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A visible-near infrared tunable waveguide based on plasmonic gold nanoshell*

Zhang Hai-Xi(张海汐), Gu Ying(古 英)†, and Gong Qi-Huang(龚旗煌)‡

State Key Laboratory for Mesoscopic Physics, Department of Physics, Peking University, Beijing 100871, *China*

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A tunable plasmonic waveguide via gold nanoshells immerged in a silica base is proposed and simulated by using the finite difference time-domain (FDTD) method. For waveguides based on near-field coupling, transmission frequencies can be tuned in a wide region from 660 to 900 nm in wavelength by varying shell thicknesses. After exploring the steady distributions of electric fields in these waveguides, we find that their decay lengths are about 5.948–12.83 dB/1000 nm, which is superior to the decay length (8.947 dB/1000 nm) of a gold nanosphere plasmonic waveguide. These excellent tunability and transmittability are mainly due to the unique hollow structure. These gold nanoshell waveguides should be fabricated in laboratory.

Keywords: waveguide, surface plasmons, energy transfer
PACC: 4280L, 7320M

1. Introduction

Ordered arrays of closely spaced metallic nanoparticles are employed to transport optical signals via near-field coupling.[1,2] Such structures, as plasmonic waveguides, allow the transport of electromagnetic energy at optical frequencies below the diffraction limit. These structures also may be used as the building blocks for the creation of nanoscale optical devices, optical circuits, and other near-field applications. Quinten *et al*[3] analytically showed that the visible light could be transferred through a linear chain of silver nanoparticles. A direct experimental demonstration of this plasmonic waveguide has been pioneered by Maier *et al.*[4] Nanosphere waveguides have been widely studied qualitatively, for example, by treating the nanospheres as a coupled dipole chain.[5,6] Other plasmonic waveguides, formed by various shaped nanoparticles, have been widely investigated as well.[7,8]

When the metallic nanoparticle waveguide is illuminated on one tip and is surveyed on another tip, there exists a transmission (resonance) frequency defined by its best transmittability. This transmission frequency is different from the surface plasmon resonance frequency of a single nanoparticle. The frequency depends on the number of the nanoparticles, the spacing, and the specific structure in the waveguide. Too little a spacing leads to an insufficient near-field coupling between these particles and a more non-radiative loss as well. Nanosphere waveguide suffers from this limitation. With the radii of the nanospheres each being 25 nm, their spacings each being 25 nm, and their immergence in a silica base, the transmission wavelength of a nanosphere waveguide is almost untunable at ∼555 nm. In this work, we employ the gold nanoshells as a block to design the tunable plasmonic waveguides. Many studies have substantiated that the gold nanoshell is a kind of versatile nanophotonic particle whose plasmon resonance can be tuned from a visible region to an infrared region by adjusting the core/shell ratio.[9−11] Oldenburg *et al*[9] fabricated gold nanoshells by way of molecular self-assembly and colloidal growth chemistry. The gold nanoshell (< 100 nm) that is to be designed here has a silica core coated with a thin gold shell. It can be fabricated by layering a gold layer onto a silica nanoparticle.[12,13] Recently, the smaller multi-layer gold nanoshells with a silica core have also been fabricated.[14]

The nanoshell waveguide in this work is composed of chain-like nanoshells each with an outer radius of 25 nm and a spacing of 25 nm. By using an oscillat-

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†E-mail: ygu@pku.edu.cn
‡E-mail: qhgong@pku.edu.cn

ing point-dipole as the zeroth excited nanoshell, and performing the Fourier transform to the time evolution of the electrical field from the FDTD simulation, we obtain the transmission frequency of the nanoshell waveguide. By changing the shell thickness, the transmission frequency is able to be tuned from a visible region to a near-infrared region, corresponding to the 660–900 nm wavelength range. For the 5 nm-thick nanoshell waveguide, the energy decay length of the steady distribution of the near-field is about 5.948 dB/1000 nm due to the hollow structure, which is superior to that of the nanosphere waveguide.[15] Compared with the nanosphere waveguide, the 5 nm-thick nanoshell waveguide shows an effective tunability and an excellent transmittability. These plasmonic gold nanoshell waveguides should have potential applications in nano-optics.

In the next section, we describe how we select the parameters of dielectric functions and how we set up the FDTD simulation at the optical frequencies. In Section 3, the simulation results on the gold nanoshell plasmonic waveguides are shown and discussed in detail. Concluding remarks appear in Section 4.

2. Modification of the dielectric function and the FDTD method

As an effective numerical algorithm for the exact solution to Maxwell's equations, the finite-difference time-domain (FDTD) method[16,17] and its ramification are a highly useful tool in studying the electromagnetic responses for a heterogeneous material of arbitrary geometry.[18−21] Here we utilize the commercially available XFDTD 6.3.8.3 software (Remcom, Inc.). First, the experimental data of the bulk gold is modified to describe the size-dependent dielectric function of the metallic nanoshell at optical frequencies. To ensure the validity of our simulations, we set the parameters such as mesh, stimulation dimension and convergence degree elaborately. Then, according to these selected parameters, we obtain the surface plasmon resonance frequency for the specific nanostructure through the use of a pulse. The results for the single nanoshells affirmed the accuracy of our simulations. This approach should be applicable to finding out the transmission frequencies for the nanoshell waveguides.

The shell thickness here is only several nanometres, much less than the gold electron mean-free path (∼42 nm). Dielectric function of a metallic nanoparticle will become size-dependent when the particle is smaller than the electron mean free path of the bulk metal. The width of the absorption peak can be described as a modification of the bulk collisional frequency as shown below:[22]

$$\Gamma = \gamma_{\text{bulk}} + A \times V_{\text{F}}/a, \tag{1}$$

where $\gamma_{\text{bulk}} = V_{\text{F}}/l_0$ is the bulk collisional frequency; V_{F} is the Fermi speed; the gold electron mean free path is $l_0 = 42\,\text{nm}$ at room temperature; a is the reduced electron mean free path due to the surface; for the gold nanoshell, a is assumed to be equal to the shell thickness; A is the parameter which is dependent on the details of the surface scattering process.[23] In the context of the simple Drude theory and isotropic scattering, we chose $A = 1$. As a result, the size-dependent dielectric function of the gold nanoshells, $\varepsilon(a, \omega)$, becomes

$$\varepsilon(a,\omega) = \varepsilon(\omega)_{\text{exp}} + \frac{\omega_{\text{p}}^2}{\omega^2 + \text{i}\omega\gamma_{\text{bulk}}} - \frac{\omega_{\text{p}}^2}{\omega^2 + \text{i}\omega\Gamma}, \tag{2}$$

where $\varepsilon(\omega)_{\text{exp}}$ is the experimental dielectric function,[24] and $\omega_{\text{p}} = 6.274 \times 10^{15}\,\text{rad/s}$ is the bulk plasmon frequency of gold. For the nanoshells in the near-infrared and the visible regions, the dielectric function obtains an increase of the imaginary part, less than 50%; and a small increase in the real part from the modification. The half-width of the dipolar Mie resonance peak of the single gold nanoshell is affected in the form of broadening and little redshift.[25] In the XFDTD software, the dielectric function $\varepsilon(\omega)$ is described as

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_{\text{s}} - \varepsilon_\infty}{1 + \text{i}\omega\tau} + \frac{\sigma}{\text{i}\omega\varepsilon_0}, \tag{3}$$

where ε_{s} is the static permittivity at zero frequency, ε_∞ is the infinite frequency permittivity, τ is the relaxation time, and σ is the conductivity term.[16] In a 600–1200 nm wavelength region, the modified data from expression (2) can be well fitted to expression (3). The parameters, obtained from the fitting to various gold nanoshells, appear in Table 1. For the following modulated Gaussian pulse sources, these parameters can be used directly.

Table 1. Parameters of gold nanoshells of different thicknesses.

thickness/nm (wavelength/nm)	3 (600–1200)	5 (600–1200)	7 (600–1000)	bulk gold (650–1000)
σ	8.03185×10^{6}	9.83187×10^{6}	1.40456×10^{7}	1.48311×10^{7}
τ	5.06739×10^{-15}	6.15573×10^{-15}	8.76852×10^{-15}	9.30635×10^{-15}
$\varepsilon_{\rm s}$	-4.58501×10^{3}	-6.82362×10^{3}	-1.38881×10^{4}	-1.55794×10^{4}
ε_{∞}	8.27306	8.40669	8.48622	8.24384

For a specific nanostructure, we find out the surface plasmon resonance frequency in two steps. First, the object is illuminated with a modulated Gaussian pulse which contains many frequencies; then, we perform the Fourier transform to the FDTD result, which traces the time evolution of the field for a certain point in the nanostructure, and take the weight of each frequency in the pulse into account. The final plots reveal the resonance frequency spectra for a certain point in the nanostructure. To verify the accuracy of this approach, we simulated the resonance frequency of a single gold nanoshell. The simulation volume consisted of a rectangular box of dimensions 120 nm×120 nm×120 nm. The 50 nm outer-diameter gold nanoshell, with a 40 nm diameter core (with a dielectric constant of 5.44) was placed at the centre of the volume. The particle was surrounded by a medium with a dielectric constant of 1.78. The nanoshell was illuminated by a plane-wave propagating in the z-direction with the electric field polarized in the x-direction . The waveform of the plane wave was chosen to be of the modulated Gaussian pulse with a width of 0.8320 fs, and its frequency was set at 4.28275×10^{14} Hz. The illumination covered the visible region and the near-infrared region. Figure 1(a) shows the time evolution of the x-direction field at the centre of the nanoshell. The Fourier transform plot displays a single dipole peak centred at 3.97603×10^{14} Hz ($\approx$ 754 nm) in Fig.1(b), which is in line with the result, about 750 nm determined by the Mie theory.[26]

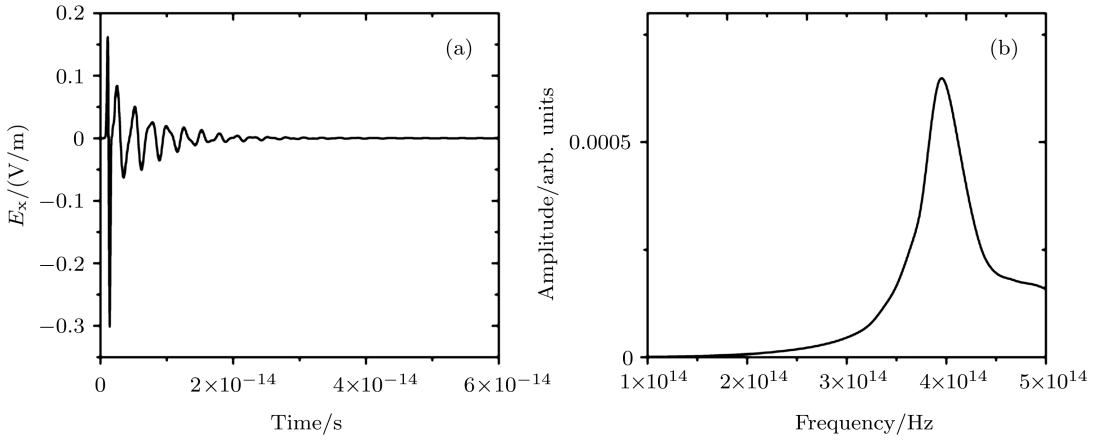


Fig.1. (a) Time evolution of the electric field in the x-direction at the centre of single nanoshell and (b) Fourier transform of $E_{\rm x}(t)$ with a dipole surface plasmon peak at 3.97603×10^{14} Hz(∼754 nm).

Mesh size in all of our numerical simulations was 1 nm, which provided both a good spatial resolution and a low level of numerical spread error. We also checked the automatic convergence function (–35 dB), the Perfectly Matched Layers (8 layers), and the time step of the XFDTD to make sure that our simulations gave a high accuracy and numerical stability in the optical frequencies. To investigate the local error that was introduced by the interaction between the nanoshell and the PML boundary, we tested the smaller computational domains ($90\times90\times90$ nm) with the same mesh. In this case, the plasmon resonance frequency was almost unchanged. For an array of seven 50 nm gold nanospheres with a spacing of 75 nm in vacuum, we also checked the resonance peak at 2.06 eV (about 602 nm).[27] The approach can be effectively used for the nanoshell waveguides if the simulation volume is correspondingly enlarged.

3. Simulation results and discussion

In our simulations, we have employed 15 or 25 gold nanoshells each with an outer radius of 25 nm and a silica core to design the chain-like plasmonic waveguides. The geometry of the nanoshell waveguide is depicted in Fig.2, where a 15–5 nm-thick nanoshell waveguide is composed of 15 nanoshells each with a thickness of 5 nm in shell. Unless otherwise stated, the centre-to-centre spacing is always 75 nm and the surrounding medium is selected to be silica with a refractive index of 1.5067. To demonstrate the optical signal propagation in a nanoshell waveguide, we used a unit intensity oscillating point-dipole, which was placed at a distance of 75 nm from the centre of the first nanoshell, to represent an imaginary excited zeroth nanoshell. The dipole, aligned parallel or perpendicular to the chain, corresponds to either the longitudinal mode (LM) excitation or the transverse mode (TM) excitation. As described in Section 2, to find out the transmission frequency, which is defined by the strongest electric field appearing at the last nanoshell, we used a modulated Gaussian pulse excitation, which covers the visual region and the near-infrared region, as a feed source. Taking the weight of each frequency in the modulated Gaussian pulse into account, the Fourier transform plots reveal the transmission spectra for the waveguides.

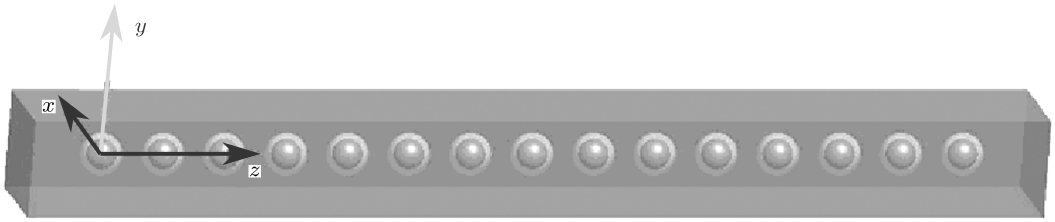


Fig.2. The geometry of a 15–5 nm-thick nanoshell waveguide, with the outer radius of each nanoshell being 25 nm, the centre-to-centre spacing being always 75 nm, and the core and the surrounding medium selected to be silica with a refractive index of 1.5067.

The final LM and TM transmission spectra for the 15–3 nm-thick, 15–5 nm-thick, and 15–7 nm-thick gold nanoshell waveguide are respectively shown in Figs.3(a) and 3(b). With the decrease in shell thickness, the transmission peaks become broadened and red-shifted, which can be seen in the transmission spectra. This broadening mainly comes from the inherent hollow structure and the many electron collisions in the shell as compared with in a nanosphere.[10,22,25] We have observed that the optical signals can be transported in certain frequency regions due to the existence of line-width in the transmission spectra. Typically, for a 15–3 nm-thick nanoshell waveguide, the transmission band covers a wide range of 600–900 nm in wavelength in its T mode. Figure 3(c) shows that the tuned transmission frequencies with the shell thickness varying in the 650–900 nm wavelength range. The nanoshell waveguides proved

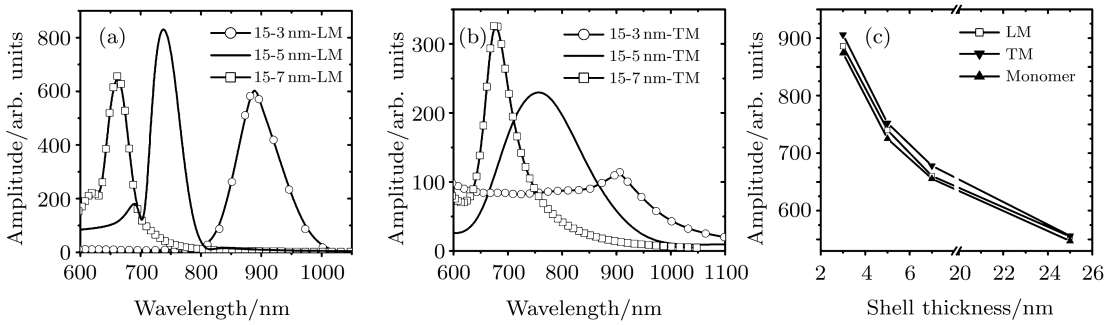


Fig.3. Simulated optical transmission spectra of a nanoshell waveguide with the amplitude of the total field at the centre of the last nanoshell versus the wavelength, for (a) L mode excitation and (b) T mode excitation. Panel (c) is for the red shift plots of the transmission frequencies for the 15-nanoshell waveguides and 15-nanosphere waveguides, where the upward triangle denotes the single nanoparticle of corresponding shell thickness.

to be superior to the nanosphere waveguides, which contain only a fixed transmission frequency (about 555 nm in wavelength). In comparison with the single nanoshells, the nanoshell waveguide is shown to have an approximate 10–20 nm red shift of the resonance position. For nanosphere waveguides, an analytical approximate model as well as FDTD simulations (coarse scanning in frequency region) reckoned the transmission frequencies just as the monomer resonance frequencies.[15,28] Taking the cluster effect contribution into account, this 10–20 nm redshift is reasonable and accordant with the result which has been demonstrated in nanosphere waveguide.[28,29] In our simulations, the transmission wavelengths in T mode are always larger than the transmission wavelengths in L mode in Fig.3(c). Further simulations indicate that, with the same shell thicknesses, a 25-nanoshell waveguide almost possesses the same transmission frequency as a 15-nanoshell waveguide. The above two results are reasonable and in line with the results obtained from gold pad waveguides as well.[8] In conclusion, by varying the nanoshell thickness, the transmission frequency of the waveguide is effectively tuned from a visible region to a near-infrared region.

To account for the energy transmittability of the plasmonic waveguides, we explored the optical near field of the nanoshells as shown for T mode of 15–5 nm-thick nanoshell waveguide in Fig.4(a) and for L mode of 15–5 nm-thick nanoshell waveguide in Fig.4(b). At the transmission frequencies, the steady amplitude distributions of the total field at the centre of each shell are shown in Fig.5. If the input tip of the waveguide is illuminated in T mode, the electromagnetic energy ceaselessly loses when it is transported along the waveguide due to the radiative scattering and nonradiative energy dissipation. When the energy is transported into the terminal section of the waveguide, the near-field coupling is not so strong as that in the forepart, which partly gives place to the effect of a far field superposition.[8] A steady transport emerges in its terminal section, in which the plot becomes an approximately straight line as shown in Figs.5(a), 5(c), 5(e) and 5(f).

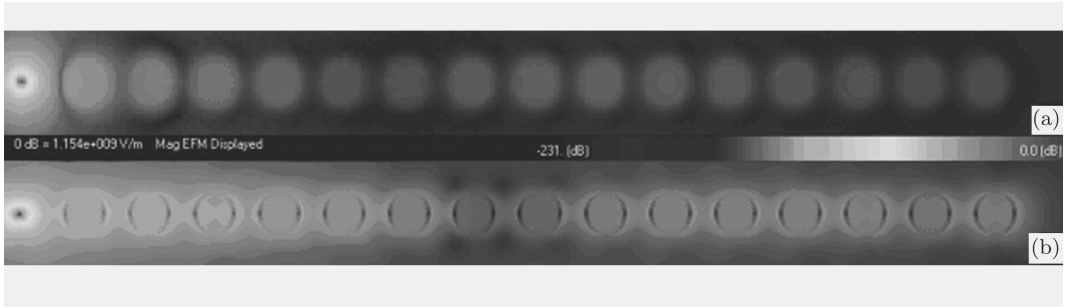


Fig.4. Distributions of steady amplitudes of the total electric field at the median section for 15–5 nm-thick nanoshell waveguides in their TM (a) and LM (b).

To estimate the energy transmissibility of T mode, we fit straight lines to these curve tails. Though it is not very strict, this choice gives an excellent fit and it allows us to compare the decay lengths with the results in the literature. The extracted energy decay lengths for the 25–3 nm-thick, and the 25–7 nm-thick nanoshell waveguides are 12.83 and 6.573 dB/1000 nm. Especially, the energy decay length for the transverse excitation of 25–5 nm-thick nanoshell waveguide is 5.948 dB/1000 nm, which is equal to about 730 nm in terms of the $1/e$ decay length. This energy decay is lower than 8.947/1000 nm of 25-nanosphere waveguide shown in Fig.5(f) and is obviously lower than those FDTD results obtained from a pulse-transporting simulation in the gold nanosphere waveguide (3 dB/140 nm for L mode; 3 dB/43 nm for T mode).[15]

For the LM, the longitudinal strong near-field coupling acts in the whole waveguide when the input tip is illuminated. In the forepart of the waveguide, the rapid exponential decay is shown. The endpoint effect for the last few nanoshells is seen clearly in our calculation results.[5] Because for the LM, the transmission mainly benefits from the longitudinal strong near-field coupling, this endpoint effect mainly comes from the longitudinal reflection of the last nanoparticle. Without the endpoint effect, a 15-nanoshell waveguide shares an overlapping decay curve with a 25-nanoshell waveguide with the same shell thicknesses. The L mode decay is undulating in its midst, like a stationary wave, which is subjected to the multiple superposition and scattering of the strong near-

field. Therefore its transmittability can be measured by surveying the total field amplitude at the output tip of the waveguide as shown in Figs.5(b), 5(d), 5(e) and 5(f). These plots show that the tunable nanoshell waveguide is superior to the nanosphere waveguide in the sense of the energy transmittability. Especially, surveying the total field amplitude at the centre of the last nanoparticle, the 15–5 nm-thick nanoshell waveguide (LM) is superior to the 15–5 nm-thick nanosphere waveguide (LM) by three folds.

The above mentioned improvement on energy transmittability mainly arises from their unique hollow structure of the nanoshell waveguides. The intrinsic tunability due to the hollow structure locates the transmission frequency in a certain optical range where the dielectric losses are weaker. At the transmission frequency of the nanosphere waveguide (about 555 nm in wavelength), the imaginary part of the dielectric constant for bulk gold is about 2.0. While, for the nanoshell waveguides with certain shell thicknesses ($\geq$5 nm), the modified imaginary parts of the dielectric constants at their transmission frequencies (660–900 nm in wavelength) are always less than 2.0. Furthermore, the hollow structure employs less metallic material, hence it reduces the nonradiative loss too.

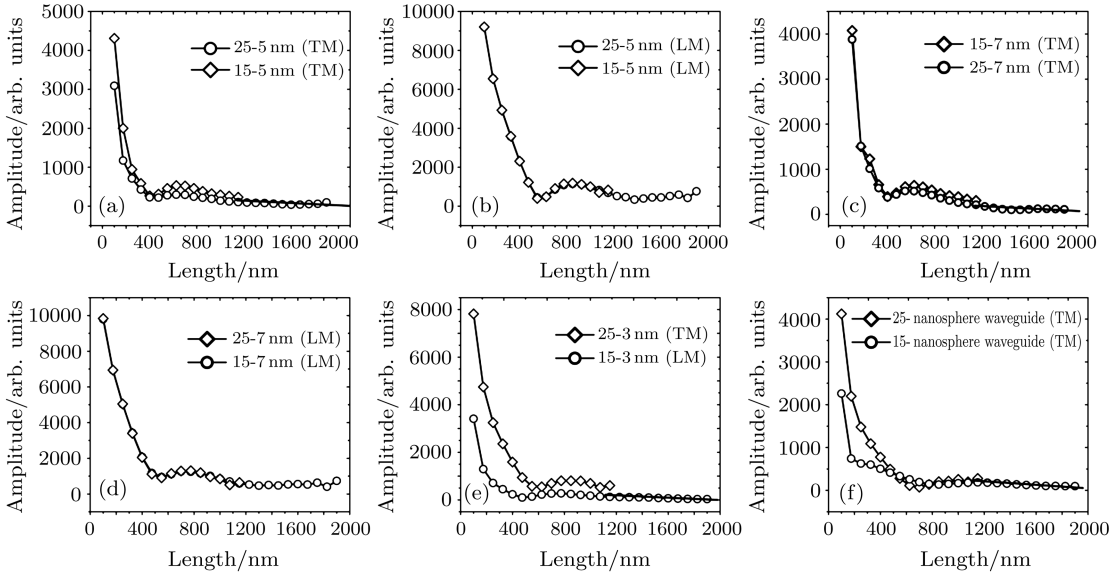


Fig.5. Distributions of steady amplitudes of the total electric field at the centre of each nanoshell versus distance in their transmission frequencies. Panels (a) and (b) are for the results for 15–5 nm-thick nanoshell waveguide and 25–5 nm-thick nanoshell waveguide (TM, LM). Panels (c) and (d) are for the results for 15–7 nm-thick nanoshell waveguide and 25–7 nm-thick nanoshell waveguide (TM, LM). Panels (e) and (f) are for the results for 25–3 nm-thick and 15–3 nm-thick nanoshell waveguides and 25- and 15- nanosphere waveguides.

4. Conclusions

We have presented a tunable plasmonic waveguide, based on the near-field coupling, and simulated it by using the FDTD method. In order to ensure the validity of the FDTD method in simulation, we carefully set and select various parameters. The transmission frequencies are tuned in the visible region and the near-infrared region (650–900 nm in wavelength) by utilizing different core/shell ratios. The transverse mode of the nanoshell waveguide is found to have a low level of energy decay as compared with the result of the gold nanosphere waveguide. For the longitudinal mode, a stronger near-field is observed in the output tip than in the nanosphere waveguide. We attribute the improvement on tunability and transmittability to the unique hollow structure of the nanoshell. Finally, we deem that this structure should be fabricated in laboratory and it might be a good candidate for plasmonic devices.

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