce multiple plasmon resonance modes. Meanwhile, since the incident E field is perpendicular to the vertical nanorods in the parallel-nanorod structure, it can only excite the TM plasmon oscillation, while for the U-shaped nanorod, the horizontal incident E field could produce excitation in the bottom nanorod, and those electrons can transport through the vertical nanorods to induced multimode LM plasmon resonance along the

vertical nanorods. Moreover, when light is incident with the wavelengths of $l = 1, 2, 3$ modes, the E fields at the bottom of the U-shaped nanostructure are at least one order of magnitude larger than those at the bottom of the parallel structure when light is incident with TM modes, and there are more surface areas that have large field distribution. These greatly benefit the SERS enhancement when U-shaped nanostructures are used compared to parallel-nanorod structured substrates.

In order to investigate how the separation L between two vertical nanorods affects the extinction spectra for a U-shaped nanostructure, L is increased systematically from $L = 13$ to 80 nm with fixed $H = 80$ nm. Figure 6(a) shows the extinction spectra of U-shaped nanostructures with $L = 13$ nm, 30 nm, and 80 nm, respectively. For the U-shaped nanostructure with $L = 13$ nm there are only TM modes. Because of the smaller gap (3 nm) between two vertical nanorods, the coupling between them is so strong that these two vertical nanorods can be treated as connected nanorods for the electron oscillation, which would increase the electron oscillation distance and red shift the plasmon peaks of two TM modes compared to those with larger L, as shown in figure 6(a). For the U-shaped nanostructures with $L = 30$ and 80 nm, the spectra all have three longitudinal modes ($l = 1$, 2, and 3). For the $L = 80$ nm U-shaped nanostructure, the extinction strength of the $l = 1$ mode is much higher than that of the $l = 2$ mode. However, the extinction strengths of the $l = 1$ and the $l = 2$ of the $L = 30$ nm U-shaped nanostructure have a similar magnitude. Figure 6(b) illustrates the plasmon peaks as a function of L for the U-shaped nanostructure. When L increases to $L = 20$ nm, the strong plasmon peaks of the $l = 1$, 2, and 3 modes appear. With the increase of L, the plasmon peaks of the $l = 1$ and 2 blue shift at the beginning and then red shift linearly with L (the solid curves in figure 6(b) are the linear fitting from $L = 40$ to 80 nm), which demonstrates that the separation L plays an important role in determining the plasmon resonance of the U-shaped nanostructure. For the $l = 1$ and 2 modes, there are similar E field distributions as shown in figures 5(a) and (b), and similar E field enhancement magnitude of $\sim 10^6$. For U-shaped nanostructures with a shorter length L, such as $L = 20$ nm, larger E fields are coupled between two vertical nanorods compared to those outside the U-shaped nanostructure. With the increase in L, the E field coupling between two vertical cylinders becomes weaker, which would decrease the effective collective oscillation distance between the two vertical nanorods and blue shift the plasmon peak ($l = 1$ and 2). When L continues to increase, there is almost no coupling between the two vertical nanorods, while the dipole oscillation distance in the bottom nanorod becomes longer and starts to play a major role, which red shifts the plasmon peak. For the $l = 3$ mode, with increasing L, the quadrupole oscillation in two vertical nanorods becomes weak and the plasmon peak disappears at $L = 55$ nm. When L continues increasing, the quadrupole oscillation in the bottom cylinder makes this mode appear again.

To investigate the effect of height, H is increased from $H = 40$ to 120 nm with fixed $L = 40$ nm. Figure 7(a) shows the extinction spectra of U-shaped nanostructures with $H = 50$ nm, 70 nm, and 100 nm, respectively. For the U-shaped nanostructure with $H = 50$ nm there are two plasmon

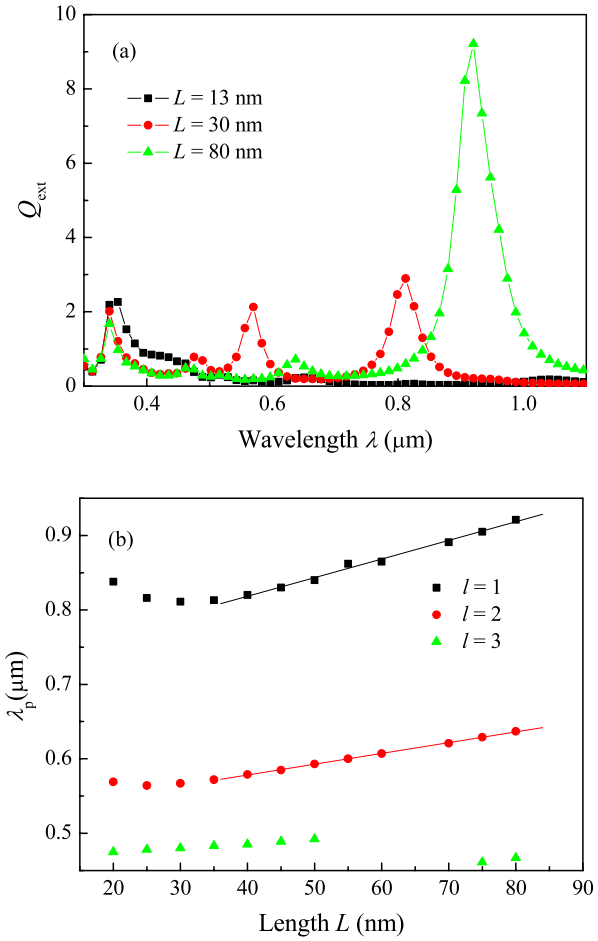


Figure 6. (a) Extinction spectra of the U-shaped nanostructures with $L = 13$ nm, 30 nm, and 80 nm at $R = 5$ nm, $H = 80$ nm, and $r = 5$ nm, respectively. (b) Plasmon peak wavelengths as a function of length L.

modes ($l = 1$ and 2). However, there are three plasmon modes for $H = 70$ nm and there are four plasmon modes for $H = 90$ nm. The plasmon peaks of the $l = 1$ and 2 modes red shift with the increase in H. The extinction strengths at TM modes of two vertical nanorods increase with H; this is probably due to the total number of dipoles increasing with H. Figure 7(b) illustrates the plasmon peak wavelengths as a function of H. When the height increases from $H = 40$ to 120 nm, the plasmon peaks of the $l = 1$ mode red shift from $\lambda_p = 0.593$ to 1.111 μm and the plasmon peaks of the $l = 2$ red shift from $\lambda_p = 0.457$ to 0.714 μm. When H increases to 70 nm, the plasmon peak of the $l = 3$ mode appears, and red shifts from $\lambda_p = 0.465$ to 0.572 μm at $H = 120$ nm. When the height H keeps increasing to 100 nm, the plasmon peak of the $l = 4$ mode appears, and also red shifts from $\lambda_p = 0.471$ to 0.502 μm when H increases to 120 nm. The solid curves in figure 7(b) are the linear fittings of the plasmon peaks. It is found that for all the modes, the plasmon peak wavelengths red shift linearly with increase of the height H and lower order mode plasmon peaks red shift faster than those of a higher order mode. For a single nanorod, with increasing height, higher order multiple modes also appear in the extinction spectra, and the

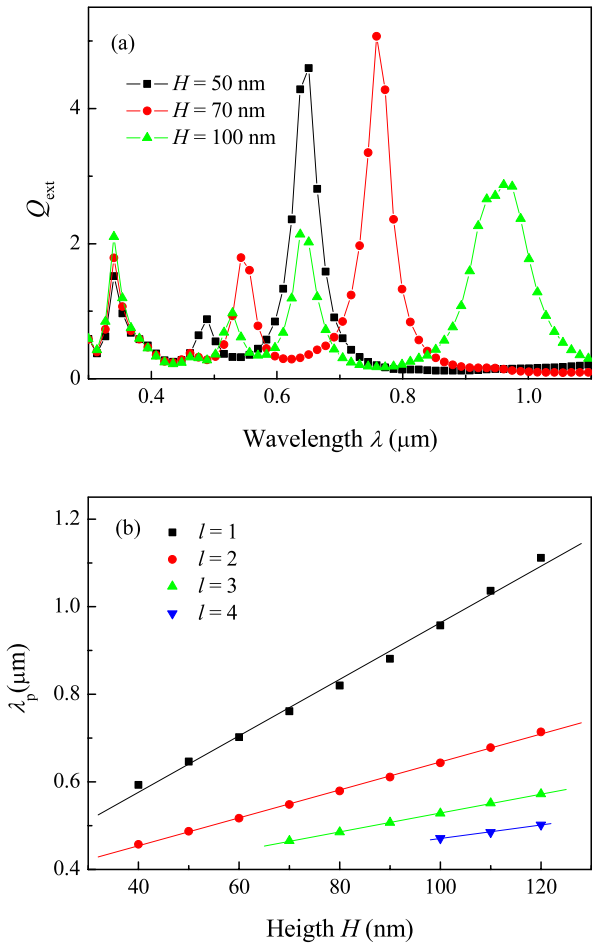


Figure 7. (a) Extinction spectra of the U-shaped nanostructures with $H = 50$ nm, 70 nm, and 100 nm at $R = 5$ nm, $L = 40$ nm, and $r = 5$ nm, respectively. (b) Plasmon peak wavelengths as a function of height H.

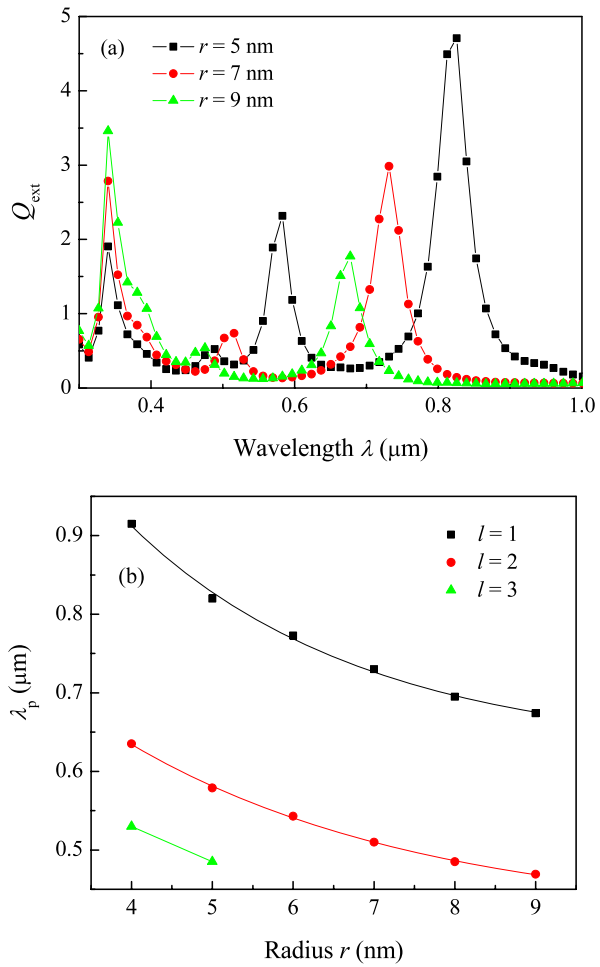


Figure 8. (a) Extinction spectra of U-shaped nanostructures with $r = 5$ nm, 7 nm, and 9 nm at $R = 5$ nm, $H = 80$ nm, and $L = 40$ nm, respectively. (b) Plasmon peak wavelengths as a function of radius r.

plasmon peaks red shift linearly with the nanorod height [11]. However, for a single nanorod with a radius of 5 nm, when the height increases to 70 nm there is no quadrupole mode. Therefore, it is easy for U-shaped nanostructures to excite multiple modes. Clearly, like the separation L, the height of the vertical nanorods H directly determines the plasmon wavelengths and the field enhancement strength. Increasing the height of vertical nanorods plays a major role in producing higher order oscillation plasmon modes.

The effect of the radius of vertical nanorods on the extinction spectra was investigated by increasing r from 4 to 9 nm. Figure 8(a) shows the extinction spectra of U-shaped nanostructures with $r = 5$ nm, 7 nm, and 9 nm, respectively. For the U-shaped nanostructure with $r = 5$ nm, there are three longitudinal modes, $l = 1, 2$, and 3. For the U-shaped nanostructures with $r = 7$ and 9 nm, there are only two longitudinal modes, $l = 1$ and 2. The plasmon peaks of the $l = 1$ and 2 modes blue shift with the increase in r. However, for the two TM modes, the plasmon peaks red shift with the increase in r. Figure 8(b) illustrates the plasmon peak wavelength as a function of r. The solid curves are the fittings using first order exponential decay. The increase in r for vertical nanorods decreases the aspect ratio of the nanorods, which could blue shift the plasmon peak and higher order plasmons would disappear. According to the Gans theory for individual particles, the decrease of the aspect ratio means a blue shift of the resonant spectra [12], which is consistent with the observed results.

The effect of the radius R of the bottom nanorod on the extinction spectra was investigated by increasing R from 4 to 10 nm. Figure 9(a) shows the extinction spectra of U-shaped nanostructures with $R = 5$ nm, 7 nm, and 9 nm, respectively. Three plasmon modes, $l = 1, 2$, and 3, are seen for all the spectra. For the $l = 1$ mode, the plasmon peak blue shift increases with the radius R, while the extinction strengths are similar. For the $l = 2$ mode, the plasmon peak also blue shift with increasing R, but the extinction strengths increase dramatically. For the $l = 3$ mode and two transverse modes, there are similar plasmon peaks. Figure 9(b) shows the plasmon peak wavelengths as a function of R. The solid curves are the fittings using first order exponential decay. The increase in the radius R will decrease the aspect ratio of the bottom cylinder, which would blue shift the dipole plasmon peak. The plasmon peak of the $l = 3$ mode is due to the quadrupole

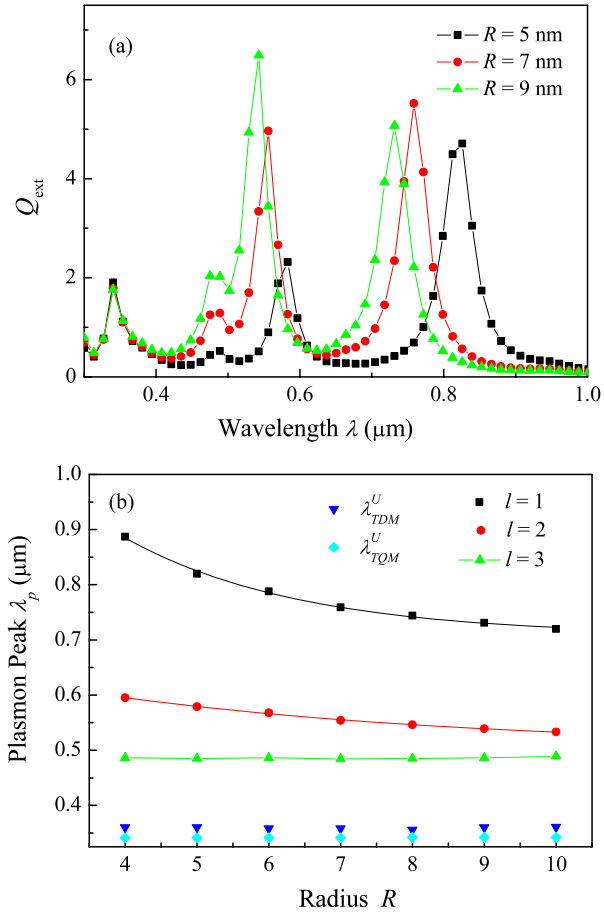


Figure 9. (a) Extinction spectra of the U-shaped nanostructures with $R = 5$ nm, 7 nm, and 9 nm at $H = 80$ nm, $L = 40$ nm, and $r = 5$ nm; respectively. (b) Plasmon peak wavelengths as a function of radius R.

oscillation in two vertical cylinders. When R is increased, the radius of two vertical nanorods and the separation between them remains unchanged. Therefore, the plasmon peaks of the $l = 3$ mode and two TM modes almost stay the same.

4. Conclusions

The optical properties of U-shaped nanostructures are calculated using the DDA method, and are compared to those of parallel-nanorod structures. The U-shaped nanostructure and the parallel-nanorod structure have the same symmetry in the horizontal direction, but the U-shaped nanostructure has a greater surface area and more corners and recesses, and at plasmon resonance wavelengths it has more hot spots. The electrons in the parallel-nanorod structure can only oscillate within the individual nanorods, and only when these two rods are close enough could the coupling affect the plasmon resonance frequency. For the U-shaped nanostructure, the bottom rod builds a path to connect the two vertical nanorods, so that electrons of the three sections are coupled together and LM plasmon oscillation along the vertical nanorods can be excited by longitudinal E field excitation. For the parallel-nanorod structure, only TM modes plasmon in the UV region can be excited, while for the U-shaped nanostructure, not only can TM modes be excited but LM modes and multiple modes can also be excited. The E field enhancements at these resonant peaks are much larger than those of the parallel-nanorod structure. The large enhancements distribute not only around two vertical nanorods but also on the bottom of the U-shaped nanostructure. Therefore, for sensing and analytical purposes, the U-shaped nanostructure has more hot surface areas to capture and detect a small number of molecules. This in part shows the importance of the underlayer in the SERS nanorod substrate in [6]. It is also found that the multiple modes can be easily excited in U-shaped nanostructures with a shorter vertical nanorod height compared to a single nanorod. In addition, the LM plasmon wavelength strongly depends on L and H, and weakly depends on r and R, even though the direction of E field excitation is perpendicular to the vertical nanorods. These properties could help us engineer nanostructures in order to tune their plasmonic properties.

Acknowledgments

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