Calculated Optical Properties of Dielectric Shell Coated Gold Nanorods *

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Optical absorption spectra of dielectric shell coated gold nanorods are simulated using the discrete dipole approximation method. The influence of the aspect ratio, shell thickness, dielectric constant of the shell, and surrounding medium on the longitudinal resonance mode is investigated. It is found that the coated dielectric shell does not affect the trend in the dependence of resonance position on the aspect ratio, while it broadens the resonant line width and reduces the sensitivity of plasmon resonance in response to changes of the surrounding medium. Furthermore, the difference of dielectric constants between the shell and surrounding medium plays an important role in determining the resonance position. The screening effect of the dielectric shell tends to be less apparent for a thicker shell thickness.

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The interest in the synthesis of gold nanostructures has grown constantly due to their attractive applications in photonics, biological sensing and imaging, and photothermal therapy. These interesting applications are mostly based on their unique surface plasmon resonance properties, which originate from the collective oscillation of conduction electrons at metal surfaces in response to optical excitation. The resonance frequencies are known to be strongly dependent on the shape, composition, and local environment of particles. Parallel to the experimental efforts, theoretical studies of optical properties have been carried out for gold nanostructure with different shapes including nanospheres,[1−5] nanorods,[6−10] nanoshells,[11−17] and nanocages.[18,19] These simulations are in good agreement with experimentally measured spectra and can be used to interpret the optical effects observed during synthesis.

As shown by experiment and calculation, optical absorption spectra of gold nanorods show two resonance modes, transversal mode (TM) and longitudinal mode (LM), corresponding to electron oscillation associated with the short and long axis of the nanorod, respectively. However, the resonance feature will be altered when dielectric shells with a different refractive index from the surrounding medium are coated onto the rods. For example, an antibody functionalized gold nanorod will respond to the presence of the corresponding antigen through a red shift in the resonance modes.[20,21] Recently, core-shell structure nanorods are synthesized and fabricated for optical sensing applications. Liz-Marzán *et al.* investigated optical properties of silica coated gold nanorods and presented their potential use for biosensing applications.[21,22] Wang *et al.* demonstrated that assembled silica coated gold nanorods can be employed for colorimetric biosensing based on their high sensitivity to the local dielectric environment.[23] Evans *et al.* reported the spectral tunability of an array of Au core-shell nanorods and exemplified the potential application as an index of refraction sensor.[24]

In this Letter, discrete dipole approximation (DDA) simulations are carried out to discuss the factors that govern the longitudinal resonance of dielectric shell coated gold nanorods. Our applications include studies of the structure (aspect ratio) dependence of absorption spectra, the influence of coated dielectric shell, and the treatment of surrounding medium.

The DDA is a numerical method to calculate scattering and absorption of electromagnetic radiation by particles with sizes of the order or less of the wavelength of the incident light. In the approximation, the object of interest is divided into a cubic lattice of N point dipoles whose positions are denoted $\boldsymbol{r}_i$, with polarizability α_i. The dipole moment of the ith element as a result of interaction with a local electric field $\boldsymbol{E}_{\mathrm{loc}}$ will be

$$\boldsymbol{P}_i = \alpha_i \cdot \boldsymbol{E}_{\mathrm{loc},i}, \qquad (1)$$

where $\boldsymbol{E}_{\mathrm{loc},i}$ is the incident field $\boldsymbol{E}_{\mathrm{inc},i}$ plus the field radiated from all the other induced dipoles,

$$\boldsymbol{E}_{\mathrm{loc},i} = \boldsymbol{E}_{\mathrm{inc},i} + \sum_{j \neq i} \boldsymbol{E}_{\mathrm{dip},j}$$
$$= \boldsymbol{E}_0 e^{i\boldsymbol{k} \cdot \boldsymbol{r}_i} - \sum_{j \neq i} \boldsymbol{A}_{ij} \cdot \boldsymbol{P}_j. \qquad (2)$$

$\boldsymbol{E}_0$ and $\boldsymbol{k}$ are the amplitude and wave vector of the

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incident light, respectively, and the interaction matrix $\boldsymbol{A}_{ij}(i \neq j)$ has the form

$$\boldsymbol{A}_{ij} \cdot \boldsymbol{P}_j = \frac{e^{ikr_{ij}}}{r_{ij}^3}\Big\{k^2 \boldsymbol{r}_{ij} \times (\boldsymbol{r}_{ij} \times \boldsymbol{P}_j) + \frac{1 - ikr_{ij}}{r_{ij}^2}$$
$$\times \left[r_{ij}^2 \boldsymbol{P}_j - 3\boldsymbol{r}_{ij}(\boldsymbol{r}_{ij} \cdot \boldsymbol{P}_j)\right]\Big\}, \quad (3)$$

where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ and $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. Substituting Eqs. (2) and (3) into Eq. (1) we can rewrite the equations as a single matrix equation:

$$\boldsymbol{A}' \cdot \boldsymbol{P} = \boldsymbol{E}. \quad (4)$$

For a system with a total of N elements, $\boldsymbol{E}$ and $\boldsymbol{P}$ are $3N$-dimensional vectors, and $\boldsymbol{A}'$ is a $3N \times 3N$ matrix built from $\boldsymbol{A}$. By solving these $3N$ complex linear equations, the dipole moment vector $\boldsymbol{P}$ is obtained, from which the absorption cross sections are evaluated:

$$C_{\text{abs}} = \frac{4\pi k}{|\boldsymbol{E}_0|^2} \sum_{i=1}^{N}\Big\{\text{Im}[\boldsymbol{P}_i \cdot (\alpha_i^{-1})^* \boldsymbol{P}_i^*] - \frac{2}{3}k^3|\boldsymbol{P}_i|^2\Big\}. \quad (5)$$

Here absorption cross sections are expressed as efficiency $Q_{\text{abs}} = C_{\text{abs}}/A$, where $A = \pi a_{\text{eff}}^2$ and a_{eff} is defined through the concept of an effective volume equal to $4\pi a_{\text{eff}}^3/3$. For this calculation, the code adapted by Draine and Flatau[25,26] is used.

The geometry of dielectric shell coated gold nanorod is shown in Fig. 1. The gold nanorod has length L_1, diameter D_1 and dielectric constant ε_0,[27] the shell has length L_2, diameter D_2 and dielectric constant ε_1, the surrounding medium has dielectric constant ε_2. Then, the uniform shell thickness $d = (D_2 - D_1)/2$, the aspect ratio AR $= L_1/D_1$.
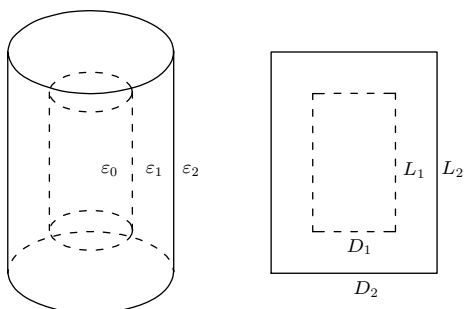
Fig. 1. Coaxial core-shell structure nanorod geometry. Here $\varepsilon_0, \varepsilon_1, \varepsilon_2$ are the dielectric constants for the gold core, dielectric shell and surrounding medium, respectively. D_1, D_2, L_1, L_2 denote the diameter and length of the core and shell, respectively.

We first consider the influence of the aspect ratio and shell thickness on the longitudinal resonance mode for silica coated gold nanorods in water. The dielectric constant ε_1 and ε_2 used in the calculations is 2.10 and 1.77, respectively. Gold nanorods with a fixed diameter ($D_1 = 8$ nm), various lengths and shell thicknesses are modelled.
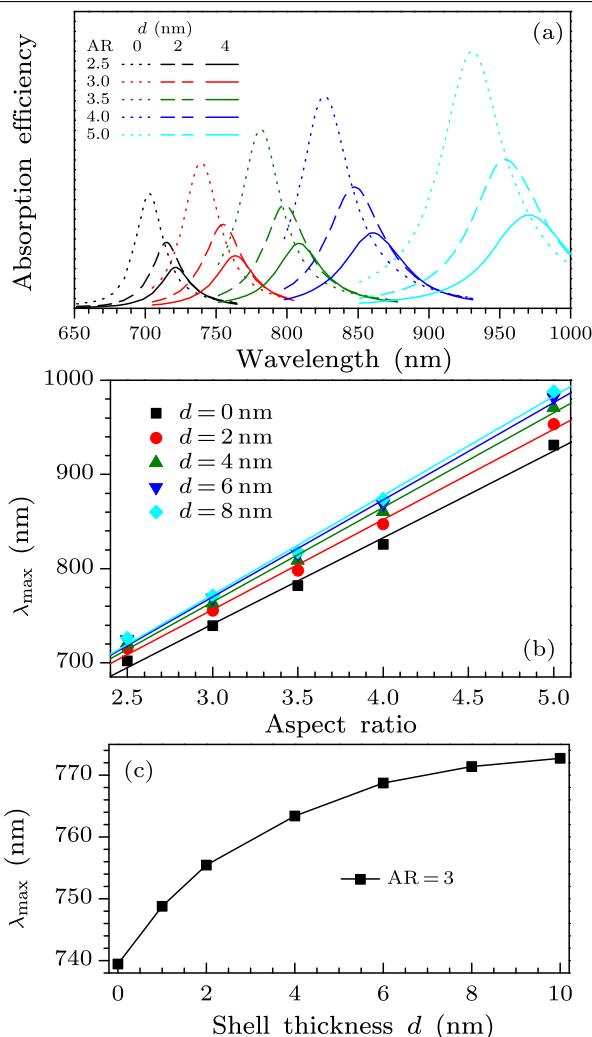

Fig. 2. (a) Simulated absorption spectra of silica coated gold nanorod with varying aspect ratio and shell thickness. (b) Resonance position λ_{max} determined from the simulated spectra plotted against the aspect ratio for varying shell thickness. The lines are linear fits to the data. (c) Resonance position λ_{max} plotted against the shell thickness when $\varepsilon_1 = 2.10, \varepsilon_2 = 1.77, \text{AR} = 3$.

The simulated absorption spectra are plotted in Fig. 2(a) for various aspect ratios and shell thicknesses. It is seen that, for gold nanorods with a fixed shell thickness, the resonance maximum λ_{max} positions of the LM show a drastic red shift with increasing aspect ratio, along with an increase of the absorption intensity. As the shell thickness is varied from 0 to 8 nm, it is interesting to show in Fig. 2(b) that the λ_{max} positions versus the aspect ratio all follow a linear relationship. It is known that the aspect ratio is the key parameter in the absorption spectrum of gold nanorods.[7] The coated silica shell does not affect the trend in the dependence of resonance position on the aspect ratio. It is also seen in Fig. 2(a) that the λ_{max} position red shifts with increasing shell thickness for gold nanorods with a given aspect ratio. This agrees with the theoretical study based on the coated ellipsoidal geometry assumed for the core-shell structure

nanorod,[21] and can be understood as follows. The coated dielectric shell polarizes in response to the plasmon field, which effectively reduces the strength of the surface charge and leads to a decreasing restoring force and consequently lowers the plasmon energies.[12,28] In Fig. 2(c) the λ_{max} positions are plotted against the shell thickness when the aspect ratio is fixed at a value of 3. Seven values of $d = 0, 1, 2, 4, 6, 8, 10$ are shown, respectively. It can be seen that, with the increasing shell thickness, λ_{max} increases rapidly first, then slows down gradually, and finally tends to be constant. This means that the screening effect of the coated shell is less apparent for a thicker shell thickness.

Now the influence of dielectric constant of the coated shell and surrounding medium are taken into account. It is well known that plasmon resonance shifts to red by increasing the dielectric constant of the solvent. The effect of the dielectric shell is similar to the effect of immersion in a medium with the same dielectric constant.[21] However the difference between dielectric constants of the shell and surrounding medium plays an important role in the changing fashion.[29] In Fig. 3(a), the λ_{max} positions are plotted against the shell thickness under the condition as the same as Fig. 2(c) except that $\varepsilon_1 = 1.44$. In opposition to the increasing dependence of λ_{max} on the shell thickness when $d < 8$ nm, the λ_{max} position blue shifts nonlinearly with increasing shell thickness. However, it also tends to be constant when $d > 8$ nm.
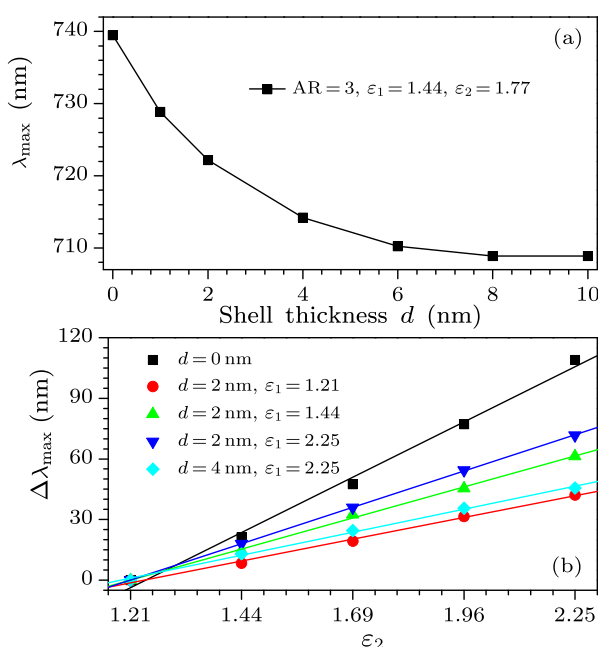
are considered for optical sensing applications, it is very important to understand the dependence of the longitudinal plasmon resonance on the dielectric constant of the surrounding medium. To ensure high analyte sensitivity, distinct changes in the resonance peak position in response to relatively small changes in the medium dielectric constant are desired. Therefore, the influence of the shell thickness and shell dielectric constant on the dielectric constant sensitivity ($\Delta\lambda_{max}/\Delta\varepsilon_2$) is investigated. The results are summarized in Fig. 3(b), where resonance shifts of dielectric coated gold nanorods are plotted against the medium dielectric constant for varying shell thickness and shell dielectric constant, while the aspect ratio is kept to be 3. From the slope of the linear fit, the dielectric constant sensitivity is obtained. It can be seen that the sensitivity of pure gold nanorods is relatively high in comparison with that of dielectric shell coated gold nanorods. It increases with increasing ε_1 for coated nanorods with a fixed shell thickness, or increases with the decreasing shell thickness for coated nanorods with a fixed shell dielectric constant. That is to say, coated shells reduce the sensitivity of plasmon resonance in response to changes of the surrounding medium. In addition, as shown in Fig. 2(a), it broadens the resonant line width, which makes the detection of the wavelength changes experimentally difficult. Therefore, gold nanorods with thin and high dielectric constant shell are preferred for optical sensing applications.

In conclusion, the DDA method is used to determine the positions of the LM resonance in the absorption spectra of dielectric-shell-coated gold nanorods. The influence of the aspect ratio, shell thickness, and dielectric constant of the shell and surrounding medium are considered. It is shown that the coated dielectric shell does not affect the trend in the dependence of resonance position on the aspect ratio, while it broadens the resonant line width and reduces the dielectric constant sensitivity. In addition, the difference of dielectric constants between the shell and surrounding medium plays an important role in determining the resonance positions. The screening effect of the dielectric shell tends to be less apparent for a thicker shell thickness.

Fig. 3. (a) Resonance position λ_{max} plotted against the shell thickness when $\varepsilon_1 = 1.44, \varepsilon_2 = 1.77, \text{AR} = 3$. (b) Resonance shift $\Delta\lambda_{max}$ plotted against the medium dielectric constant ε_2 for varying shell dielectric constant and shell thickness when AR = 3. The lines are linear fits to the data points.

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