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Research Article

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Posted Date: May 5th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-446158/v1>

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Version of Record: A version of this preprint was published at Results in Physics on January 1st, 2022. See the published version at <https://doi.org/10.1016/j.rinp.2022.105209>.

Photoacoustic response optimization of gold nanorods in the near-infrared region

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Abstract

Photoacoustic imaging (PAI) combines the advantage of optical and ultrasonic imaging, which have a high signal-to-noise ratio, penetration depth, and spatial resolution. To further improve the performance of PAI, gold nanorods (AuNRs) can be utilized as exogenous contrast agents. Therefore, in the present work, the photoacoustic properties of AuNRs in an aqueous solution in the near-infrared region are studied by the finite element method. The effects of different factors including orientation of AuNRs, incident laser wavelength, aspect ratio, and equivalent radius on the absorption efficiency, photothermal response, photoacoustic response, and the photoacoustic conversion efficiency of AuNRs are analyzed. Results show that the photoacoustic properties of AuNRs are highly related to their absorption efficiency which alters with the orientation of AuNRs and wavelength of the incident light. Moreover, the aspect ratio and equivalent radius significantly influence the heat transfer characteristics of AuNRs, which further leads to a variation of the photothermal response, photoacoustic response, and photoacoustic conversion efficiency of the AuNRs. Finally, we provide strategies to improve the photoacoustic signal of AuNRs at specific wavelengths. The structure of AuNRs at 808 nm and 1064 nm is optimized, and the size of AuNRs, which can obtain the maximum photoacoustic signal is obtained theoretically. Meanwhile, considering that it is difficult to achieve uniform size when synthesizing nanorods, the size range of nanorods with a photoacoustic efficiency threshold of 95% is given.

Keyword: Photoacoustic; gold nanorods; conversion efficiency; localized surface plasmon resonance; structural optimization

1. Introduction

Photoacoustic imaging (PAI) combines the advantages of optical imaging and ultrasonic imaging, which has a high signal-to-noise ratio, penetration depth, and spatial resolution. As a non-ionizing and non-invasive imaging method, it has great potential in biomedical imaging [1]. The generation of a photoacoustic (PA) signal has four different mechanisms: thermal expansion, vaporization, photochemical reaction, and optical breakdown depending on the laser intensity and other factors [2]. For photoacoustic imaging of biological tissues, the only safe method is the photoacoustic effect based on thermal expansion [2]. However, in terms of photoacoustic conversion efficiency, the photoacoustic effect based on the medium's thermal expansion mechanism is relatively weak, causing photoacoustic imaging based on an endogenous contrast agent to have some defects such as low sensitivity and insufficient contrast [3]. Different exogenous contrast agents have been developed to correct these defects, including small chromophores, fluorescent proteins, carbon nanoparticles, semiconductors, and plasmonic nanomaterials [4], [5]. Plasmonic nanomaterials, represented by gold nanoparticles (AuNPs), have been investigated due to their unique advantages. First, AuNPs have strong light absorption/scattering characteristics due to the localized surface plasmon resonance (LSPR) effect [6]. Second, because of their simple fabrication, various synthesis methods, and various forms, such as rods, cages, and shells, they have numerous choices in practical application [7], [8]. Most importantly, their stable surface chemistry makes them biologically inert [9] and easy to bind with targeted ligands [10]. Therefore, gold nanoparticles as contrast agents have been widely utilized in photoacoustic imaging [11]-[14].

With the successful application of photoacoustic imaging of biological tissues with gold nanoparticles as a contrast agent, research on the photoacoustic response mechanism and influencing factors of gold nanoparticles has garnered a great deal of attention. Due to the simplicity of their structure, research on the mechanism of the photoacoustic effect of gold nanoparticles is mostly focused on spherical nanoparticles, and some important results have been obtained. Chen et al. [15] theoretically calculated the photoacoustic signal of the ideal model of gold nanospheres in water. Combined with the experimental verification, it was proved that the photoacoustic signal generated by AuNP in the medium mainly came from the surrounding medium. Moreover, they found that the photoacoustic signal generated by AuNP is responsible for less than 1% of the detected signal strength. Hatef et al. [16] calculated the photothermal/photoacoustic responses of Au-Ag nanospheres with different proportions under the action of nanosecond pulse laser using the finite element method, and proved that the photothermal/photoacoustic response of Au-Ag alloy nanospheres is better than that of pure Au or Ag. Yu et al. [17] systematically studied the effects of geometry, surrounding media, laser intensity, and laser pulse width on the photoacoustic response of SiO₂-coated gold nanoshell in the near-infrared band by using the finite element method,

and optimized the structure of the gold nanoshell. Kumar et al. [18] studied the effects of the arrangement, proportion, and thickness of Au and SiO₂ in nanospheres on photoacoustic signals using the finite element method, providing an optimization strategy for practical application. Shahbazi et al. [19] obtained the analytical solution for the photoacoustic response of core-shell nanospheres. On this basis, the effects of interface thermal resistance and the pulse laser waveform on photoacoustic signals of nanospheres are studied, and the proportion of photoacoustic signals generated by the shell and water layer is investigated. It is proved that the water layer radius that can generate photoacoustic signals is twice that of the spherical radius.

While the photoacoustic effect of gold nanospheres has been investigated thoroughly, the LSPR wavelength of gold nanospheres is generally located in the visible region [20]-[22], which has a relatively small penetration depth in biological tissue. Therefore, the gold nanosphere is not the best choice for photoacoustic imaging in the near-infrared region. Compared with other morphologies, nanorods have more potential applications in the near-infrared region due to their advantages of simple synthesis and easily spectral tuning [25]. The photoacoustic effect of gold nanorods has been studied. Chen et al. [26] proposed a synthesis method for miniature gold nanorods, which proved that the properties of miniature gold nanorods were theoretically and experimentally more effective compared to regular-sized gold nanorods (AuNRs). Shi et al. [27] studied the quantitative relationship between the photoacoustic conversion efficiency and the size of gold nanospheres and nanorods. It was found that the optimal sizes of gold nanospheres and gold nanorods were 60 nm in diameter and 56 nm × 16 nm in length and width respectively. However, the optimization of gold nanorods is carried out under the condition of a fixed aspect ratio, and the optimization results are not valid for typical excitation wavelengths (the optimization is carried out at the positions of LSPR peaks of different sizes of nanorods). The mechanism for the photoacoustic effect of uncoated gold nanorods is understood, but there is a lack of theoretical guidance for selecting the size of uncoated gold nanorods under different incident lasers. At present, there is still a lack of discussion on the size range of gold nanorods with optimal photoacoustic conversion ability at typical excitation wavelengths.

In this work, the finite element method is used to study the photoacoustic effect of AuNRs in an aqueous solution. The effects of orientation of AuNRs, incident laser wavelength, and size of AuNRs on the photothermal response, photoacoustic response, and photoacoustic conversion efficiency of AuNRs are systematically analyzed through simulation. The principle of size selection of gold nanorods at specific wavelengths is proposed. Furthermore, the structures of AuNRs at typical excitation wavelengths (808 nm and 1064 nm) are optimized to achieve the highest photoacoustic signal.

2. Photoacoustic response model of the AuNP

2.1 Physical process

The LSPR effect of the gold nanoparticle in an aqueous solution occurs due to laser irradiation. The gold nanoparticle scatters part of the pulse laser energy, and the other part is absorbed and converted into thermal energy, which leads to a rapid temperature rise of the gold nanoparticle within a short period. The temperature difference between the gold nanoparticle and the surrounding water induces a nanosecond heat transfer process, causing a rapid temperature change of the surrounding water. As a result, thermal expansion occurs in the surrounding water, which means that the water will produce elastic stress and strain, resulting in pressure changes. The pressure change will cause acoustic wave-propagation, which can be detected as a real-time PA signal. The whole physical process is shown in Figure 1.

Figure 1

2.2 PA response model

When the gold nanoparticle is illuminated by a linearly polarized plane wave with frequency ω , the electric field $\mathbf{E}(\mathbf{r})$ can be calculated by the Helmholtz equation [28]:

$$\nabla \times \mu_r^{-1} [\nabla \times \mathbf{E}(\mathbf{r})] - k_0^2 (\varepsilon_r - j \frac{\sigma}{\omega \varepsilon_0}) \mathbf{E}(\mathbf{r}) = 0 \quad (1)$$

where μ_r , ε_r , and σ are relative permeability, relative permittivity, and conductivity, respectively; k_0 is the wavenumber.

C_{abs} , C_{sca} , and C_{ext} are the absorption, scattering, and extinction cross sections of the gold nanoparticle respectively, which can be calculated by:

$$C_{\text{abs}} = \frac{1}{I_0} \iiint q_r dV \quad (2a)$$

$$C_{\text{sca}} = \frac{1}{I_0} \iint (\mathbf{n}_1 \cdot \mathbf{S}_{\text{sca}}) dS \quad (2b)$$

$$C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}} \quad (2c)$$

where q_r is the resistive heating, I_0 is the incident laser fluence, $\mathbf{n}_1$ denotes the normal vector pointing outwards from the particle surface, and $\mathbf{S}_{\text{sca}}$ is the Poynting vector.

The absorbed electromagnetic energy is converted into thermal energy of the gold nanoparticle, which can be calculated as the resistive heating q_r [16]:

$$q_r = \mathbf{J} \cdot \mathbf{E} \quad (3)$$

where $\mathbf{J}$ is the current density, and $\mathbf{E}$ is the electric field strength.

For non-spherical nanoparticles, the equivalent radius r_{eff} is usually used to represent its size, which is defined as:

$$r_{\text{eff}} = \sqrt[3]{\frac{3V}{4\pi}} \quad (4)$$

where V is the volume of the gold nanoparticle. For gold nanorods, the aspect ratio is defined as the ratio of the total length of the long axis to the total radial length. The absorption and scattering efficiency (Q_{abs} and Q_{sca}) of the gold nanoparticle are defined as:

$$\begin{cases} Q_{\text{abs}} = C_{\text{abs}} / (\pi r_{\text{eff}}^2) \\ Q_{\text{sca}} = C_{\text{sca}} / (\pi r_{\text{eff}}^2) \end{cases} \quad (5)$$

The temperature of the gold nanoparticle rises rapidly because of resistance heating. When illuminated by a nanosecond pulsed laser, the electron temperature of the gold nanoparticle is equal to the lattice temperature. Therefore, the heat transfer between the gold nanoparticle and water is in thermodynamic equilibrium [29]. The heat transfer and temperature distribution in the gold nanoparticle and surrounding water can be calculated by the transient Fourier heat conduction equation [30]:

$$\rho c \frac{\partial T}{\partial t} = \nabla \kappa \nabla T + q_r * f(t) \quad (6)$$

where ρ , c , κ , and T are the density, heat capacity, thermal conductivity, and temperature, respectively. Here, the function, $f(t)$, represents the temporal Gaussian-shaped laser pulse, which is defined as:

$$f(t) = \frac{1}{\delta \sqrt{2\pi}} \exp \left[-\frac{(t - t_0)^2}{2\delta^2} \right] \quad (7)$$

where t is the time, t_0 is the time position of the center of the peak, and $\delta = t_w / (2\sqrt{2\ln 2})$ is the standard deviation.

Here, t_w is the full width at half-maximum of the Gaussian profile.

Linear thermal expansion occurs due to an increased temperature in the gold nanoparticle and the surrounding water. The corresponding stress-strain tensor can be calculated by the Duhamel-Hookes equation [29]:

$$\mathbf{s} = \mathbf{C} : (\boldsymbol{\varepsilon} - \alpha (T - T_0)) \quad (8)$$

where $\mathbf{s}$ is the total stress tensor, $\mathbf{C}$ is the fourth-order elasticity tensor related to shear and bulk modulus, “:” is defined as the double-dot product, $\boldsymbol{\varepsilon}$ is the total strain tensor, α is the thermal expansion coefficient, and T_0 is the

reference temperature.

The convection of fluid in the whole process of thermal expansion is ignored. Therefore, the water medium around the gold nanoparticle can be regarded as a solid, and its elastic properties can be represented by shear and bulk moduli [32].

The thermal expansion-induced total displacement $\mathbf{u}$ can be calculated from the total stress tensor $\mathbf{s}$ through the following equation [16]:

$$\nabla \mathbf{s} = \rho \frac{\partial^2 \mathbf{u}}{\partial t^2} \quad (9)$$

The acoustic pressure change can be calculated from the thermal expansion-induced total displacement $\mathbf{u}$ by [16]:

$$\mathbf{n}_2 \cdot \left(\frac{1}{\rho} \nabla p_t \right) = -\mathbf{n}_2 \cdot \frac{\partial^2 \mathbf{u}}{\partial t^2} \quad (10)$$

where $\mathbf{n}_2$ is the outward normal to the boundary, and $p_t = p + p_b$ is the total acoustic pressure. Here, p is the PA signal and p_b is the ambient pressure.

The propagation and pressure distribution of the PA signal in the surrounding medium can be obtained by solving the following acoustic wave equation [17]:

$$\frac{1}{\rho v_s^2} \frac{\partial^2 p_t}{\partial t^2} - \nabla \cdot \left[\frac{1}{\rho} (\nabla p_t) \right] = 0 \quad (11)$$

where v_s is the speed of sound.

2.3 Method and verification

In this paper, the commercial software COMSOL Multiphysics based on the finite element method is used to solve a system of coupled partial differential equations in the 3D PA response model of the gold nanoparticle (shown in Figure 2). In order to solve the electromagnetic partial differential equation, the frequency-domain electromagnetic model is used in Domain-I and Domain-II. To solve the partial differential equation of heat transfer, the transient solid heat transfer model is used in Domain-I. To solve the partial differential equation of thermal expansion, the transient structural mechanics model is used in Domain-I; the transient pressure acoustic model is used in Domain-II to solve the partial differential equation of acoustic wave propagation. The coupling variable of electromagnetic and heat transfer is the general heat source of the transient heat transfer model, as shown in Eq. (6). The coupling variable of heat transfer and thermal expansion is the gold nanoparticle's temperature and the

surrounding media. The linear thermal expansion model is used in the transient structural mechanics model. The coupling variables of thermal expansion and sound propagation are the total displacement and total sound pressure at Boundary-I, as shown in Eq. (10). To eliminate the reflected electromagnetic wave's influence on the calculation, the perfectly matched layer (PML) is used as the boundary condition in Domain-II. The spherical wave radiation boundary condition is used at Boundary-II to reduce the influence of reflected sound wave.

Figure 2

The verification of the electromagnetic model has been completed in our previous work [33]. The dielectric constant of gold nanoparticles is the same as that in reference [34]. In order to verify the transient heat transfer calculation model in this paper, the temperature distribution of the gold nanosphere center under a nanosecond Gaussian pulse laser is calculated. Meanwhile, the spherical nanoparticle's acoustic signal distribution is calculated to prove the validity of the structural mechanics model and the sound propagation model. The calculation results are compared with those in Refs. [19] and [35], as shown in Figure 3. It can be seen that the results of our model match with the results of the references. The physical parameters in the verification cases are the same as those in the references, as shown in Table 1.

Figure 3

Table 1

3. Results and discussion

This study investigated the photoacoustic response and photoacoustic conversion efficiency of gold nanorods in an aqueous solution. The physical parameters of Au and H₂O are shown in Table 2.

Table 2

3.1 Orientation of AuNRs

Due to the asymmetrical nature of nanorods, there are two angles θ_1 and θ_2 between the orientation of the nanorods and the incident laser, which will affect the absorption characteristics and photoacoustic response of the

gold nanorods, as shown in Figure 4. θ_1 is defined as the angle between the wave number direction $\mathbf{k}$ of the incident laser and the long axis direction $\mathbf{l}$ of the AuNRs. It can be seen from Figure 4(a) that when $\theta_1 = 90^\circ$, the absorption efficiency of AuNRs reaches the maximum value, and the symmetrical distribution gradually decreases on both sides of the peak. On the contrary, when $\theta_2 = 90^\circ$, the absorption efficiency of AuNRs is the minimum, and the absorption efficiency increases gradually on both sides, as shown in Fig. 4 (b). The LSPR effect of AuNRs with laser radiation will change with different θ_1 and θ_2 , which leads to the change of absorption efficiency of AuNRs. In Figure 4(c) and Figure 4(d), the distribution of maximum temperature rise and maximum pressure is similar to that of the absorption efficiency. The results show that the fitting curves are all in the form of $y = y_0 + A \sin(\pi(\theta - \theta_0) / \omega)$ with different fitting coefficients, which indicates that the influence of θ_1 and θ_2 on the photothermal and photoacoustic response of AuNRs is realized by changing the absorption efficiency of AuNRs (The quantitative relationship between the absorption efficiency of gold nanorods and photothermal and photoacoustic responses will be discussed in Section 3.2).

Figure 4

For non-spherically-symmetric nanoparticles, the orientation-averaged absorption efficiency is of practical significance because of the random distribution of nanoparticles in biological tissues. However, it requires a large amount of calculation, especially when considering the photoacoustic response model. Therefore, we compared the absorption characteristics of AuNRs at specific angles ($\theta_1 = 90^\circ$ and $\theta_2 = 0^\circ$) and orientation-averaged absorption characteristics of AuNRs in the optical window of interest (NIR-I: 650-900 nm and NIR-II: 1000-1200 nm [26]), as shown in Figure 5. It can be seen that the spectral absorption efficiencies of gold nanorods with different morphologies for $\theta_1 = 90^\circ$ and $\theta_2 = 0^\circ$ have the same trend as their orientation-averaged counterpart. Therefore, in the following content, the calculation results are all for $\theta_1 = 90^\circ$ and $\theta_2 = 0^\circ$.

Figure 5

3.2 Incident laser wavelength

The absorption, scattering, and photoacoustic properties of AuNRs are highly related to the incident laser wavelength. Figure 6 shows the absorption and scattering efficiencies of the AuNRs with equivalent radius $r_{\text{eff}} = 40$

nm and aspect ratio $AR = 5$ in an aqueous solution in the wavelength range of 600-1400 nm. It can be seen that due to the longitudinal LSPR effect, the absorption efficiency and scattering efficiency of the AuNRs reach a maximum at 1125 nm, and they have a similar distribution. However, as the resonance wavelength is approached, the scattering effect is stronger than the absorption effect. In the present work, it is assumed that all the laser energy absorbed by the AuNRs is converted into thermal energy, and the absorption capacity of the AuNRs depends on the absorption efficiency. Therefore, when the incident laser wavelength is the same as the resonance wavelength, the photothermal conversion ability of the AuNRs is maximized. Therefore, the temperature of the AuNRs is the highest.

Figure 6

The photoacoustic effect is derived from the photothermal effect. The analysis of photothermal properties of gold nanorods is beneficial to understand the variation in the photoacoustic response. The photothermal responses of the AuNRs in an aqueous solution at different laser wavelengths are studied when the peak pulse fluence of the pulse laser I_0 is 1 MW/cm² and the pulse half-width t_w is 5 ns, as shown in Figure 7. It can be seen that when the laser incidence fluence is the same, the change of the maximum temperature rise of the AuNRs at different laser wavelengths is due to the different absorption efficiency, which means that the photothermal conversion ability of the AuNRs changes.

All media that undergo temperature change, including gold nanorods and water, generate sound pressure signals. Therefore, the temperature distributions of gold nanorods and water in radial and axial directions at different incident laser wavelengths are studied when the gold nanorods reach the maximum temperature, as shown in Figure 7(b) and Figure 7(c), respectively. It can be seen that the temperature distribution of gold nanorods and surrounding water media changes at different incident laser wavelengths. However, because the thermal conductivity of the AuNRs is far greater than that of water, the radial temperature distribution of the AuNRs is basically uniform, while the water medium presents a large temperature gradient. Meanwhile, in Figure 7(c), the central temperature of the AuNRs is slightly higher than that of the two ends. The longitudinal size of the AuNRs is several times larger than the transverse size, and the higher the temperature of the AuNRs, the more inhomogeneous the temperature distribution inside the AuNRs. When the incident laser wavelength is 1125 nm, the maximum temperature difference between the center temperature and the two ends of the gold nanorods is 2.2 K, that is, the central temperature of the gold nanorods is $0.58\% < 1\%$ higher than that of the two ends, which can be ignored. Therefore, the internal temperature of AuNRs can be regarded as uniform.

However, a larger temperature rise does not necessarily represent a stronger sound pressure signal. In fact, the sound pressure signal's strength is affected by many factors, such as temperature gradient, thermal expansion range, and detection point. Here, the effect of temperature gradient on the sound pressure signal is analyzed. It can be seen from Figure 7(d) that the temperature gradient mainly exists in the water medium, while the temperature gradient inside the gold nanorods can be ignored compared with the surrounding water medium. Therefore, the sound pressure signal detected mainly comes from water, while the gold nanorods themselves could barely generate photoacoustic signal, which has also been pointed out by Ref. [15] that the photoacoustic signal generated by the gold nanosphere accounts for less than 1% of the total photoacoustic signal.

Figure 7

Furthermore, the photoacoustic response and photoacoustic conversion efficiency of gold nanorods at different incident laser wavelengths are investigated, as shown in Figure 8. The photoacoustic conversion efficiency of the AuNRs in an aqueous solution is defined as [26]:

$$\Phi_{PA} = \frac{E_{acoustic}}{E_{thermal}} = \frac{\iint p^2 / R dS dt}{\int C_{abs} I dt} \quad (12)$$

where, $E_{acoustic}$ is the sound energy of the photoacoustic system, $E_{thermal}$ is the thermal energy, $R = \rho_{H_2O} c_{H_2O}$ is the acoustic impedance of water, and S is the spherical surface with enough size containing the gold nanorods, so that the heat will not escape from the S plane.

Figure 8(a) shows that the sound pressure signal profile at different incident laser wavelengths is the same, but the amplitude of the sound pressure signal is different. According to Figure 7(a) and Figure 8(a), the change of the sound pressure signal's amplitude is similar to that of the central temperature of the gold nanorods at different incident laser wavelengths, that is, the higher the absorption efficiency of the gold nanorods corresponding to the incident laser wavelength, the greater the maximum temperature rise of the gold nanorods and the amplitude of the sound pressure signal. Therefore, the photothermal and photoacoustic response of the AuNRs in an aqueous solution has a positive correlation with the absorption efficiency of the AuNRs which are highly related to the incident wavelength. The quantitative relationship between the maximum temperature rise of the AuNRs and the absorption efficiency, and the quantitative relationship between the amplitude of the sound pressure signal and the absorption efficiency are studied. It can be seen in Figure 8(b) that the maximum temperature rise and the amplitude of sound pressure signal are directly proportional to the absorption efficiency. It also means that the amplitude of the sound

pressure signal is proportional to the maximum temperature rise in the center of the AuNRs, consistent with the conclusion in Ref. **Error! Reference source not found.**

As contrast agents, gold nanorods with higher photoacoustic conversion efficiency can improve the signal-to-noise ratio of photoacoustic imaging [27]. The thermal and acoustic energy corresponding to different absorption efficiency of AuNRs is studied according to Eq. (12) as shown in Figure 8(c). It can be seen that the thermal energy is directly proportional to the absorption efficiency, while the sound energy is in second order in proportion to the absorption efficiency. Furthermore, Figure 8(d) shows that the photoacoustic conversion efficiency of the AuNRs in an aqueous solution is proportional to the absorption efficiency of the AuNRs. Because of the higher absorption efficiency, the maximum temperature rise of the AuNRs will be larger, the temperature gradient mode in the water medium will be larger, and the thermal expansion effect of the water medium will be more significant, which will improve the photoacoustic conversion efficiency of the whole system.

Figure 8

3.3 Size of the AuNRs

Different sizes of AuNRs show significant differences in absorption and photoacoustic properties. An equivalent radius and aspect ratio can accurately describe the size of AuNRs. We first study the influence of these two factors on the absorption characteristics of AuNRs, as shown in Figure 9. Results in Figure 9(a) show that with the increase of aspect ratio, the wavelength of the longitudinal resonance peak of the AuNRs is red shifted, which is similar to the variation of equivalent radius as shown in Figure 9(c). However, in terms of the LSPR effect and maximum absorption efficiency, the aspect ratio and equivalent radius show the opposite trend. Meanwhile, the wavelength of the longitudinal resonance peak of the AuNRs has a positive linear relationship with the aspect ratio AR, and is second order in proportion to the equivalent radius, which can be seen in Figure 9(b) and Figure 9(d). Therefore, when it is necessary to adjust the resonant peak position of the AuNRs, changing the aspect ratio AR will be an effective method.

Figure 9

Then, the effects of size on photothermal and photoacoustic effects of the AuNRs are studied. When the incident laser wavelength is 1125 nm, the absorption efficiencies of gold nanorods with different aspect ratios and

equivalent radius are not equal, as shown in Figure 9. To eliminate the influence of absorption efficiency on the photothermal and photoacoustic effects of the AuNRs, the fluence of the pulsed laser $I_{AR=i}$ for different aspect ratio gold nanorods satisfies $\int I_{AR=i} C_{abs}^{AR=i} dt = \int I_0 C_{abs}^0 dt$. Here, I_0 and C_{abs}^0 are constants and $C_{abs}^{AR=i}$ is the absorption cross section at 1125 nm for $AR = i$. Meanwhile, the incident laser radiation fluence $I_{r_{eff}=j}$ satisfies

$$\int I_{r_{eff}=j} \frac{Q_{abs}^{r_{eff}=j}}{r_{eff}} dt = \int I_0 \frac{Q_{abs}^0}{r_{eff}} dt \quad \text{for gold nanorods with different equivalent radius.}$$

It can be seen in Figure 10(a) and Figure 10(b) that when the equivalent radius of the AuNRs is set as constant, the surface area of the AuNRs increases with the increase of aspect ratio. Meanwhile, the maximum temperature rise decreases linearly with the surface area, while the amplitude of detected sound pressure signal increases, and the photoacoustic conversion efficiency increases linearly with the surface area of AuNRs. The reason is that the surface area of AuNRs increases, which makes the heat transfer area of AuNRs increase. With the heat transfer ability of AuNRs increasing, the water medium gains more thermal energy. For the sound pressure generated by water around the gold nanospheres, there is an approximate formula $p = Q_r \frac{\rho_{H_2O}}{4\pi r_{probe}} \left(\frac{\beta}{\rho c_p} \right)_{H_2O}$ [27]. Therefore, the amplitude of the detected sound pressure signal is significantly increased, and the photoacoustic conversion efficiency is significantly improved. Similar trends can be seen in Figure 10(c) and Figure 10(d). However, compared with the aspect ratio, with the variation of equivalent radius the maximum temperature rise and photoacoustic conversion efficiency of AuNRs change nonlinearly. The reason for the non-linear trend may be that the variation of equivalent radius changes the range of the surrounding water medium which can produce a thermal expansion effect (This range is generally twice the equivalent radius [19]).

Figure 10

3.4 AuNRs size optimization

When gold nanoparticles are used for tissue therapy or imaging in vivo, particle transmission through cell membrane will be affected by an increase in particle size, and it may also cause additional problems [36]. Therefore, the size of gold nanoparticles should be controlled in the application. An existing study has shown that the size limit of gold nanoparticles in vivo should be less than 100 nm [37]. In the present work, the total length L of nanorods is between 30 nm and 100 nm, and the aspect ratio AR is between 2 and 8. In order to facilitate the process in the

above discussion, the equivalent radius r_{eff} is used to describe the size of nanorods, and it ranges from 10.2 nm to 14.1 nm.

According to the above discussion, in order to obtain the highest photoacoustic conversion efficiency of AuNRs at a specific incident laser wavelength, it is necessary to optimize the AuNRs from the following three aspects:

- (1) At the incident laser wavelength, the absorption cross section of unit volume $Q_{\text{abs}}/r_{\text{eff}}$ should be as large as possible;
- (2) The aspect ratio AR of AuNRs should be as large as possible;
- (3) The equivalent radius r_{eff} of AuNRs should be as small as possible.

In the NIR-I and NIR-II, the typical excitation wavelengths are 808 nm and 1064 nm, respectively. We calculate the unit volume absorption cross-sections of different sizes of AuNRs at 808 nm and 1064 nm, as shown in Figure 11(a) and Figure 11(b), respectively. The calculation interval of equivalent radius and aspect ratio is 0.1. When the incident laser wavelength is 808 nm, the absorption cross-section in a unit volume of AuNRs ($Q_{\text{abs}}/r_{\text{eff}}$) with aspect ratio AR of 4.0 and equivalent radius r_{eff} of 10.2 nm is the largest (marked in Fig. 11(a)). Meanwhile, when the incident laser wavelength is 1064 nm, the $Q_{\text{abs}}/r_{\text{eff}}$ value of AuNRs with aspect ratio AR of 6.5 and an equivalent radius of r_{eff} of 10.2 nm is the largest (marked in Fig. 11(b)). Since the photoacoustic effect is the derivative effect of the photothermal effect of AuNRs, the size of maximum $Q_{\text{abs}}/r_{\text{eff}}$ should be noted first. The photoacoustic conversion efficiency of the region near the size of interest is then calculated. The structure of AuNRs with the largest photoacoustic signal (the strongest photothermal conversion ability and the highest photoacoustic conversion efficiency) is obtained, as shown in Table 3. However, it is difficult to synthesize gold nanorods with the same morphology (aspect ratio and equivalent radius) in practical applications. Therefore, it is necessary to obtain the size range in which the photoacoustic conversion efficiency exceeds a certain threshold. Here, we take 95% of the maximum photoacoustic efficiency of AuNRs at a specific wavelength as the threshold, and obtain the corresponding size range, as shown in Table 3. When observing and counting the morphology of gold nanorods, the equivalent radius and aspect ratio are not intuitive enough. Therefore, the optimized size range is expressed by the length L and circumference radius r of gold nanorods, as shown in Figure 12.

Figure 11

Table 3

Figure 12

4. Conclusions

In this work, the effects of nanorod orientation, incident laser wavelength, aspect ratio, and equivalent radius, on the photothermal response, photoacoustic response, and photoacoustic conversion efficiency of AuNRs in an aqueous solution are studied by using the finite element method. It is found that the absorption efficiency distribution of gold nanorods for $\theta_1 = 90^\circ$ and $\theta_2 = 0^\circ$ is quite similar to that of gold nanorods with average anisotropy in the near-infrared band, which means that the results for $\theta_1 = 90^\circ$ and $\theta_2 = 0^\circ$ are meaningful for practical application when studying other factors. The incident laser wavelength affects the photoacoustic response and photoacoustic conversion efficiency of AuNRs by changing the absorption efficiency, and the photoacoustic conversion efficiency of AuNRs is directly proportional to the absorption efficiency. The change of the size of AuNRs (including aspect ratio and equivalent radius) will affect the heat transfer efficiency of the AuNRs. Generally, the increase of aspect ratio and the reduction of the equivalent radius are expected to increase the heat transfer efficiency and improve the photoacoustic characteristics.

Stronger photoacoustic signals are more favorable for photoacoustic image reconstruction. Therefore, the size of AuNRs at 808 nm and 1064 nm are optimized and the structures of AuNRs with the strongest photoacoustic signals at the two wavelengths are obtained. Meanwhile, considering that the size of gold nanorods can not be completely consistent in practical application, all the sizes with photoacoustic efficiency above 95% of the maximum photoacoustic efficiency at two excitation wavelengths are given. The discussion in this paper helps explain the photoacoustic effect of gold nanorods and provides a reference for the practical application of gold nanorods. The focus of this research is a single gold nanorod, which suggests the results obtained are suitable for a dilute colloidal solution of gold nanorods. It should be noted that gold nanoparticles may aggregate in cells. In the future, the effect of LSPR enhancement and scattering between particle aggregates on the photoacoustic effect will be further studied.

Declarations

Funding

This project has received funding from the National Natural Science Foundation of China (51806047), China Postdoctoral Science Foundation (2019T120264), Natural Science Foundation of Heilongjiang Province (LH2019E047), Heilongjiang Postdoctoral Science Foundation (LBH-Z18094), and the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 839641.

Conflicts of interest/Competing interests

The authors have no conflicts of interest to declare that are relevant to the content of this article.

Availability of data and material

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Code availability

Not applicable.

Authors' contributions

J.P.S.: Investigation, Methodology, Data analysis, Writing - original draft, Writing - review & editing. **Y.T.R.:** Conceptualization, Methodology, Supervision, Writing - review & editing. **D.H.J.:** Investigation, Methodology, Data analysis. **M.J.H.:** Methodology, Data analysis, Writing - review & editing. **B.H.G.:** Methodology, Data analysis, Writing - review & editing. **H.Q.:** Conceptualization, Supervision, Writing - review & editing.

Ethics approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

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Table Captions

Table 1 Settings of physical parameters in the verification examples

Table 2 Physical parameters have been used for PA model in this paper

Table 3 Results of AuNRs optimization

Figure Captions

- Fig. 1** Schematic of physical process of photoacoustic effect of the gold nanoparticle.
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- Fig. 3** Validation of present model: (a) Gaussian profile of pulsed laser and temperature profile distribution of the gold nanosphere; (b) temporal profile of the normalized PA pulse generated by a gold nanosphere heated by Gaussian pulse.
- Fig. 4** The absorption efficiency, photothermal response and photoacoustic response of AuNRs with equivalent radius $r_{\text{eff}} = 30$ nm and aspect ratio $AR = 3$ at 774 nm (longitudinal resonance wavelength): (a) absorption efficiency as a function of θ_1 when $\theta_2 = 0^\circ$; (b) absorption efficiency as a function of θ_2 when $\theta_1 = 90^\circ$; (c) maximum temperature rise and maximum pressure as a function of θ_1 irradiated by a 5 ns, 1 MW/cm² Gaussian pulse laser; (d) maximum temperature rise and maximum pressure as a function of θ_2 irradiated by a 5 ns, 1 MW/cm² Gaussian pulse laser.
- Fig. 5** Absorption efficiency of gold nanorods with different structures: (a) $\theta_1 = 90^\circ$ and $\theta_2 = 0^\circ$; (b) orientation average.
- Fig. 6** Optical efficiency of AuNRs with equivalent radius $r_{\text{eff}} = 40$ nm and aspect ratio $AR = 5$.
- Fig. 7** Photothermal response of AuNRs with equivalent radius $r_{\text{eff}} = 40$ nm and aspect ratio $AR = 5$ under different laser wavelengths: (a) central temperature distribution of AuNRs; (b) temperature distribution of radial section at $t = 11.4$ ns; (c) temperature distribution of axial section at $t = 11.4$ ns; (d) temperature gradient mode distribution along the axial central section at 1125 nm.
- Fig. 8** PA response and photoacoustic conversion efficiency of AuNRs at different incident laser wavelengths: (a) temporal profile of sound pressure signal at different incident laser wavelengths; (b) maximum temperature rise and maximum pressure as a function of absorption efficiency; (c) thermal and acoustic energy distribution as a function of absorption efficiency; (d) photoacoustic conversion efficiency as a function of absorption efficiency.
- Fig. 9** Absorption characteristics of gold nanorods with different sizes: (a) absorption efficiency distribution of gold nanorods with different aspect ratio and equivalent radius $r_{\text{eff}} = 50$ nm; (b) longitudinal resonance wavelength as a function of aspect ratio; (c) absorption efficiency distribution of gold nanorods with different equivalent radius and aspect ratio $AR = 3$; (d) longitudinal resonance wavelength as a function of equivalent radius.
- Fig. 10** Photothermal and photoacoustic properties of AuNRs with different size: (a) distribution of maximum temperature rise and maximum pressure of AuNRs with different aspect ratio and equivalent radius $r_{\text{eff}} = 50$ nm; (b) photoacoustic conversion efficiency as a function of surface area; (c) distribution of maximum temperature rise and

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Fig. 11 Distribution of absorption cross section per unit volume $Q_{\text{abs}}/r_{\text{eff}}$ of AuNRs with different size and aspect ratio at wavelength: (a) 808 nm; (b) 1064 nm.

Fig. 12 Circumference radius and length of gold nanorods at an excitation wavelength of 808 nm and 1064 nm, ensuring that the photoacoustic conversion efficiency is larger than 95% of the maximum conversion efficiency.

Table 1 Settings of physical parameters in the verification examples [19]

Parameters	Symbol	Value
Density of gold	ρ_{Au}	18900 kg/m ³
Density of water	$\rho_{\text{H}_2\text{O}}$	1000 kg/m ³
Thermal conductivity of gold	κ_{Au}	318 W/m/K
Thermal conductivity of water	$\kappa_{\text{H}_2\text{O}}$	0.6 W/m/K
Shear modulus of gold	G_{Au}	28×10^9 N/m ²
Bulk modulus of gold	K_{Au}	165×10^9 N/m ²
Shear modulus of water	$G_{\text{H}_2\text{O}}$	0 N/m ²
Bulk modulus of water	$K_{\text{H}_2\text{O}}$	2.0×10^9 N/m ²
Linear expansion coefficient of gold	α_{Au}	42×10^{-6} 1/K
Linear expansion coefficient of water	$\alpha_{\text{H}_2\text{O}}$	70×10^{-6} 1/K
Heat capacity of gold	c_{Au}	130 J/kg/K
Heat capacity of water	$c_{\text{H}_2\text{O}}$	4200 J/kg/K

Table 2 Physical parameters have been used for PA model in this paper.

Parameters	Formula	Unit
Density Au [31]	$\rho_{Au} = 19501.44 - 0.6933844T - 2.041944 \times 10^{-4}T^2 + 4.297982 \times 10^{-8}T^3$	kg/m ³
Density H ₂ O [31]	$\rho_{H_2O} = 838.466135 + 1.40050603T - 0.0030112376T^2 + 3.71822313 \times 10^{-7}T^3$	kg/m ³
Thermal conductivity Au [31]	$\kappa_{Au} = 330.6431 - 0.02536626T - 8.191375 \times 10^{-5}T^2 + 6.792908 \times 10^{-8}T^3 - 2.15362 \times 10^{-11}T^4$	W/(m·K)
Thermal conductivity H ₂ O [31]	$\kappa_{H_2O} = -0.869083936 + 0.00894880345T - 1.58366345 \times 10^{-5}T^2 + 7.97543259 \times 10^{-9}T^3$	W/(m·K)
Poisson coefficient Au [31]	$\nu_{Au} = 0.4403494 + 8.884688 \times 10^{-6}T - 1.158876 \times 10^{-8}T^2 + 1.023495 \times 10^{-11}T^3$	1
Young modulus Au [31]	$Y_{Au} = 7.736733 \times 10^{10} + 425187.2T - 20070.07T^2$	GPa
Shear modulus H ₂ O [17]	$G_{H_2O} = 1.3 \times 10^{-5}$	N/m ²
Bulk modulus H ₂ O [17]	$K_{H_2O} = 2.15 \times 10^9$	N/m ²
Linear expansion coefficient Au [31]	$\alpha_{Au} = \frac{a_{Au}(T) + \frac{(T_0 - 293)[a_{Au}(T) - a_{Au}(T_0)]}{T - T_{ref}}}{1 + a_{Au}(T_0)(T_0 - 293)}$ $a_{Au} = 1.310696 \times 10^{-5} + 2.762787 \times 10^{-9}T$	1/K
Linear expansion coefficient H ₂ O [16]	$\alpha_{H_2O} = 7 \times 10^{-5}$	1/K
Heat capacity Au [31]	$c_{Au} = 399352.2T^{-2} + 114.8987 + 0.03228805T$	J/(kg·K)
Heat capacity H ₂ O [31]	$c_{H_2O} = 12010.1471 - 80.4072879T + 0.309866854T^2 - 5.38186884 \times 10^{-4}T^3 + 3.62536437 \times 10^{-7}T^4$	J/(kg·K)

Table 3 Results of AuNRs optimization

Wavelength λ [nm]	Equivalent radius r_{eff} [nm]	Aspect ratio AR	Photoacoustic conversion efficiency
808 nm	10.2	4.0	Maximum
	[10.2, 11.8]	4.0	95% of the maximum
1064 nm	10.2	6.5	Maximum
	[10.2, 11.6]	6.4	95% of the maximum
	[10.2, 10.8]	6.5	95% of the maximum

Fig. 1 Schematic of physical process of photoacoustic effect of the gold nanoparticle.

Fig. 2 Schematic of the PA response model of the gold nanoparticle.

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Fig. 7 Photothermal response of AuNRs with equivalent radius $r_{\text{eff}} = 40$ nm and aspect ratio $AR = 5$ under different laser wavelengths: (a) central temperature distribution of AuNRs; (b) temperature distribution of radial section at $t = 11.4$ ns ; (c) temperature distribution of axial section at $t = 11.4$ ns ; (d) temperature gradient mode distribution along the axial central section at 1125 nm.

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Fig. 9 Absorption characteristics of gold nanorods with different sizes: (a) absorption efficiency distribution of gold nanorods with different aspect ratio and equivalent radius $r_{\text{eff}} = 50$ nm; (b) longitudinal resonance wavelength as a function of aspect ratio; (c) absorption efficiency distribution of gold nanorods with different equivalent radius and aspect ratio AR = 3; (d) longitudinal resonance wavelength as a function of equivalent radius.

Fig. 10 Photothermal and photoacoustic properties of AuNRs with different size: (a) distribution of maximum temperature rise and maximum pressure of AuNRs with different aspect ratio and equivalent radius $r_{\text{eff}} = 50$ nm; (b) photoacoustic conversion efficiency as a function of surface area; (c) distribution of maximum temperature rise and maximum pressure of AuNRs with different equivalent radius and aspect ratio $AR = 3$; (d) photoacoustic conversion efficiency as a function of surface to volume ratio.

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Figures

Figure 1

Schematic of physical process of photoacoustic effect of the gold nanoparticle.

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Schematic of the PA response model of the gold nanoparticle.

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