Influence of dielectric core, embedding medium and size on the optical properties of gold nanoshells

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Abstract

The amplitudes of the dipole and quadrupole modes for gold nanoshells have been investigated with various dielectric constants for the core and the embedding medium and with various size of the nanoshells by means of Mie theory. With the increase in the dielectric constant of the core, it is found that the strengths of dipole and quadrupole modes become weak. We also observe with the increasing dielectric constant of the embedding medium that the strength of the quadrupole mode is enhanced quickly, whereas that of dipole mode increases first and then decreases. We further find that the amplitude maximum of the dipole mode appears when the total radius of the nanoshell reaches to 50 nm even if the ratio of the inner and outer shell radii is fixed. We have ascribed the changes of the dipole and quadrupole modes to the competition among the variations of induced surface charges, conduction electrons and oscillation electrons.

Gold nanoshell, a particularly interesting structure consisting of a dielectric core coated with a gold layer, has received much attention due to its special electronic and optical properties \cite{1–3}. In contrast to solid metal nanoparticle, the plasmon resonance frequency in the gold nanoshell geometry is sensitive to the relative dimensions of the core and the gold shell, and can be moved from the visible region into the near-infrared region of 800–1200 nm, where the transparent window of biological tissues is located \cite{4}. Recent studies have indicated that the optically excitable plasmon of the nanoshell geometry is remarkably sensitive to the changes such as dielectric environment, size, shape etc. \cite{5–7}, which may lead to applications such as nanoscale plasmon waveguides \cite{8}, chemical or biological sensors \cite{9} and even photothermal cancer therapy \cite{10}.

In order to characterize the fascinating optical features of the metal nanoshells, a number of theoretical approaches have been developed \cite{11–16}. For small nanoparticles, when their dimensions are much smaller than the wavelength of incident light, the far-field extinction can be described by the dipole term. In this case, the quasi-static equations are useful for the calculations of nonlinear optical effects \cite{11} and influences of the dielectric core and embedding medium on nanoshells \cite{12}. As the overall size of the nanoshell is larger than the quasi-static limit, the optical extinction changes from primarily absorbing to primarily scattering \cite{13} and hence the high-order multipole modes dominate the extinction spectra \cite{14}. In this case, Mie theory is more useful for the investigation of the optical properties of metallic nanoshells. In addition, the time-dependent local density approximation (TDLDA) has been used to calculate the electronic structure and optical properties of gold nanoshells \cite{15}. Prodan et al. \cite{16} mainly described the effects of dielectric core and dielectric embedding medium on the plasmon resonance of metallic nanoshells by means of TDLDA. They have shown that the TDLDA results agree well with the predictions from classical Mie theory. On the other hand, the effects of the geometrical parameters on the plasmon resonance were also reported in metal nanocrystals \cite{17,18}. However, little work has been carried out on the exact
shifting of plasmon resonance amplitude in gold nanoshells, especially for the detailed investigation of contributions from higher-order multipole modes. The amplitude of plasmon resonance for gold nanoshells is important to the photothermal conversion and the surface-enhanced Raman spectroscopy (SERS). The resonant excitation of larger or aspherical particles gives rise to broad extinction spectra with significant contributions from higher-order multipole modes. In addition, when the geometrical parameters of gold nanoshells change continuously, the variation of the plasmon resonance amplitude of gold nanoshells should be caused by competition of the different mechanisms, which have not been discussed in detail.

In this Communication, we have systematically investigated the influence of the dielectric core and embedding medium as well as the size effect on the plasmon resonant amplitude of gold nanoshells. The dipole and quadrupole modes have been simulated by means of Mie theory. We have obtained the three-dimensional plots of extinction spectra, which distinctly display sensitivity of the plasmon resonance of nanoshell with various dielectric constants for the core and embedding medium. We further have investigated the effect of the size for gold nanoshells on the dipole resonant mode, and found a maximum for the dipole mode amplitude when the total radius of the shell reaches to 50 nm even if the ratio of the inner and outer shell radii is fixed at 0.8. Furthermore, changes of the plasmon resonance amplitudes have been discussed in terms of competition among the variations of induced surface charges, conduction electrons and oscillation electrons.

First, let us investigate the optical response of gold nanoshells due to the plasmon resonance. Gold nanoshell consists of a nanometer-scaled dielectric core with radius \( r_1 \) surrounded by a thin gold shell with thickness \( r_2 - r_1 \). The permittivities of the core, shell and embedding medium are \( \varepsilon_1 \), \( \varepsilon_2 \) and \( \varepsilon_3 \), respectively. In gold nanoparticles, \( \varepsilon_2 \) has real and imaginary frequency-dependent components, and the dielectric function should be affected by the scattering of the conduction electrons in the particle surface. Thus, \( \varepsilon_2 \) is usually accounted by replacing the ideal Drude part in the dielectric function with a size-dependent one [11,19], and can be expressed as

\[
\varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma} + \chi_\infty, \tag{1}
\]

where the background susceptibility \( \chi_\infty \) arises from the core electron polarizability and interband \((d \rightarrow sp)\) transitions, \( \omega_p \) is the bulk plasma frequency, and \( \gamma \) is the modified collision frequency. \( \gamma \) can be expressed as

\[
\gamma = \gamma_f + \frac{V_f}{a}, \tag{2}
\]

where \( \gamma_f \) is the bulk collision frequency, \( V_f \) is the Fermi velocity, and the reduced electron mean free path \( a \) equates with the shell thickness \((r_2 - r_1)\). The parameters can be obtained by fitting the dielectric function to a particular frequency range of bulk dielectric data for Au [20]. The extinction spectra of the gold nanoshells were simulated by the computer program BHC0AT employing Mie scattering for concentric sphere geometry [21]. The Mie total extinction efficiency \( Q_{\text{ext}} \) for concentric sphere geometry can be expressed as

\[
Q_{\text{ext}} = \frac{2}{\lambda^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}(a_n + b_n). \tag{3}
\]

The scattering coefficients \( a_n \) and \( b_n \) are given in Ref. [21]. We investigated the contributions from dipole and quadrupole modes with \( n = 1 \) (dipole) and \( n = 2 \) (quadrupole), respectively. The numerical calculation results of Au@SiO\(_2\) (\( \varepsilon_1 = 2.04 \)) suspended in water (\( \varepsilon_3 = 1.7689 \)) are shown in Fig. 1. Here, the inner and outer shell radii \( r_1 \) and \( r_2 \) are fixed at 50 nm and 60 nm, respectively. The dotted and dashed curves represent the dipole and quadrupole resonance modes, respectively. The strong peaks at 799 nm and 636 nm have been ascribed to the dipole and quadrupole resonance modes, respectively. We also note that a weak peak appears at 458 nm in both the contributions of the dipole and quadrupole modes. Wang et al. [22] have reported that the octupole resonance mode would be highly damped and not discernible due to the contributions of interband transitions in the Au layer at wavelengths shorter than 500 nm. Thus, this peak may be ascribed to the interband transition in the Au state. We have not found the contribution of the octupole mode due to the weak intensity.

Fig. 2(a) shows the extinction spectra of gold nanoshells with variation of the core dielectric constant \( \varepsilon_1 \). Here, the \( \varepsilon_3 \)-value is fixed at 1.7689 of water. With the increasing \( \varepsilon_1 \)-value from 1 to 6.25, the dipole resonance shifts from 769 to 928 nm (solid curve), while the quadrupole resonance shifts from 614 to 750 nm (dashed curve), as shown in Fig. 2(b). In Fig. 2(c), we have observed with the increasing core dielectric constant that the strengths of the dipole and quadrupole peaks are decreased, and ascribed the behavior to the plasmon hybridization [23]. In plasmon hybridization model, the higher energy mode \( \omega_+ \) corresponds to an antisymmetric coupling between the surface plasmon on the surface of a solid sphere with energy \( \omega_S \) and dipolar cavity plasmon on the inner surface with energy \( \omega_C \). The lower energy mode \( \omega_- \) corresponds to a symmetric coupling between \( \omega_S \) and \( \omega_C \). The increase in the \( \varepsilon_1 \)-value
Fig. 2. (a) Three-dimensional plot of extinction spectra for gold nanoshells ($r_1 = 50$ nm, $r_2 = 60$ nm) suspended in water ($\varepsilon_3 = 1.7689$) with the increasing core dielectric constant $\varepsilon_1$ from 1 to 6.25. (b) Positions of dipole (solid line) and quadrupole (dashed line) peaks versus $\varepsilon_1$. (c) Strengths of dipole (solid line) and quadrupole (dashed line) peaks versus $\varepsilon_1$.

decreases the inner surface charges and hence the reduced restoring force. In this case, the energy of $\omega_C$ should be decreased, which suppresses the energies of the $\omega_-$ and $\omega_+$ modes and hence the reduced spectral weight of the $\omega_-$ mode [16].

We have further investigated the influence of the embedding medium on the dipole and quadrupole modes. Fig. 3(a) shows the extinction spectra of gold nanoshells with variation of the dielectric constant $\varepsilon_3$ for the embedding medium. Here, the $\varepsilon_1$-value is fixed at 2.04 of SiO$_2$. With the increasing $\varepsilon_3$-value from 1 to 6.25, the dipole (quadrupole) peak shifts from 695 nm (587 nm) to 1283 nm (906 nm), as shown in Fig. 3(b). It is found that the influence of the embedding medium on the dipole mode is more sensitive than that on the quadrupole mode. Fig. 3(c) shows the changes of the strengths for dipole and quadrupole peaks with $\varepsilon_3$. We have found that the strength of the dipole peak increases from 8.07 at $\varepsilon_3 = 1$ to 8.75 at $\varepsilon_3 = 1.8$, and then decreases to 7.73 at $\varepsilon_3 = 6.25$, while the strength of the quadrupole peak increases from 0.36 at $\varepsilon_3 = 1$ to 2.35 at $\varepsilon_3 = 6.25$. Note that the $\varepsilon_3$-dependence of the strengths for dipole and quadrupole modes has different behavior with the $\varepsilon_1$-dependence. The increase in the $\varepsilon_3$-value decreases the outer surface charges, which suppresses the energy of $\omega_S$. In this case, the energy of the $\omega_-$ mode is decreased and the spectral weight is increased [16]. For large particles, with the increasing $\varepsilon_3$-value, the reduced spatial wavelength of the light enhances the phase retardation and hence the decrease in dipole amplitude [24]. Therefore, when the $\varepsilon_3$-value is small, the contribution of the decrease in outer surface charges on the dipole mode is stronger than that of the reduced spatial wavelength of the light, and then the enhanced strength of dipole peak appears. With the increase in the $\varepsilon_3$-value, when the contribution of the reduced spatial wavelength of the light outweighs that of the decrease in the outer surface charges, the strength of dipole peak is suppressed. On the other hand, the strength of quadrupole mode is enhanced by both the facts, i.e., the decrease in outer surface charges and the reduced spatial wavelength of the light with the increasing $\varepsilon_3$-value.

Finally, let us investigate the variation of the extinction spectra with the total radius of gold nanoshell. In quasi-static theory, the resonance condition in small metal shell is expressed as a function of wavelength [19]

$$
\frac{r_1}{r_2} = \left[ 1 + \frac{3}{2} \frac{\varepsilon_1'\epsilon_2'\epsilon_1 + 2\epsilon_3}{\varepsilon_2'\epsilon_2\epsilon_1 + \epsilon_3} \right]^{1/3},
$$

(4)
Fig. 3. (a) Three-dimensional plot of extinction spectra for Au@SiO$_2$ ($\varepsilon_1 = 2.04$, $\varepsilon_3 = 1.7689$) with the increasing embedding medium dielectric constant $\varepsilon_3$ from 1 to 6.25. (b) Positions of dipole (solid line) and quadrupole (dashed line) peaks versus $\varepsilon_3$. (c) Strengths of dipole (solid line) and quadrupole (dashed line) peaks versus $\varepsilon_3$.

where $\varepsilon'_2$ and $\varepsilon''_2$ are real and imaginary portions of $\varepsilon_2$, respectively. This expression indicates that the wavelength of plasmon resonance is determined by the ratio of the inner radius to the outer radius $r_1/r_2$. Fig. 4(a) shows the extinction spectra of Au@SiO$_2$ suspended in water with variation of the outer shell radius $r_2$, here the $r_1/r_2$-value is fixed at 0.8. We have found that the plasmon resonance frequency shows a red-shift with the increasing $r_2$-value even if the $r_1/r_2$-value is fixed, as shown in Fig. 4(b). Fig. 4(c) shows the variations of the dipole and quadrupole mode amplitudes with $r_2$. It is found that the strength of the quadrupole mode increases from 0.02 at $r_2 = 20$ nm to 1.70 at $r_2 = 70$ nm, whereas the strength of the dipole mode increases from 3.43 at $r_2 = 20$ nm to 9.07 at $r_2 = 50$ nm and then decreases to 8.20 at $r_2 = 70$ nm. 

Evanoff et al. [17] have investigated the influence of particle size on the extinction efficiency, and found that two counteracting factors simultaneously affect the efficiency with the increasing particle size: the increase in the conduction electrons that are available for the plasmon resonance and the phase retardation decreasing the number of electrons that collectively oscillate at the dipole resonance frequency. When the particle size is small, the effect of the increase in conduction electrons outweighs that of the phase retardation, which causes the increase in dipole extinction efficiency. With the increasing total size, when the effect of phase retardation outweighs that of the increase in conduction electrons, the dipole extinction efficiency should be decreased. Thus, the influence of size on the dipole mode amplitude is the result of the competition between the changes of the conduction and oscillation electrons. On the other hand, the enhanced amplitude of quadrupole mode is mainly due to the optical extinction changes from primarily absorbing to primarily scattering with the increasing size and hence the high-order multipole modes dominate the extinction spectra [14].

In summary, we have investigated the plasmon resonance amplitudes of gold nanoshells with various dielectric constants for the core and the embedding medium and with various size of the nanoshell by means of Mie theory. We have found that the hollow gold nanoshell has the maximum extinction efficiency. With the increase in the dielectric constant of embedding medium, the quadrupole mode amplitude is enhanced quickly, whereas the dipole mode amplitude increases first and then decreases. When the $r_1/r_2$-value is fixed at 0.8, the increase in the total size causes the appearance of the maximum in the extinction efficiency at $r_2 = 50$ nm. Thus, the maximum amplitude of the plasmon resonance can be obtained in gold nanoshells by controlling the dielectric constants and the size of nanoshell, which is advantageous for practical applications.
Fig. 4. (a) Three-dimensional plot of extinction spectra for Au@SiO$_2$ ($\varepsilon_2 = 2.04$) suspended in water ($\varepsilon_3 = 1.7689$) with the increasing outer radius $r_2$ from 20 nm to 70 nm, while ratio of the inner and outer shell radii ($r_1/r_2$) is fixed at 0.8. (b) Positions of dipole (solid line) and quadrupole (dashed line) peaks versus $r_2$. (c) Strengths of dipole (solid line) and quadrupole (dashed line) peaks versus $r_2$.

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