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Optical resonance of metal-coated nanoshell*

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Metal-coated nanoshell, the nanoparticle consisting of a nanometre-scale dielectric core coated with a thin metallic shell, exhibits three distinct optical resonant forms, the sphere cavity resonance (SCR), plasmon resonance (PR), and concentric dielectric sphere resonance (CDSR). The SCR, PR and CDSR of the metal-coated nanoshell reveal a geometric tunability controlled by the core radius and by the ratio of the core radius to the total radius. Classical electrodynamics and Mie scattering theory are used to treat the resonant forms and the transition state between the resonant forms. Based on previous experimental research, we present a group of resonant equations for all the resonant forms, which depend on the geometric structure of the metal-coated nanoshell.

Keywords: metal-coated nanoshell, optical resonance, resonant wavelength, skin effect
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1. Introduction

Metal nanoparticles bridge the gap between the atomic and the bulk levels, and exhibits mesoscopic properties unique to this size. Hence the need for communication between nanoscale devices and the outside world is prerequisite, both for supplying energy to drive a device and for transmitting or receiving signals to control or extract information from a device. Now, most efforts in this area have been focused on electrical communication with semiconductor or molecule-based devices, where electrical contacts and interconnects are made to each individual device.[1−5] For the distinct resonant properties, the metal-coated nanoshells and dielectric/metal concentric spherical nanoparticles can be used to couple between electromagnetic radiation and nanoscale structures. Oldenburg *et al* found that the metal-coated nanoshells could be made into "nanoantennas" that can selectively couple to incident electromagnetic waves at their resonant wavelength.[6]

The structure of a metal-coated nanoshell (namely a gold-coated Au_2S nanoshell) is shown in Fig.1. Figure 1(a) is the TEM image of the gold-coated nanoshell obtained by JEM 200CX, and Fig.1(b) shows the ideal geometry of the metal-coated nanoshell, which is a spherical dielectric nanoparticle (radius R_1) coated with a thin, homogeneous metallic layer (thickness R_2–R_1). Practically, with the help of chemical reactions, the gold-coated Au_2S and gold-coated silica nanoshells can be fabricated, and the fabrication method allows us to independently control both the size of the core and the thickness of the shell.[7,8]

In this paper, we present the results of theoretical studies of the resonant forms of the metal-coated nanoshell based on previous experimental research on the sphere cavity resonance (SCR), plasmon resonance (PR), and concentric dielectric sphere resonance (CDSR).[7,8] Classical electrodynamics and Mie scattering theory for the metal-coated nanoshell geometry quantitatively account for the observed resonant wavelength and resonant energy, and a group of resonant equations for all the resonant forms of the metal-coated nanoshell is obtained. The resonant form, energy and linewidth of the metal-coated nanoshell are all dominated by the thickness of the metal shell. Owing to these properties, the metal-coated nanoshell can be used in nanometre-scale machines or devices for signal conduction and storage, as well as in sensitive optically based chemical detectors.

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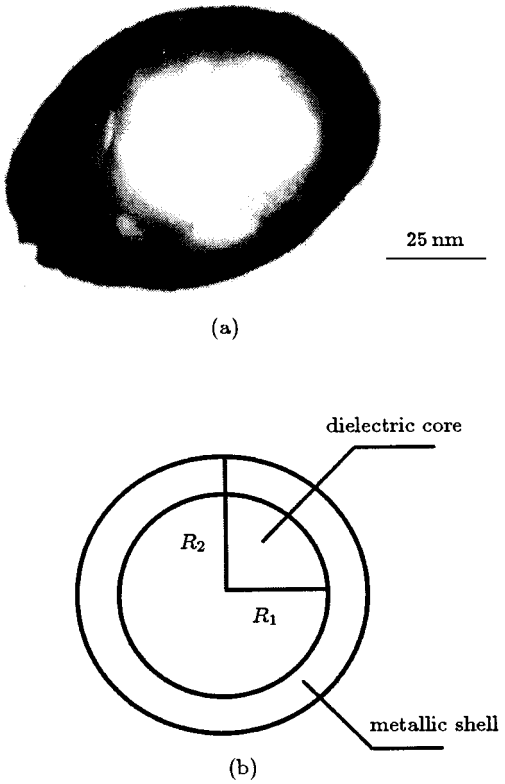


Fig.1. The structure of the gold-coated Au_2S nanoshell. (a) TEM micrograph of the nanoshell sample. (b) The ideal nanoshell geometry. R_1 and R_2 are the radii of the core and whole particle.

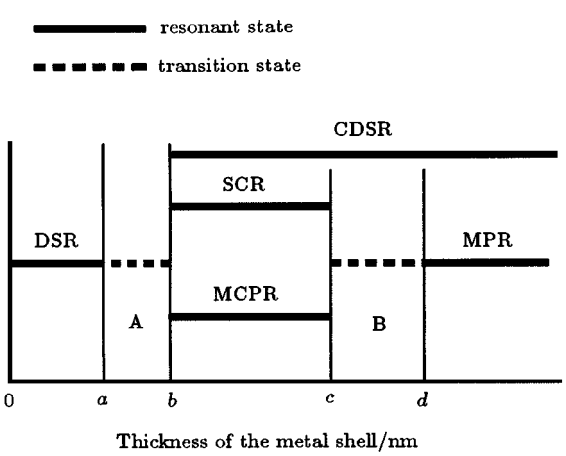


Fig.2. Variation of the resonant forms of the metal-coated nanoshell with the thickness of the metal shell.

When the metal shell is too thin to influence the electromagnetic field of the dielectric core, the SCR turns to the special case of dielectric sphere resonance (DSR). For the PR, there exist two different forms: the metal-coated nanoshell PR (MCPR) and metal nanoparticle PR (MPR). The MPR is also a special case on condition that the metal shell is quite thick and the effect of the dielectric core can be neglected. When the frequency of the electromagnetic wave is so high that the gold can be regarded as dielectric, the gold nanoshell can be treated as a concentric dielectric sphere. There will be a novel resonant form of the gold nanoshell, the CDSR. The thickness of the metal shell is responsible for the synchronous resonant forms of the SCR and MCPR, as it does to the DSR and the MPR, which lead to the discovery that the thickness of the metal shell determines the resonant forms of the metal-coated nanoshell. The variation of the resonant forms of the metal-coated nanoshell with the thickness of the metal shell is shown in Fig.2.

There are five regions shown in Fig.2, regions A and B are for the transition states while others are for resonant states. The parameters of the thickness a, b, c, and d will be discussed in the next sections.

2. SCR and DSR

As a sphere cavity, the metal-coated nanoshell is a mini-resonator. The characteristic equations of SCR can be written in terms of Bessel functions and their derivatives such that:

TE mode

$$\mathrm{J}_{n+1/2}(kR_1) = 0; \tag{1}$$

TM mode

$$\mathrm{J}'_{n+1/2}(kR_1) = 0; \tag{2}$$

where R_1 is the sphere radius, both $\mathrm{J}_{n+1/2}$ and $\mathrm{J}'_{n+1/2}$ are the $(n+1/2)_{\mathrm{th}}$ order Bessel function, and $k = \omega\sqrt{\varepsilon_d\mu_d}$, ε_d and μ_d are the wavenumber, permittivity and permeability of the dielectric core, respectively. Waves with electric fields perpendicular to the radial directions are designated as TE modes. The field components with magnetic field perpendicular to the radial directions are designated as TM modes. The roots of the above equations are pure real numbers, and the resonance is undamped. TE_{101} is the main mode of the SCR with the longest-wavelength and the highest energy. Respecting the resonant modes of SCR, all the high-order modes complex together, only the low-order main mode is notable enough to be discussed.[9] The resonant wavelength of the main mode is given as

$$\lambda_{\mathrm{SCR}} = \frac{\pi c\sqrt{\varepsilon_d\mu_d}}{1.372}R_1, \tag{3}$$

where c is the velocity of light in vacuum. Concerning the gold-coated Au_2S nanoshell, the cavity resonant absorption (CRA) of the main mode is obtained notably which shows the redshift during the reaction.

Equation (3) has been proved by the CRA of gold-coated Au_2S nanoshell, and the results of the experiments agree well with the theoretical calculation.[9]

The coupling of this nanocavity is transmission coupling which is due to the quite thin metal shell (near the skin effect depth of the metal).[9] Therefore, the thickness of the metal shell is a very important factor of the SCR, which is responsible for the influences on the Q-factor, the resonant linewidth, and the resonant energy of the SCR. The Q-factor of the main mode of the SCR is given as

$$Q_{\mathrm{SCR}} = \left(\frac{R_1\mu_d}{\mu'\delta}\right)\left(1+\frac{1}{3.755R_1^2}\right), \qquad (4)$$

where μ' and δ are the permeability and the skin effect depth of the metal shell, respectively. The skin effect depth of the metal shell is generally given as $\delta = 1/\sqrt{\pi f\mu'\sigma}$, where f and σ are the frequency of the electrodynamic wave and the resistivity of the metal shell. In general, the thickness of the metal is much thicker than the skin effect depth. But for this kind of nanocavity, the thickness of the metal is often less than the skin effect depth. We assume an equivalent skin effect depth, δ' given as: $\delta' = A(\delta - h) + h$. Where A is the incident depth coefficient of the proportionality between metal shell and the medium for the metal-coated nanoshell, and h is the thickness of the metal shell. δ' is the equivalent thickness of the metal only in the case that the thickness is less than the skin effect depth. Figure 3 shows how the Q-factor varies with the thickness of the metal shell (δ=2 nm).

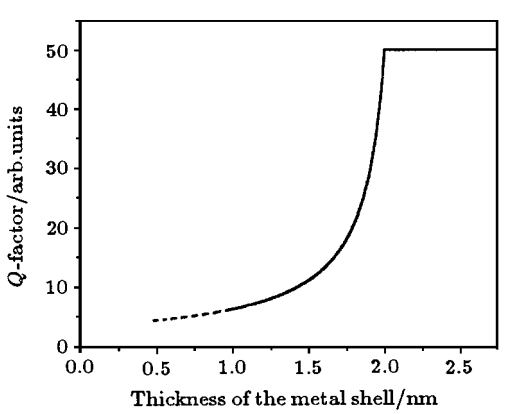


Fig.3. Variation of the Q-factor with the thickness of the metal shell (when δ=2 nm, $\mu_d = \mu'$=1).

The coupling of this nanocavity being via transmission, the thickness of the metal shell affects the incident energy of the electrodynamic wave. The relationship between external energy and internal energy is described by $E_{\mathrm{i}} = E_0 \mathrm{e}^{-h/\delta}$, where E_0 is the external electrodynamic wave energy out of the sphere. δ should be replaced by equivalent skin effect depth δ' on condition that h is less than the skin effect depth.

The resonant energy of the SCR main mode can be obtained, provided that only magnetic field exists in the nanocavity.

$$|E(\omega)|^2 = \frac{E_{\mathrm{i}}^2}{(\omega-\omega_0)^2+(\omega_0/2Q)^2}, \qquad (5)$$

where ω and ω_0 are the angular frequency of the electromagnetic wave and the resonant angular frequency of the SCR, and E_{i} is the incident energy of the electromagnetic wave. In the presence of perturbations, the shift of the resonant angular frequency $\Delta\omega$ will occur. The resonant energy and the linewidth of the resonant peak are affected by the Q-factor, which, actually, is determined by the thickness of the metal shell. The resonant energy distribution with the thickness of the incident electromagnetic wavelength is given in Fig.4 for three different thicknesses of the metal shell (λ_{SCR}=50 nm, δ=2 nm).

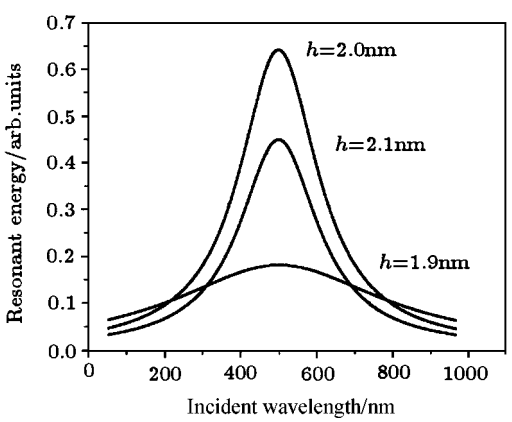


Fig.4. Resonant energy distribution with incident electromagnetic wavelength for three different thicknesses of the metal shell h=2.1, 2.0 and 1.9 nm (when λ_{SCR}=500 nm, δ=2 nm).

Figures 3 and 4 indicate that the Q-factor and the peak of resonant energy diminish dramatically on condition that h is less than the skin effect depth, which can be explained as that a great part of the resonant electromagnetic waves transmit out through the thin metal shell, and the amount of the lost resonant energy varies with the thickness of the metal shell remarkably when h is less than the skin effect depth. From Fig.4, we can also find that the linewidth of SCR varies with the thickness of the metal shell. Actually, it is affected not only by the thickness of the metal shell, but also by the size distribution of metal-coated nanoshell.

For the DSR, the characteristic equations can be obtained from the denominators of the expansion coefficients in the normal mode-field expansions given by Chen.[10]

TE mode

$$\sqrt{\varepsilon_d\mu_x}\hat{\mathrm{H}}_n^{(2)}(k_xR)\hat{\mathrm{J}}_n'(k_dR) - \sqrt{\varepsilon_x\mu_d}\hat{\mathrm{H}}_n^{(2)'}(k_xR)\hat{\mathrm{J}}_n(k_dR) = 0; \quad (6)$$

TM mode

$$\sqrt{\varepsilon_x\mu_d}\hat{\mathrm{H}}_n^{(2)}(k_xR)\hat{\mathrm{J}}_n'(k_dR) - \sqrt{\varepsilon_d\mu_x}\hat{\mathrm{H}}_n^{(2)'}(k_xR)\hat{\mathrm{J}}_n(k_dR) = 0; \quad (7)$$

where $\hat{\mathrm{J}}_n$ and $\hat{\mathrm{H}}_n$ are nth-order modified spherical Bessel and Hankel functions. The subscript "x" and "d" designate the external and internal medium. In this paper, it is assumed that the external medium is air, $\varepsilon_x = \varepsilon_0$, and $\mu_x = \mu_0$ (free-space). As in the case of SCR, we only discuss the main mode of the DSR, TE_{101}. The resonant wavelength of the main mode is given as

$$\lambda_{\mathrm{DSR}} = \frac{\pi c\sqrt{\varepsilon_d\mu_d}}{1.525}R_1. \quad (8)$$

Eq.(8) has the same form as Eq.(3) because the DSR is a special case for the SCR on condition that the metal shell is extremely thin. The difference between the DSR and the SCR is merely determined by the different boundary conditions, dielectric for DSR and conducting for SCR. The variation of the metal shell thickness leads to the change from DSR to SCR, as shown in Fig.5.

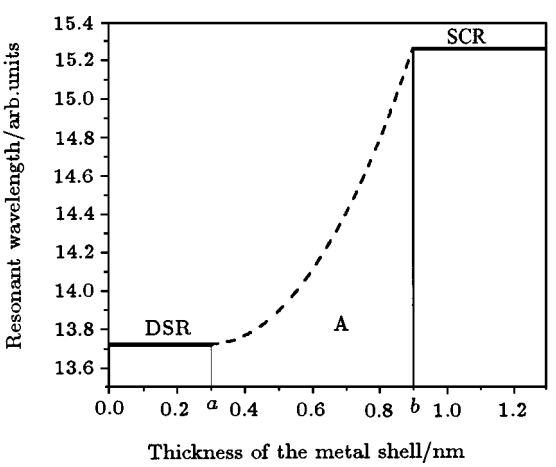


Fig.5. Change of processes between the DSR and the SCR with the variation of thickness of metal shell.

Region A is the transition state between the DSR and the SCR. Actually: the metal shell cannot surround the dielectric core as the ideal mode. For gold-coated silica nanoshell, to coat the silica particles with gold in an aqueous environment, a seeded growth technique was used where small gold particles were first attached to the silica core nanoparticle using amine-terminated silane as linker molecules. Additional gold was reduced on to the attached gold "seed" particles until the seed particles coalesced into a complete shell. As a result, there is a transition state between the DSR and the SCR. The thickness of the metal shell for the DSR is less than one atomic layer, $a > 0.3$ nm, and the thickness for the SCR is more than two or three atomic layers, $b < 1$ nm.[9] The thickness of the metal is not homogeneous at the beginning of the reaction, so the parameters a and b given above are the average values, which are affected by the material of the metal shell and the interfacial condition between dielectric core and metal shell. In region A between a and b, The DSR and SCR complex together, and there is no dominant form or mode. The variation of processes between the DSR and the SCR of metal-coated nanoshell, being sensitive to the local chemical environment at the nanoparticle interface, leads to the possibility of sensitive optically based chemical detectors.[11]

3. MCPR and MPR

The metal-coated nanoshell has the new and tunable optical properties, whereas solid metal nanoparticles do not.[12] The MCPR displays the expected geometric tunability controlled by the ratio of the core radius to the total radius. For gold-coated $\mathrm{Au_2S}$ nanoshell, the ratio of R_1/R_2 varies from 0.6 to 0.9, yielding a plasmon resonance tunable from 600 nm to greater than 1000 nm. During the reaction of the gold-coated $\mathrm{Au_2S}$ nanoshell, the MCPR initially shows the redshift; about 20 min later, it shows the blueshift.[8]

A theoretical description based on Mie scattering theory for the MCPR of the metal-coated nanoshell has been given.[13] Mie scattering theory is the solution to Maxwell's equations in spherical coordinates with boundary conditions appropriate for a sphere. For the metal-coated nanoshell, the general solution to the potential in each part of the metal-coated nanoshell is given as[6]

$$\Pi_{(x,m,d)}(r,\theta) = [A_{(x,m,d)}r + (B_{(x,m,d)}/r^2)]\cos\theta, \quad (9)$$

where $A_{(x,m,d)}$ and $B_{(x,m,d)}$ are the constants multiplying the monopole and the dipole terms, respec-

tively. Using Eq.(9), with the boundary conditions, the following expression for the resonance condition of the metal-coated nanoshell is obtained.[8]

$$\frac{R_1}{R_2}=\left[1+\frac{3}{2}\frac{\varepsilon'_m(\lambda)(\varepsilon_d+2\varepsilon_x)}{[\varepsilon'_m(\lambda)]^2-\varepsilon'_m(\lambda)(\varepsilon_d+\varepsilon_x)+\{\varepsilon_d\varepsilon_x-[\varepsilon''_m(\lambda)]^2\}}\right]^{1/3}, \tag{10}$$

where $\varepsilon_m(\lambda)$ is the dielectric function of the metal shell with the incident wavelength; ε_x and ε_d are the permittivity of the external and internal medium. This expression gives the ratio of the core radius to the total radius needed to obtain a resonant condition at a particular wavelength, and it embodies the geometrical tunability that metallic nanoshell possess.

From Fig.2, we know that the thickness of the metal shell for the MCPR is in the same region as SCR. On condition that the metal shell is so thick that the dielectric core can be ignored, the resonant form of the metal-coated nanoshell is MPR, whose resonant wavelength is identical with the plasmon resonant wavelength of the metal nanoparticle (λ_m). For example, solid gold nanoparticles have a resonant peak at 520 nm, and the silver nanoparticles show a resonance at 390 nm. Region B in Fig.2 is the transition state between the MCPR and MPR. The thickness of the metal shell for the MCPR is less than about 20 nm (c <20 nm) as compared with that for the MPR, which is greater than about 20 nm (d >20 nm).[7]

4. CDSR

The condition for the CDSR requires the gold being regarded as dielectric. For the dielectric constant of the gold, the electronic transitions in a solid are more directly related to the complex dielectric constant $\tilde{\varepsilon}=\varepsilon_A+\mathrm{i}\varepsilon_B$ rather than the complex index of refraction $\tilde{n}=n+\mathrm{i}k$. They are connected by $\tilde{\varepsilon}=\tilde{n}^2$, so that $\varepsilon_A=n^2-k^2$ and $\varepsilon_B=2nk$. The dielectric constant is determined by the relaxation time and the optical mass of the electrons according to the Drude free-electron theory,[14]

$$\tilde{\varepsilon}(\omega)=1-\frac{\omega_{\mathrm{p}}^2}{\omega(\omega+\mathrm{i}/\tau)}, \tag{11}$$

where $\omega_{\mathrm{p}}^2=4\pi Ne^2/m_0$. Here N is the density of the conduction electrons, m_0 is their effective optical mass, and τ is the relaxation time. Separating $\tilde{\varepsilon}$ into its real and imaginary parts, we obtain

$$\varepsilon_A=1-\frac{\omega_{\mathrm{p}}^2\tau^2}{1+\omega^2\tau^2}, \tag{12}$$

and

$$\varepsilon_B=\frac{\omega_{\mathrm{p}}^2\tau}{\omega(1+\omega^2\tau^2)}. \tag{13}$$

When $\omega>(\omega_{\mathrm{p}}-1/\tau)$, the real part of the gold dielectric constant ε_A is positive, and for gold, $\omega_{\mathrm{p}}=9.4\times10^{15}$ rad/s, $\tau=(9.3\pm0.9)\times10^{-15}$s, thus $\omega_{\mathrm{p}}\gg1/\tau$ implies that the imaginary part can be ignored.[14] Under that condition, the gold shell of the nanoshell can be regarded as a dielectric shell, and the dielectric constant of gold at high frequency ($\omega>\omega_{\mathrm{p}}$) is given as

$$\varepsilon_2=1-\frac{\omega_{\mathrm{p}}^2}{\omega^2}. \tag{14}$$

Then the gold nanoshell can be treated as the concentric dielectric sphere (CDS). The equivalent dielectric constant of this CDS is given as[8]

$$\varepsilon_{\mathrm{CDS}}=\frac{\varepsilon_2[\varepsilon_1(3-2P)+2\varepsilon_2P]}{\varepsilon_3[\varepsilon_1P+\varepsilon_2(3-P)]}, \tag{15}$$

where $P=1-(R_1/R_2)^3$ is the ratio of the shell volume to the total particle volume. Under the consideration that dielectric constant of the Au_2S core does not vary with the electromagnetic wave notably, ε_1 is assumed unchanged and given as ε_1=5.44. It is determined by using an estimate of the calculated bandgap of Au_2S (2.6 eV) and the empirical expression $\varepsilon^2E_{\mathrm{g}}$=77, where E_{g} is the bandgap.[8] In this paper, it is assumed that the external medium is air, $\varepsilon_3=\varepsilon_0$, and the permeabilities in all regions are equal to that in air, $\mu_1=\mu_2=\mu_3=\mu_0$ (free-space).

From Eqs.(8), (14) and (15), the expression for the resonant angular frequency of the CDSR (of gold-coated Au_2S nanoshell) can be obtained

$$\omega_{\mathrm{CDSR}}=\left[\frac{B+(B^2-4AC)^{1/2}}{2A}\right]^{1/2}, \tag{16}$$

where

$$A=16.32-8.88P,$$

$$B=(16.32-6.88P)\omega_{\mathrm{p}}^2+(3+4.44P)\frac{9.3c^2}{R_2^2},$$

$$C=\omega_{\mathrm{p}}^2\left[2\omega_{\mathrm{p}}^2P+(3-P)\frac{9.3c^2}{R_2^2}\right], \tag{17}$$

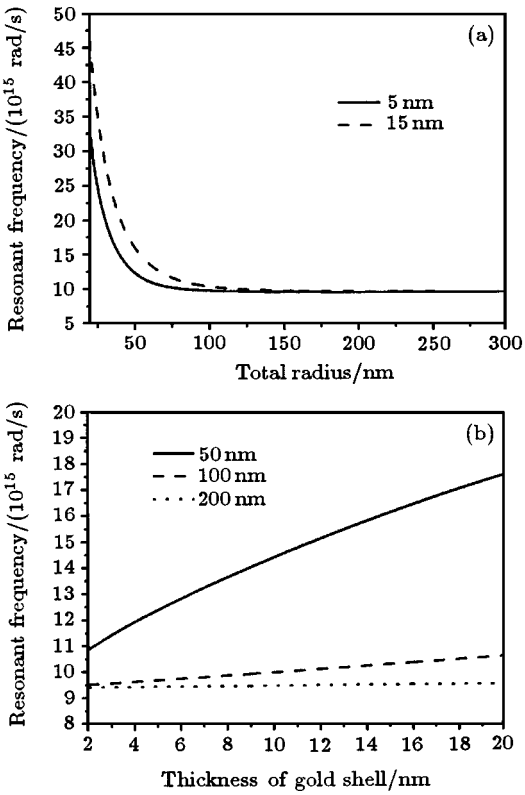


Fig.6. Variation of resonant angular frequency: (a) for the general gold nanoshell with the total radius (R_2) of the nanoshell (the thickness of gold shell $R_2 - R_1$=5 and 15 nm), (b) for the general gold nanoshell with the thickness ($R_2 - R_1$) of the nanoshell (total radius R_2=50, 100 and 200 nm).

where c is the speed of light in a vacuum. The sizes of the general gold nanoshell are 300 nm$> R_2 >$20 nm, and 20 nm$> R_2 - R_1 >$2 nm,[7] and the angular frequency of the general gold nanoshell given by Eq.(16) conforms to the condition of CDSR, $\omega > \omega_{\rm p}$. From Eqs.(16)–(17), we can find the resonance frequency of CDSR as functions of the core radius and the total radius of the gold nanoshell. The variation of resonant angular frequency for the general gold nanoshell with the total radius (R_2) of the nanoshell (the thickness of gold shell $R_2 - R_1$=5 and 15 nm), and for the general gold nanoshell with the thickness ($R_2 - R_1$) of the nanoshell (total radius R_2=50, 100 and 200 nm) are given in Fig.6.

From Fig.6, we can find that the CDSR is notable when the nanoshell is small and the shell is thick. And the limiting condition of the CDSR is the resonant angular frequency approaches to the $\omega_{\rm p}$. The CDSR is the coupling result of the macroscopic dielectric resonance of Au_2S and the microscopic plasmon resonance of gold, and it is a special resonance form for the macroscopic nanoshell, only when the nanoshell is small enough that the resonant angular frequency of Au_2S dielectric resonance conforms to the condition that gold can be regarded as dielectric, $\omega > \omega_{\rm p}$. Accordingly, the thickness of the gold shell is very important in that the plasmon resonance of gold heavily influence the CDSR.

5. Conclusion

We have investigated the resonant properties of the nanoparticles consisting of dielectric cores and gold shells. There are five resonant forms for the metal-coated nanoshell. Based on classical electrodynamics and Mie scattering theory, a group of resonant equations for all the resonant forms of the metal-coated nanoshell is obtained.

DSR form

$$\lambda_{\rm DSR} = \frac{\pi c\sqrt{\varepsilon\mu}}{1.525}R_1; \tag{18}$$

SCR form

$$\lambda_{\rm SCR} = \frac{\pi c\sqrt{\varepsilon\mu}}{1.372}R_1; \tag{19}$$

MCPR form

$$\frac{R_1}{R_2} = \left[1 + \frac{3}{2}\frac{\varepsilon'_m(\lambda)(\varepsilon + 2\varepsilon_0)}{[\varepsilon'_m(\lambda)]^2 - \varepsilon'_m(\lambda)(\varepsilon + \varepsilon_0) + \{\varepsilon\varepsilon_0 - [\varepsilon''_m(\lambda)]^2\}}\right]^{1/3}; \tag{20}$$

MPR form

$$\lambda_{\rm MPR} = \lambda_m; \tag{21}$$

CDSR form (gold-coated Au_2S nanoshell)

$$\lambda_{\rm CDSR} = \frac{2\pi c}{\left[\dfrac{B + (B^2 - 4AC)^{1/2}}{2A}\right]^{1/2}}; \tag{22}$$

where ε, μ are the permittivity and permeability of the dielectric core. The resonant forms of the metal-coated nanoshell depend on the thickness of the metal shell. The SCR of the metal-coated nanoshell reveals a geometric tunability controlled by the radius of the core, and the PR and CDSR are functions of the core radius to shell thickness. This paper provides theoretical foundations for the applications of the metal-coated nanoshells.

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