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# Optimal design of gold nanoshells for optical imaging and photothermal therapy

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ABSTRACT

Gold nanoshells are of great interest in optical imaging based on their light scattering properties and photothermal therapy due to their light absorption properties. Strong light scattering is essential for optical imaging, while effective photothermal therapy requires high light absorption. In this article, the optimal core radii and shell thicknesses of silica–gold and hollow gold nanoshells, possessing maximal light scattering and absorption at wavelengths between 700 and 1100 nm, are obtained using the Mie theory of a coated sphere. The results show that large-sized gold nanoshells of high aspect ratios (the aspect ratio is defined as the ratio of core radius to shell thickness) are the efficient contrast agents for optical imaging, while smaller gold nanoshells of high aspect ratios are the ideal therapeutic agents for photothermal therapy. From the comparison of the numerical results for silica–gold and hollow gold nanoshells, the latter are seen to offer a little superior light scattering and absorption at smaller particle size. Fitting expressions for the optimal core radii and shell thicknesses are also obtained, which can provide design guidelines for experimentalists to optimize the synthetic process of gold nanoshells.



## 1. Introduction

Metal nanoparticles can strongly scatter and absorb light at plasmon resonance wavelength in the visible and near-infrared regions. The strongly enhanced light scattering and absorption by metal nanoparticles are attributable to the localized surface plasmon resonance (LSPR) of metal nanoparticles while interacting with light. A localized surface plasmon (LSP) is a collective spatial oscillation of the free electrons in a metal nanoparticle; it can be directly excited by light and resonate at a specific wavelength (i.e., the plasmon resonance wavelength). These special optical properties of metal nanoparticles make them have tremendous potential applications in many research fields such as photothermal cancer therapy and imaging [1], biosensing [2], surface-enhanced Raman scattering (SERS) [3], solar cells (SCs) [4], and light-emitting diodes (LEDs) [5].

Gold nanoshells, consisting of a nanoscale dielectric core coated with an ultrathin gold shell, are a new type of composite metal nanoparticles invented by Halas and co-workers [6]. By varying the dimension and composition of each layer of the nanoshell structure, the plasmon resonance wavelength can be tuned to any wavelength desired across a large region of the visible and near-infrared spectra, and the extent of light scattering and absorption enhancement also can be changed [7–10]. Owing to these advantages, gold nanoshells can be used as contrast agents for optical imaging and therapeutic agents for photothermal therapy. Gold nanoshells have been studied specifically for their potential as contrast agents with dark-field microscopy [11], two-photon-induced photoluminescence [12], reflectance confocal microscopy [13], and optical coherence tomography [14]. Hirsch et al. [15] were the first to demonstrate photothermal therapy using gold nanoshells. Gold nanoshells have been tested as targeted-therapy probes for human breast [16], prostate [17], brain [18], and liver [19] cancers.

The effectiveness of gold nanoshells as contrast agents for optical imaging and therapeutic agents for photothermal therapy depends on their light scattering and absorption properties. Strong light scattering is essential for optical imaging, while effective photothermal therapy with minimal laser dosage requires high light absorption. For both optical imaging and photothermal therapy, the laser needs to penetrate biological tissue, so the plasmon resonance wavelength of gold nanoshells is strongly desired to be in the near-infrared region between 700 and 1100 nm, where the light transmittance of biological tissue is the highest [20]. Thus the optimal design of gold nanoshells with maximal light scattering and absorption in the near-infrared region is an important first step in the ultimate selection of gold nanoshells for optical imaging and photothermal therapy. In this paper, we provide the optimal core radii and shell thicknesses of silica–gold and hollow

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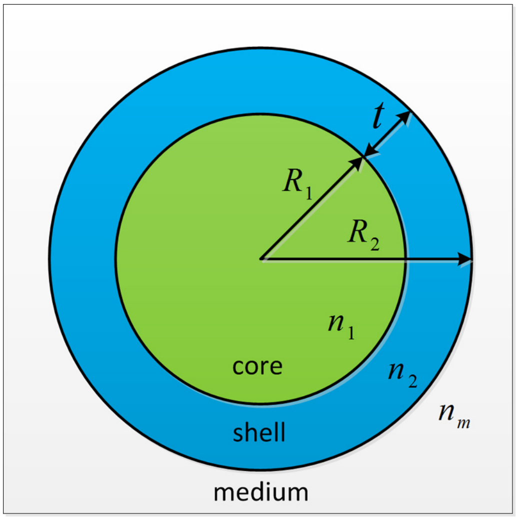


**Fig. 1.** Schematic of a nanoshell. $R_1$, $R_2$, and $t$ are the core radius, shell radius, and shell thickness, respectively. $n_1$, $n_2$, and $n_m$ are the refractive indices of the core, shell, and surrounding medium, respectively.

gold nanoshells, possessing maximal light scattering and absorption at wavelengths between 700 and 1100 nm, by using the Mie theory of a coated sphere.

This paper is organized as follows. The Mie theory of a coated sphere and the size-dependent dielectric function of metal nanoparticles are introduced in Section 2. In Section 3, the effects of the core radius and shell thickness on the spectra of the volume scattering and absorption coefficients are systematically simulated and quantitatively analyzed; maximal volume scattering and absorption coefficients and the corresponding optimal core radii and shell thicknesses are obtained, and the fitting expressions for the optimal core radii and shell thicknesses of silica–gold and hollow gold nanoshells are provided. Section 4 is devoted to the conclusion.

## 2. Theoretical background

When a particle is illuminated by a beam of light, a part of light is scattered by the particle, and a part of light is absorbed if the particle is opaque. The total energy loss of the incident light is the sum of the scattered and absorbed energies by the particle. The scattered and absorbed energies are usually expressed by the scattering and absorption cross sections, $C_{sca}$ and $C_{abs}$, respectively. The total extinction cross section $C_{ext}$ is given by $C_{ext} = C_{sca} + C_{abs}$. $C_{sca}$, $C_{abs}$, and $C_{ext}$ have units of area because they represent an equivalent cross sectional area of the particle that contributes to the scattering, absorption, and extinction of the incident light.

The absolute magnitude of the cross section does not provide a reliable measure for the optical properties of an ensemble of nanoparticles employed in real-life applications, because smaller particles can be loaded in a given volume in greater numbers as compared to particles of a larger size. Therefore, the more meaningful parameters for comparison across a range of sizes are the cross sections per unit particle volume, which are called volume extinction, scattering, and absorption coefficient, $\mu_{ext}$, $\mu_{sca}$, and $\mu_{abs}$, respectively [21,22]. It should be noted that we assumed the spacing between nanoparticles is wide enough to neglect the coupling effects on the surface plasmon resonance.

In this work we have considered and studied the nanoshells with geometries shown in Fig. 1. The calculation of the light scattering and absorption by gold nanoshells were performed by using Mie theory of a coated sphere proposed by Aden and Kerker [23]. For a coated sphere (a homogeneous sphere coated with a homogeneous layer of uniform thickness), the volume extinction, scattering, and absorption coefficients are

$$\mu_{ext} = \frac{C_{ext}}{V} = \frac{2\pi}{Vk^2}\sum_{n=1}^{\infty}(2n+1)Re\{a_n + b_n\} \quad (1)$$

$$\mu_{sca} = \frac{C_{sca}}{V} = \frac{2\pi}{Vk^2}\sum_{n=1}^{\infty}(2n+1)\left(|a_n|^2 + |b_n|^2\right) \quad (2)$$

$$\mu_{abs} = \mu_{ext} - \mu_{sca} \quad (3)$$

where $V$ is the volume of the coated sphere, $k$ is the wavenumber in the surrounding medium, $a_n$ and $b_n$ are the scattering coefficients.

We developed a computer code employing the algorithm proposed by Bohren and Huffman [22]. The results of the code were checked against the Mie theory results for homogeneous spheres for three cases: vanishing shell, vanishing core, and vanishing refractive index difference between core and shell materials. There was excellent agreement in the numerical results by the two methods, verifying the accuracy of our code for gold nanoshells. The required parameters for the code are the vacuum wavelength of incident light $\lambda$, the core and shell radii, $R_1$ and $R_2$, and the refractive indices of the core, shell, and surrounding medium, $n_1$, $n_2$, and $n_m$, respectively.

When the light interacts with the small metal nanoparticles (especially for the size smaller than the mean free path of the free electrons), the dielectric function of the nanoparticles deviates from the bulk value [24]. That is because the collision of the free electrons with the particle surface becomes important as an additional relaxation process. The dielectric function of small metal nanoparticles should thus be modified to account for the surface scattering of the free electron, which is expressed as [24]

$$\varepsilon(\omega, L_{eff}) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega v_f/l_\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\left(v_f/l_\infty + Av_f/L_{eff}\right)} \quad (4)$$

where $\varepsilon_{bulk}$ is bulk dielectric function, $\omega$ is the angle frequency of incident light, $\omega_p$ is the plasma frequency, $v_f$ is the Fermi velocity, $l_\infty$ is the mean free path of the free electrons, $A$ is a dimensionless parameter, usually assumed to be close to unity, and $L_{eff}$ is the reduced effective mean free path of the free electrons. For gold nanoshells, $\omega_p = 9.03$ eV [25], $v_f = 1.40 \times 10^{15}$ nm/s [8], $l_\infty = 42$ nm [8], $A = 1$ [8], $L_{eff} = R_2 - R_1$ [8], and the values of the bulk dielectric function at different wavelengths were obtained from Johnson and Christy [26], cubic interpolation was used to calculate the complex refractive indices at intermediate wavelengths, where data was not available directly from Johnson and Christy. The refractive index of the gold sell is calculated by $n_{Au} = \varepsilon^{1/2}$. In this paper, the core material of gold nanoshells was considered to be silica, refractive index given by Malitson [27], or vacuum, and the surrounding medium was considered to be water with a refractive index given by Daimon and Masumura [28].

## 3. Results and discussion

In order to investigate the effect of the core radius and shell thickness on the spectra of the volume scattering and absorption coefficients ($\mu_{sca}$ and $\mu_{abs}$), silica–gold nanoshells of various dimensions are selected as the subjects of study. Calculated spectra of the $\mu_{sca}$ and $\mu_{abs}$ for silica–gold nanoshells embedded in water are shown in Fig. 2. The core radius increases from 10 to 100 nm and the shell thickness is 5 nm in Fig. 2(a) and (b). The shell thickness increases from 2 to 20 nm and the core radius is 50 nm in Fig. 2(c) and (d). The figures show that the plasmon resonance wavelength