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Optical Tunability of Silver-Dielectric-Silver Multi-Layered Cylindrical Nanotubes Using Quasi-Static Approximation *

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Local surface plasmon resonances (LSPRs) of silver-dielectric-silver multi-layered (SDS-ML) nanotubes are studied by theoretical calculations. Based on quasi-static approximation, the absorption cross section of SDS-ML nanotubes is plotted as a function of wavelength. The results show that SDS-ML nanotubes exhibit strong coupling between the cylindrical silver and nanotubes. The absorption spectra of LSPRs are strongly influenced by changing the radius of the inner core and outer nanotube shell. The longer wavelength is red-shifted by increasing the radius of the inner core and outer shell, while the short wavelength shows the opposite properties. These phenomena are explained by the plasmon hybridization theory. In addition, for clarity, the distributions of electric field intensity at their plasmon resonance wavelengths are also studied.

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Optical properties of noble metal nano-structures have received great attention due to their plasmonic properties, especially the optical absorption effects induced by local surface plasmon resonances (LSPRs) have attracted much attention in recent years.[1,2] Due to their geometry-dependent properties, nanostructures with specific shapes are designed for some applications such as surface enhancement Raman scattering (SERS) and waveguides. The tunable properties of LSPR peak positions can be tuned by varying the parameters such as the surrounding media, the particle shapes and different components.[3] The optical properties of dielectric-metal core-shell nanoshell structures are well explained by plasmon hybridization theory,[4−6] which can view optical responses of complex nanostructures as the hybridization of elementary plasmons supported by nanostructures of elementary geometries, providing a simple and intuitive description of their plasmon excitations.

In recent years, there have been many studies investigating the interactions for nano-spheres with theory and experiments. Wu *et al.* have studied the optimization of the bimetallic Ag-Ag alloy nanoshell biomedical applications in vivo.[7] Sharma *et al.* have prepared Au-Ag alloy nanoparticles in experiments.[8] Au-Ag nanoshell has also been applied in the antibody detection in vitro, drug delivery and medical applications.[9] Xia *et al.* have synthesized a three-layered gold-silica-gold nanoshell,[10] which could generate a strong surface plasmon resonance. Zhu *et al.* have studied the optical properties of multi-layered nano-spheres, and the results show that the optical properties could be well tunable by adjusting the particle sizes and its components.[11,12] In addition, plasmon hybridization in metallic nanotubes has also been studied. Moradi has given a theoretical formula about the plasmon hybridization between capillary plasmon and wire with neglecting the dielectric effects.[13] Daneshfar *et al.* have studied the light scattering by two concentric gold cylindrical hollow nanoshell, the results show that the intensity and position of scattering peak depend on the parameters of concentric cylindrical nanoshell.[14]

However, optical properties of silver-dielectric-silver multi-layered nanotubes have rarely been reported. In this work, we investigate the influence of inner core radius, the radius of middle dielectric layer and outer shell to SDS-ML nanotubes. The LSPR properties of SDS-ML nanotubes are studied in detail based on the quasi-static approximation. The results are well explained by the plasmon hybridization theory.

Firstly, let us briefly introduce the schematic structure and theoretical method. A single silver cylinder is inserted into a silver nanotube to fabricate a composite silver nanotube structure (SDS nanotubes), which has four regions, and the theoretical schematic nanotube structure is given in Fig. 1(a). The first region is the single cylindrical silver core with radius r_1 and dielectric constant ε_1, the second region is the dielectric layer with thickness $r_2 - r_1$ and dielectric constant ε_2, the third region is the silver nanotube shell with thickness $r_3 - r_2$ and dielectric constant ε_3, and the final region is the surrounding medium with dielectric constant ε_4. The shell thickness of SDS-ML nanoshell is much smaller than the incident wavelength, and then the quasi-static approximation[15] can be used in calculation. In this case, the electrostatic solution could be obtained by the solution of Laplace's equation for the potential

$$\nabla^2\phi = 0. \tag{1}$$

The general solution for the potential $\phi_i(r,\theta)$ of Eq. 1 in each region could be expressed as[16]

$$\phi_i(r,\theta) = (A_i r + B_i/r)\cos\theta, \tag{2}$$

where ϕ_i is the electric potential in region i, r and θ are the radial distance and the polar angle, respec-

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tively. The coefficients A_i and B_i could be solved under the electric field boundary conditions.[16] Thus the electrical field magnitude $\boldsymbol{E}_i$ in each region i could be obtained with a gradient of the potential relation $\boldsymbol{E}_i = -\nabla\phi_i(r,\theta)$. SDS-ML nanotubes are much smaller than wavelength, thus the induced field in the region of the outer side of the shell is the same as a dipole with an effective dipole moment $\boldsymbol{P}$ by the relation $\boldsymbol{P} = \varepsilon_4\alpha\boldsymbol{E}_4$, where α is the polarizability. Then the absorption cross section could be obtained from the polarizability with the optical scattering theory $C_{\rm abs} = k{\rm Im}(\alpha)$,[17] where $k = \frac{2\pi}{\lambda}$ is the wave number, and Im denotes the imaginary part.

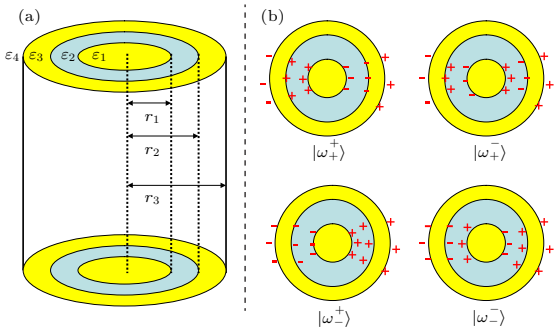

Fig. 1. (a) The schematic structure of SDS-ML nanotubes used for this study, where r and ε are the radius and dielectric constant, respectively. (b) Distributions of induced charges of the four SDS-ML nanotube plasmon modes.

In this study, an SDS-ML nanotube could be considered as a single cylindrical silver inserted into a dielectric-silver core-shell nanotube (seen in Fig. 1(a)). According to the plasmon hybridization theory,[5] core-shell nanotube can be considered as an interaction between the plasmon responses of a single cylindrical silver with its energy mode $|\omega_{\rm s}\rangle$ and a cavity with $|\omega_{\rm c}\rangle$. Then two new plasmon modes $|\omega_+\rangle$ and $|\omega_-\rangle$ could be obtained in the core-shell nanotube. When a single cylindrical silver core is inserted into the dielectric-silver core-shell nanotube, four new plasmon resonance modes $|\omega_+^+\rangle$, $|\omega_+^-\rangle$, $|\omega_-^+\rangle$ and $|\omega_-^-\rangle$[5,6] could be obtained in SDS-ML nanotubes, which could be considered as the interaction between a single cylindrical silver core and the nanotube ($|\omega_{\rm s}\rangle$ and $|\omega_+\rangle$, $|\omega_{\rm s}\rangle$ and $|\omega_-\rangle$). The distributions of induced charges for four plasmon modes are given in Fig. 1(b). The first plasmon mode $|\omega_+^+\rangle$ is an antisymmetric coupling between the inner single cylindrical silver core $|\omega_{\rm s}\rangle$ and outer antibonding nanotube plasmon mode $|\omega_+\rangle$. In this plasmon mode, the distributions of induced charges on the surface of the single cylindrical silver core are oppositely aligned with plasmon of the nanotube, which reduce the dipole moment, thus the absorption peak is too weak to be observed in experiments. The second plasmon mode $|\omega_+^-\rangle$ is a symmetric coupling between $|\omega_{\rm s}\rangle$ and $|\omega_+\rangle$, where the distributions of induced charges on the surface of single cylindrical silver core are the same as that of the nanotube. The third plasmon mode $|\omega_-^+\rangle$ is a symmetric coupling between $|\omega_{\rm s}\rangle$ and $|\omega_-\rangle$. In this mode, the charge distribution on the single nanosphere is the same as that of the nanotube. The fourth plasmon mode $|\omega_-^-\rangle$ is an anti-symmetric coupling between $|\omega_{\rm s}\rangle$ and $|\omega_-\rangle$. In this mode, the charge distribution on the single sphere oppositely is aligned with the plasmon of the nanotube. The last two plasmon modes $|\omega_-^+\rangle$ and $|\omega_-^-\rangle$ are induced by the bonding nanoshell plasmon, which have larger dipole moments, thus the absorption peaks could be easily observed in experiments. The influences of $|\omega_-^+\rangle$ and $|\omega_-^-\rangle$ modes are discussed in detail.

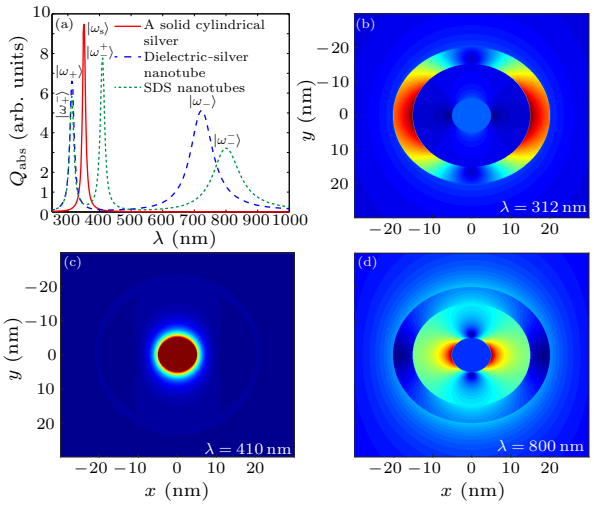

Fig. 2. (a) Absorption spectra of the SDS-ML nanotubes calculated for a single cylindrical silver, the dielectric-silver nanotube and the SDS-ML nanotubes, and (b)–(d) the local field intensity distribution of the SDS-ML nanotubes at LSPR wavelengths $\lambda = 312$ nm, $\lambda = 410$ nm and $\lambda = 800$ nm.

Firstly, to fully understand the plasmon modes of SDS-ML nanotubes, the absorption spectra of a single cylindrical silver, the dielectric-silver nanotube and the SDS-ML nanotubes with the surrounding medium $\varepsilon_4 = 1.0$ are given in Fig. 2(a), where the radii r_1, r_2 and r_3 are 10 nm, 15 nm and 20 nm. Figure 2(a) shows that the single cylindrical silver has only one plasmon resonance peak at about $\lambda = 352$ nm, the dielectric-silver nanotube has two peaks at about $\lambda = 314$ nm and $\lambda = 722$ nm, and the SDS-ML nanotube exhibits three peaks at about $\lambda = 312$ nm, $\lambda = 410$ nm and $\lambda = 800$ nm. To make the plasmon modes of SDS-ML nanotubes easily understood, the distributions of local electric field intensity at each LSPR wavelength of SDS-ML nanotubes are calculated in Figs. 2(b)–2(d). As shown in Fig. 2(b), at the higher-energy $\lambda = 312$ nm mode, the local electric field intensity is stronger in the nanotube silver shell than those in the middle dielectric layer and the inner sliver core. Because the topology of electric filed distribution inside and around the nanotube could be understood by terms of the polarization charges. We consider that $\lambda = 312$ nm is from the $|\omega_+^-\rangle$ mode shown in Fig. 1(b), which is a symmetric coupling between $|\omega_{\rm s}\rangle$ and $|\omega_+\rangle$. The induced charges on the inner and outer surfaces of nano-shell are opposite in this mode, and then the local electric field intensity is concentrated in the outer-shell of nanotubes.[6] Figure 2(c) shows that the local electric field intensity is concentrated outside of the silver core whereas the middle dielectric layer and the outer silver nanotube are very weak at

the $\lambda = 410\,\text{nm}$ mode. Here $\lambda = 410\,\text{nm}$ is from the $|\omega_-^+\rangle$ mode, which is a symmetric coupling between $|\omega_s\rangle$ and $|\omega_-\rangle$. The same kind of induced charges used on the inner surface of the outer shell and the inner surface of the silver core, and then the outer surfaces of the nanoshell repel each other, which results in a very weak interaction between the inner and outer surfaces of the nanoshell. The distribution of local electric field intensity at $\lambda = 800\,\text{nm}$ is shown in Fig. 2(d). Both the local electric field intensities of the single cylindrical silver and the outer nanotube shell are very weak, while the middle dielectric layer is stronger. In this plasmon mode, different kinds of induced charges are used on the inner core and the outer-shell surface. Here $\lambda = 800\,\text{nm}$ is considered from the $|\omega_-^-\rangle$ mode, which is an anti-symmetric coupling between $|\omega_s\rangle$ and $|\omega_-\rangle$.

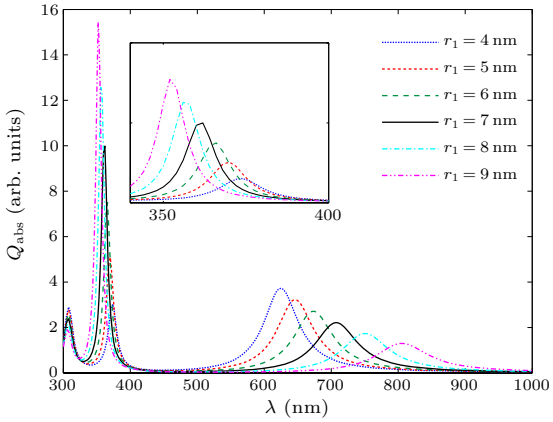

Fig. 3. The absorption spectra of the SDS-ML nanotubes versus wavelengths with the inner radius from $r_1 = 4\,\text{nm}$ to $r_1 = 9\,\text{nm}$.

Secondly, Fig. 3 shows the absorption spectra of the SDS-ML nanotubes suspended in medium $\varepsilon_4 = 1.0$ with variation of inner silver core radius r_1 from $r_1 = 4\,\text{nm}$ to $r_1 = 9\,\text{nm}$, where the radii of r_2 and r_3 are fixed at 15 nm and 20 nm, respectively. Figure 3(a) shows that three LSPR peaks appear in the absorption spectra. The longest wavelength of the $|\omega_-^-\rangle$ mode shows a red shift from $\lambda = 624\,\text{nm}$ with $r_1 = 4.0\,\text{nm}$ to $\lambda = 808\,\text{nm}$ with $r_1 = 9.0\,\text{nm}$ and its intensity reduces. The $|\omega_-^+\rangle$ mode has a slight blue shift from $\lambda = 374\,\text{nm}$ with $r_1 = 4.0\,\text{nm}$ to $\lambda = 352\,m$ with $r_1 = 9.0\,\text{nm}$ and its intensity enhances gradually, which is in good agreement with previous studies.[14] These phenomena could be explained by the plasmon hybridization theory. The attraction between the inner silver core and the outer silver nanotube is strengthened with increasing the inner silver core radius in the $|\omega_-^-\rangle$ mode due to the induced charges of single sphere oppositely aligned with that of the nanotube (seen Fig. 1(b)), and then the restoring force is strengthened. The plasmon energy of the nanotube ($|\omega_+\rangle$ and $|\omega_-\rangle$) could be considered to be constant when the radii of the middle dielectric layer (r_2) and outer nanotube shell (r_3) are fixed. In other words, the energy of the SDS-ML nanotubes depends on the inner core energy $|\omega_s\rangle$. An increase in the inner silver core radius will reduce the middle dielectric layer thickness, the reduced middle dielectric layer enhances the coupling between $|\omega_s\rangle$ and $|\omega_-\rangle$. The energy of $|\omega_-^-\rangle$ is reduced and $|\omega_-^+\rangle$ is enhanced. In other words, $|\omega_-^-\rangle$ shows a red shift and $|\omega_-^+\rangle$ is a blue shift with increasing the inner core radius.

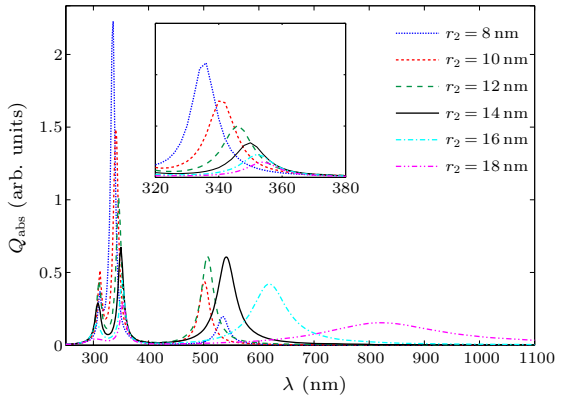

Fig. 4. The absorption spectra of the SDS-ML nanotubes versus wavelengths with the middle dielectric radius from $r_2 = 8\,\text{nm}$ to $r_2 = 18\,\text{nm}$.

Figure 4 shows the influences of middle dielectric layer thickness on absorption spectra of the SDS-ML nanotubes, where the radii of the inner core (r_1) and the outer silver nanotube shell (r_3) are fixed at 5 nm and 20 nm, respectively, while the middle dielectric layer radius r_2 is changed from $r_2 = 8\,\text{nm}$ to $r_2 = 18\,\text{nm}$. Figure 4 shows that the $|\omega_-^-\rangle$ mode exhibits a blue shift from $\lambda = 540\,\text{nm}$ with $r_2 = 8.0\,\text{nm}$ to $\lambda = 498\,\text{nm}$ with $r_2 = 10.0\,\text{nm}$ firstly and then a distinct red shift from $\lambda = 506\,\text{nm}$ with $r_2 = 12.0\,\text{nm}$ to $\lambda = 828\,\text{nm}$ with $r_2 = 18.0\,\text{nm}$ as the middle dielectric layer radius increases, which is very similar to that of nanosphere.[6,11,18] In addition, the intensity of the $|\omega_-^-\rangle$ mode increases firstly and then decreases, and the full widths at half maximum (FWHMs) are always increased. The $|\omega_-^+\rangle$ mode shows a red shift from $\lambda = 336\,\text{nm}$ to $\lambda = 354\,\text{nm}$ and its intensity reduces rapidly with increasing the middle dielectric layer radius. These phenomena could be explained by the plasmon hybridization theory, and the plasmon coupling is controlled by the thickness of the nanoshell. The separation between the inner core and the outer shell is increased with the middle dielectric layer radius. The attractive strength between the inner core and outer shell will be reduced with the increasing middle dielectric layer radius in the $|\omega_-^-\rangle$ mode due to the opposite signs of charges on each surface (seen Fig. 1(b)), thus the LSPR peak of the $|\omega_-^-\rangle$ mode shows a blue shift, while the $|\omega_-^+\rangle$ mode is a blue shift due to the same kind induced charges on the surface. On the other hand, the radius ratio (r_2/r_3) is enlarged with increasing the middle dielectric layer radius r_2. The LSPR for higher energy mode ω_+ increases and for the lower energy ω_- reduces. Then plasmon coupling between the nanotube and silver core is influenced by the nanotube, and the $|\omega_-^-\rangle$ mode shows a red shift and the $|\omega_-^+\rangle$ mode shows a blue shift. In addition, the intensity of LSPR increases firstly and then reduces gradually with increasing the inner core radius. This behavior could be explained such that, although the coupling is stronger with thin

thickness, there are less electrons to participate in oscillating when the thickness becomes much thinner, thus the resonance becomes less and absorption gets less intense.

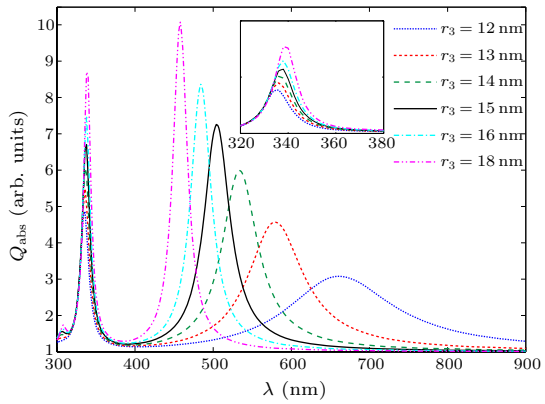

Fig. 5. The absorption spectra of SDS-ML nanotubes versus wavelengths with the outer radius from $r_3 = 12$ nm to $r_3 = 18$ nm.

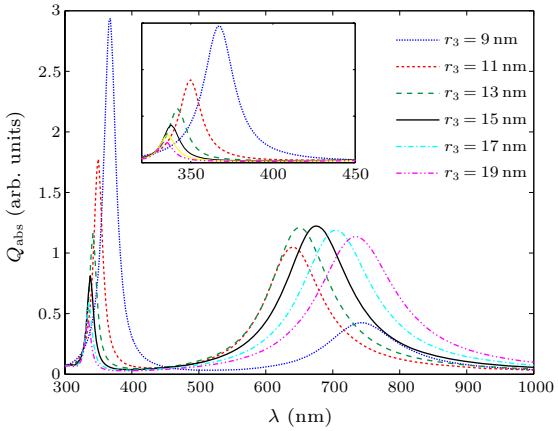

Fig. 6. Absorption spectra of SDS-ML nanotubes at $r_3 - r_2 = 5$ nm with the outer radius from $r_3 = 9$ nm to $r_3 = 19$ nm.

The influences of outer nanotube radius r_3 to LSPRs are also studied, and the results are shown in Fig. 5, where the radii of inner core (r_1) and the middle dielectric layer (r_2) are fixed at 5 nm and 10 nm, while the outer radius r_3 is varied from $r_3 = 12$ nm to $r_3 = 18$ nm. The results show that the $|\omega_-^-\rangle$ mode exhibits a distinct blue shift from $\lambda = 662$ nm with $r_3 = 12$ nm to $\lambda = 458$ nm with $r_3 = 18$ nm, and the intensity increases with the outer nanotube radius r_3. The $|\omega_-^+\rangle$ mode has a slight red shift from $\lambda = 334$ nm to $\lambda = 338$ nm with increasing r_3. According to the plasmon hybridization theory, the higher energy mode ω_+ reduces and the lower energy ω_- increases with the outer radius r_3, in other words, ω_- is a blue shift and ω_+ is a red shift.[6,14] Then the intensity of the $|\omega_-^-\rangle$ mode is increased and the $|\omega_-^+\rangle$ mode is reduced between the $|\omega_-\rangle$ mode and $|\omega_s\rangle$. In addition, there are more electrons to participate in oscillating when the thickness becomes much greater, thus the absorption gets more intense.

Lastly, the absorption spectra of the outer nanotube thickness at $r_3 - r_2 = 5$ nm are given in Fig. 6. Here the radius of inner core (r_1) is fixed at 5 nm while the outer nanotube radius r_3 is changed from $r_3 = 9$ nm to $r_1 = 19$ nm. Figure 6 shows that the $|\omega_-^-\rangle$ mode exhibits a distinct blue shift from $\lambda = 744$ nm with $r_3 = 9.0$ nm to $\lambda = 642$ nm with $r_3 = 11.0$ nm firstly and then a red shift from $\lambda = 650$ nm with $r_3 = 11.0$ nm to $\lambda = 736$ nm with $r_3 = 19.0$ nm. The intensity increases firstly and then keeps at a constant. The $|\omega_-^+\rangle$ mode has a slight blue shift from $\lambda = 368$ nm to $\lambda = 334$ nm with increasing r_3 and its intensity reduces rapidly. The mechanism of these properties could be explained by the plasmon hybridization theory. As the inner core radius r_1 is fixed, the plasmon energy of the $|\omega_s\rangle$ mode is fixed. An increase in the outer nanotube radius r_3 will increase the separation between the middle dielectric layer and the inner core. The increased separation reduces the coupling between the nanotube and the inner core, which makes the $|\omega_-^-\rangle$ mode blue-shift and the $|\omega_-^+\rangle$ mode red-shift.[5] In addition, the total size of the SDS-ML nanotubes is also enlarged with increasing the outer nanotube radius r_3, and then the increased nanotube size will cause the phase retardation.[7,15] The phase retardation will lead to the reduction of $|\omega_-^-\rangle$ plasmon energy. In other words, the $|\omega_-^-\rangle$ plasmon is a red shift. With the increase of the total size of nanotubes, the phase retardation effect is more dominant than the coupling effect between the nanotubes and the inner core. In other words, the $|\omega_-^-\rangle$ plasmon is a blue shift when the coupling plays a more dominant role than the phase retardation. On the contrary, $|\omega_-^-\rangle$ plasmon has a red shift.

In conclusion, SDS-ML nanotubes have been studied using the quasi-static approximation, analyzed by plasmon hybridization theory and the distribution of induced charges. The results show that the $|\omega_-^-\rangle$ mode could be well tunable by varying the inner core radius, dielectric radius or outer shell thickness. The $|\omega_-^-\rangle$ mode shows a red shift with increasing the inner core radius, a blue shift with increasing outer nanotube radius. This work may provide an alternative approach to analyzing the property of the core-shell nanoshell particles based on the plasmon hybridization theory and the induced charge interaction.

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