Understanding the Spatiotemporal Resolution of Near-Field Photoacoustics from Nanostructures

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It is well known that gold nanoparticles can readily tune the optical absorption spectrum by their size and geometry, which can resonantly enhance photoacoustic imaging, targeted photothermal therapy and stimulation, as well as drug delivery. When gold nanorods are molecularly targeted to cells, they can act as nanoscale transducers that amplify the acoustic signals triggered by light, known as the photoacoustic effect. However, the majority of the existing studies focus on the far-field photoacoustic signals that can be measured with an ultrasound transducer, much less is known in the near-field regime where the photoacoustic signal strongly interacts with the cells and cell membrane molecules. Here we discuss the theory and numerical studies of near-field photoacoustic distribution generated by a single gold nanorod upon pulsed laser illumination. Our results show
that the near-field region is much smaller than the wavelength of the associated acoustic pulse, and has a distinct spatial distribution controlled by the geometry of the nanorod. Specifically, the near-field photoacoustic distribution of the nanorod is anisotropic and converges to an isotropic spherical wave at 100 nm away from the nanorod surface. Immediately around the nanorod, the near-field photoacoustic signals decay dramatically, depending on the orientation. The nanorod shows ~75% stronger photoacoustic signal amplitude in the transverse direction (along the short axis of the nanorod) than in the longitudinal direction (along the long axis). We show that the spatial confinement of the photoacoustic signal is also related to the laser pulse width and identify an optimal pulse width in the range of 0.01 ns to 10.44 ns depending on the nanorod’s dimension.

**KEYWORDS:** gold nanoparticles, nano-transducer, near-field, photoacoustics

Gold nanoparticles are one of the most versatile nanoparticles that have been widely used in biomedical research and preclinical studies. Owing to its high tunability, gold nanorods can generate strong absorption in the first and second near-infrared optical windows, where the biological tissues produce relatively low absorption, allowing for a deeper light penetration in the millimeter ranges. Therefore, gold nanorods have also been widely used as contrast and molecular agents for photoacoustic imaging\(^1\)–\(^3\), targeted stimulation\(^4\), and photothermal cancer therapy\(^5\)–\(^7\). It has been shown that the far-field photoacoustic signal of gold nanorods can be optimized with certain nanorod designs, such as miniature nanorod\(^1\), silica-coating\(^8,9\), Polyethylene glycol (PEG) coating\(^10\), and lipid-coating\(^11\). However, the near-field spatiotemporal profiles of the nanorods as nano-transducers are less studied. This might be attributed to the fact that most of the studies employed gold nanorods as photoacoustic imaging agents, where the far-field imaging signals are recorded by an ultrasound transducer, and the near-field photoacoustic signals at the targeted cell are less related to the imaging signals. However, the situation differs dramatically in the case of photothermal therapy, stimulation, and drug release, where the vicinity of a cell is more relevant.
In this paper, we focus on the near-field photoacoustic effect of an individual gold nanorod. To characterize the performance, we calculate the near-field acoustic distribution of the nanorods using analytical approaches and multi-physical simulations. We show that the near-field distribution is anisotropic, yielding 74.6% higher intensity along the transverse direction than in the longitudinal direction. Therefore, the nanorod should be placed in parallel with the targeting molecule for the most effective interaction. We analyze the influence of the laser pulse width and show that it is related to the attenuation rate of the acoustic field. We demonstrate an optimal laser pulse width of 0.01 ns to 10.44 ns depending on the nanorod dimension. We further provide a design principle of the nanorod’s dimension and material composition (coating) to achieve an optimal near-field photoacoustic amplitude.

As illustrated in Fig. 1a, a pulsed laser illuminates a gold nanorod to generate near-field photoacoustic pressure. The gold nanorod absorbs energy from light and induces a photothermal expansion. The time-varying photothermal expansion further generates an acoustic wave. The attenuation rate of the acoustic amplitude over distance is dependent on the laser pulse width (Fig. 1b). The near-field acoustic distribution of the nanorod is anisotropic and is dependent on the laser pulse width (Fig. 1c).

The photoacoustic pressure as a function of the space and the time, \( p(\mathbf{r}, t) \), can be described with the equation:

\[
(\nabla^2 - \frac{1}{v_s^2} \frac{\partial}{\partial t^2}) p(\mathbf{r}, t) = -\frac{\beta}{\kappa v_s^2} \frac{\partial^2 T(\mathbf{r}, t)}{\partial t^2},
\]

where \( v_s \) is the acoustic speed, \( \beta \) is the thermal expansion coefficient, \( \kappa \) is the isothermal compressibility, \( \kappa = \frac{C_p}{\rho v_s^2 C_v} \), \( C_p \) is the heat capacity at constant pressure, and \( C_v \) is the heat capacity at constant volume.
To analyze the near-field photoacoustic pressure, we first calculate the time-dependent thermal profile of a gold nanorod. We simulate the absorption spectrum with a finite element solver (COMSOL Multiphysics 5.5, Electromagnetic Wave, Frequency domain module). By choosing a gold nanorod with 160 nm in length, an aspect ratio of 5.33, and water as the media, the absorption peak of the longitudinal mode of the nanorod falls in the second near-infrared window (Fig. 2a). The temporal profile of the laser pulse is modeled with a Gaussian function, \[ I = P_0 \cdot \exp\left(-\frac{1}{2} \frac{(t-t_0)^2}{\sigma^2}\right), \] where \( P_0 \) is the peak power,

\[ P_0 = \frac{F}{\sqrt{2\pi \sigma}}, \] \( F \) is the fluence, \( \sigma \) is the variance \( \sigma = \frac{w}{2.3548} \), \( w \) is the full width at half maximum of the laser pulse, \( t_0 \) is the center time of the pulse. We assume the laser fluence and pulse width to be 1 mJ/cm\(^2\) and 0.1 ns, respectively; the pulse width is varied in later analysis. The laser pulse width associates with thermal confinement of the nanorod. If the pulse width is much shorter than the thermal relaxation time of the nanorod, the photoacoustic process is thermally confined; otherwise, the photoacoustic process is not thermally confined, where the heat transfer to the immediate media of the nanorod competes with the photothermal heating process. The thermal relaxation time of the nanorod, \( \tau \), defined as the time required to dissipate \( 1 - e^{-1} \) of the thermal energy with an impulse laser input \(^{13}\), is 0.0633 ns (Supplementary Note 3). If one assumes the thermal confinement, the heat transfer between the nanorod and its media is negligible, second derivative of temperature in Eq. (1) can be simplified as

\[ \frac{\partial^2 T}{\partial t^2} = \frac{1}{C_{nr} m_{nr}} \frac{\partial H}{\partial t}, \] (2)

where \( C_{nr} \), \( m_{nr} \), and \( H \) are the heat capacity, mass, and the total absorption power of the nanorod (in a unit of watts). \( H = \sigma_{abs} I \), \( \sigma_{abs} \) is the absorption cross-section of the nanorod. The time derivative of the laser’s intensity is \[ \frac{\partial I}{\partial t} = -\frac{(t-t_0)}{\sigma^2} P_0 \cdot \exp\left(-\frac{1}{2} \frac{(t-t_0)^2}{\sigma^2}\right). \]
The assumed pulse width of Fig. 2, 0.1 ns, is longer than the thermal relaxation time, so the process is not thermally confined. The simulation considering both the heating and cooling processes results in a lower photoacoustic amplitude than the analytical calculation by assuming thermal confinement (Fig. 2b). Fig. 2c shows the time evolution of the acoustic wave generated by the nanorod, which propagates through space with a far-field profile similar to a spherical wave but a distinct feature in the near-field.

The anisotropy of the near-field photoacoustic distribution is attributed to the nanorod’s geometry and acoustic interference. Ignoring the acoustic scattering, we can calculate the photoacoustic field using

$$\delta(t-t' - \frac{|\mathbf{r} - \mathbf{r}'|}{v_s})$$

Green’s function in water $G(\mathbf{r}, \mathbf{r}', t') = \frac{v_s}{4\pi |\mathbf{r} - \mathbf{r}'|}$. The photoacoustic pressure can be simplified as

$$p(\mathbf{r}, t) = \frac{\beta}{4\pi\kappa v_s^2} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial^2 T(\mathbf{r}', t')}{\partial t'^2} \bigg|_{v_s t' = \frac{|\mathbf{r} - \mathbf{r}'|}{v_s}}.$$

When the acoustic source region (the nanorod and its immediate media) is comparably small to their distance to the measurement point, $|\mathbf{r}'| \ll |\mathbf{r}|$, the term $\frac{1}{|\mathbf{r} - \mathbf{r}'|} \approx \frac{1}{|\mathbf{r}|}$. Furthermore, when the laser pulse width is long, the time-shift of the acoustic wave from different part of the acoustic source region is comparably small to the time in a few pulse widths (where the photoacoustic pressure is non-zero), $\frac{|\mathbf{r} - \mathbf{r}'|}{v_s} \ll t$, thus, $t' \approx t$.

With these two approximations, the photoacoustic distribution can be further simplified into a spherical wave:

$$p_{\text{sph}}(\mathbf{r}, t) = \frac{\beta}{4\pi\kappa v_s^2} \frac{1}{|\mathbf{r}|} \int d\mathbf{r}' \frac{\partial^2 T(\mathbf{r}', t)}{\partial t'^2}.$$
However, the assumption $|r| \gg |r'|$ fail to hold in the near-field. Moreover, when the pulse width is short, the time-shift $\frac{|r-r'|}{v}$ becomes significant to the time. Specifically, the positive acoustic pressure generated by one part of the source region may destructively interference with a negative acoustic pressure generated by another part. Both of these two effects lead to the difference of the photoacoustic field distribution comparing to the spherical wave described by Eq. (4).

We define the photoacoustic amplitude as the difference between the maximum and the minimum of the photoacoustic pressure over time, $P(r) = \max(p(r,t), t) - \min(p(r,t), t)$. Note that the temporal profile of the photoacoustic pressure is asymmetrical under thermal non-confinement, so

$$\max(p(r,t), t) - \min(p(r,t), t) \neq 2 \max(p(r,t), t).$$

The calculated 2D map of the photoacoustic amplitude with Eq. (3) using the simulated thermal profile, $P(r)$, of a nanorod is shown in Fig. 2a. For comparison, $P(r)$ of a spherical wave given by Eq. (4), basing on the simulated thermal profile, is shown in Fig. 2b. To elaborate on the anisotropic near-field property of the nanorod, we define a unitless correction coefficient to the spherical wave, $R_p$, which is the differential ratio of the photoacoustic near-field to the spherical wave:

$$R_p(r) = \frac{P(r)}{P_{sph}(r)}.$$  \hspace{1cm} (5)

Fig. 2c shows the 2D distribution of $R_p$, given by the ratio of Fig. 2a and Fig. 2b. Fig. 2d shows the line-profiles of photoacoustic amplitude along the transverse (x) and longitudinal (y) directions, being different from the isotropic spherical waves in the near-field. The near-field pattern of a nanorod is distinct along the two directions within ~50 nm away from the nanorod’s surface and converges with the spherical wave at a longer distance. Fig. 2e also compares the simulated photoacoustic amplitudes and the photoacoustic amplitudes given by Eq. (3). The analytical result is slightly larger than the simulated
value, because the Green’s function method neglects the acoustic energy loss at the boundary of the nanorod. However, the influence of this effect is minor, with a difference smaller than 5% for laser with a pulse width of 0.1 ns and will be even smaller for longer pulse widths. \( R_p \) along the two cutlines are shown in Fig. 2e.

According to Eq. (4) and Eq. (5), the distribution of the photoacoustic amplitude can be written as

\[
P(\mathbf{r}) = \frac{R_p A_0}{|\mathbf{r}|},
\]

(6)

where \( A_0 \) is the photoacoustic source intensity, \( A_0 = \max(A(t),t) - \min(A(t),t) \),

\[
A(t) = -\frac{\beta}{4\pi\kappa\nu_s^2} \int d\mathbf{r}' \frac{\partial^2 T(\mathbf{r}',t)}{\partial t^2}. \]

The absolute distance \(|\mathbf{r}|\) start from the center of the nanorod.

\( R_p \) at the surface of the nanorod is 58.9% along the longitudinal direction and -38.3% along the transverse direction (Fig. 3e). Although the \( R_p \) along the transverse direction is negative, considering its smaller absolution distance, \(|\mathbf{r}|\), the photoacoustic amplitude along the transverse direction is still 74.6% higher than the longitudinal direction (Fig. 3d).

The photoacoustic amplitude varies with the laser pulse width due to both heat transfer and acoustic interference. As shown in Fig. 4a, as the pulse width increases, the heat transfer between the nanorod and its media becomes more significant. At a fixed laser’s fluence of 1 mJ/cm², the second derivative of the nanorod’s thermal energy diverges from the N-shape given by the thermal confinement, and the normalized peak intensity decreases. The thermal energy of the nanorod is calculated as \( Q = \rho C_{\text{nr}} \int_{nr} T dv \).

The N-shape pulse under thermal confinement is calculated as the time derivative of the absorbed energy of the nanorod (according to Eq. (2), see details of the normalization under different pulse widths in Supplementary Note 1). So, the source intensity of the photoacoustic wave, being proportional to the
second derivative of the nanorod’s thermal energy (Eq. (1)), decreases with a higher pulse width. When the pulse width is higher than 0.5 ns, the heat transfer is significant, and the photoacoustic amplitude decreases with the pulse width (Fig. 4c).

On the other hand, when the laser pulse width is short, with a pulse length, defined as the laser pulse width multiply by the acoustic speed $w v_a$, close to or smaller than the nanorod’s size, the positive and negative peaks of the photoacoustic wave generated by a different part of the source region destructively interfere with each other in the near-field (Fig. 4b), which undermines the photoacoustic amplitude. When the pulse width is lower than 0.5 ns, the acoustic interference effect is significant, and the photoacoustic amplitude increases with the pulse width (Fig. 4c). The simulated photoacoustic amplitude shows the same trend with the analytical solution in this region. The difference at a longer pulse width is caused by the thermal non-confinement.

According to Eq. (6), the attenuation of the photoacoustic amplitude over distance is related to $R_p$, and consequently, the laser pulse width. In other words, the laser pulse width will influence the confinement of the photoacoustic field. As shown in Fig. 5a and 5b, when fixing the far-field photoacoustic amplitude at 1 $\mu m$, the near-field photoacoustic distribution is more confined with pulse widths of 0.1 ns and 1 ns. There is an optimal laser pulse width for the most confined photoacoustic field. Since the photoacoustic amplitude will converge to the spherical wave (Eq. (4)) at a distance larger than 100 nm (being far-field), $R_p$ will approach to 1 at a long distance. Considering the typical size of a mammalian cell, which is in a few tens of micrometers \(^ {14}\), anything besides the cell membrane protein that is conjugated (for example, using antibodies) to the nanorod is beyond the near-field region. According to Eq. (6), the far-field photoacoustic amplitude can be written as

$$P_{\text{farfield}} = \frac{P_{\text{nearfield}}}{R_{p,t}} \left| \frac{\mathbf{r}_i}{\mathbf{r}} \right|,$$

where $P_{\text{farfield}}$ and $P_{\text{nearfield}}$ are the far-field and near-field photoacoustic amplitude, $\mathbf{r}_i$ and $R_{p,t}$ are the displacement (with respect to the
nanorod’s center) and $R_p$ of the targeting point. The confinement of the photoacoustic field is uniquely reflected by $R_{p,t}$. A higher $R_{p,t}$ results in a lower far-field amplitude with certain near-field amplitude, in other words, more confined near-field. By comparing $R_p$ in Fig. 4c and the field distribution in Fig. 5b, we can see that $R_p$ is at its peak value with the pulse width between 0.1 ns and 1 ns (Fig 4c), where Fig. 5b shows the most confined near-field.

Given by the simulation shown in Fig. 4c, to reach over 70% of the peak $R_p$, the laser should have a pulse length higher than 0.46 of the nanorod’s length, i.e.,

$$v_s \cdot w > 0.46 \cdot l,$$

and a pulse width shorter than 165.06 of the thermal relaxation time, i.e.,

$$w < 165.06 \cdot \tau .$$

For nanorods with different physical dimensions, both the photoacoustic equation (Eq. (1)) and the heat transfer equation (Supplementary Eq. (S4)) can be scaled up or down of its dependent variables without changing the correction coefficient, $R_p$. Eq. (7) and Eq. (8) remain valid regardless of the nanorod’s size (Supplementary Note 2).

The size of the nanorod can be optimized for the photoacoustic amplitude. We define the scaling factor, $a$, as the ratio of the nanorod’s length with 160 nm. In the multi-physical process of the photoacoustic field generation, there are two differences led by the nanorod’s size: optical absorption and heat transfer. First, nanorods with different sizes yield various absorption efficiency, $Q_{abs} = \frac{\sigma_{abs}}{\sigma_{np}}$, where $\sigma_{np}$ is the physical cross-section of the nanorod. When maintaining the aspect ratio of the nanorod, the resonance wavelength of the nanorod remains
similar in the near-IR regime, and the absorption efficiency also varies marginally with different scaling factors \( a \) (Fig. 6a). The absorption power density per unit volume is \( W = \frac{\sigma_{abs} I}{v_{np}} \), and can be simplified as

\[
W = \frac{Q_{abs}}{a} W_0 ,
\]

where \( W_0 \) is the absorption power density with a nanorod’s length of 160 nm. In general, a smaller nanorod yields a higher absorption power density (Fig. 6b). On the other hand, a smaller nanorod also results in a faster heat transfer, and consequently, stronger cooling effect from the media (Supplementary Note 2). Considering both effects, there is an optimal nanorod dimension for generating photoacoustic near-field amplitude at a given laser pulse width (Fig. 6c). The optimal nanorod size is dependent on the laser pulse width and is approximately linear to the logarithm of the pulse width. For example, for laser pulse widths of 0.1 ns, 1 ns, and 10 ns, the optimal nanorod length is around 50 nm, 65 nm, and 80 nm (Fig. 5c), respectively. Due to the increased thermal energy loss to the media, the photoacoustic amplitude decreases with the pulse width. Note that the photoacoustic amplitude is different from \( R_p \) discussed previously, which measures the differential ratio of the photoacoustic amplitude with the spherical wave amplitude. Both the photoacoustic amplitude and the \( R_p \) decreases with the pulse width for long pulses, but with a different rate. Through linear fitting of the optimal scaling factor with the logarithm of the laser pulse width, the optimal scaling factor is approximately

\[
a_{opt} = c_1 + c_2 \cdot \log(w/1\text{ns}) ,
\]

where the two coefficients are \( c_1 = 0.0591 \) and \( c_2 = 0.402 \). With the optimal dimension, the photoacoustic amplitude can be increased by 64.91%, 56.56%, and 48.36% respectively compared to the nanorod with a length of 160 nm (as shown in Fig. 3c).
The near-field photoacoustic signal can be enhanced by a thermally isolative coating, such as lipid\textsuperscript{11,15,16}, because the nanorod becomes more thermally confined at the same physical length. The second time derivative of the temperature increases with the coating thickness (Fig. 6a). However, the increased separation between the targeting spot and the nanorod undermines the photoacoustic intensity. Due to these two effects, there is an optimal thickness of the shell layer, which is related to the laser pulse width (Fig 6b). The optimal thickness is approximately linear to the pulse width (Fig 6c). By fitting the simulation, we get the relationship as

\[ a_{c, opt} = c_3w + c_4, \]  

where \( a_{c, opt} \) is the ratio of the optimal coating thickness to the nanorod’s length (as 160 nm in Fig. 6), and the two coefficients are \( c_3 = 0.025\text{ns}^{-1} \) and \( c_3 = 0.0487 \).

According to Eq. (7) and Eq. (8), and the optimal nanorod size and lipid coating thickness given by Eq. (10) and Eq. (11), the overall optimal nanorod design and laser pulse width is shown in Fig. 8 to maximize the near-field photoacoustic signal. Specifically, the green region between the black and red curves offers the most confined photoacoustic field; the relationship of the laser pulse width and the nanorod’s size for the optimal photoacoustic amplitude is shown as the blue curve (given by Eq. (10)). Considering all the three conditions, the scaling factor should be between 0.2 and 0.47, which corresponds to a nanorod’s length of 32 nm to 75.2 nm, and the laser pulse width should be 0.011 ns to 4.6 ns depending on the nanorod’s size. The nanorod’s size and the laser pulse width should follow Eq. (10) for the optimal photoacoustic intensity. We can use a thermal isolative coating to further boost the photoacoustic amplitude. The optimal thickness of a lipid coating given by Eq. (11) is shown as the green curve in Fig. 7. The optimal coating for the lower optimal point (intersection of the blue curve and the black curve) is 0.053, corresponding to a thickness of 8.5 nm, and for the higher optimal point (intersection of the blue curve and the red curve) is 0.16, corresponding to 25.6 nm.
In this paper, we develop a systematic analysis of the near-field photoacoustic signals from a gold nanoparticle controlled by the excitation laser pulse width and nanoparticle structures. The laser pulse width is related to the confinement of the photoacoustic field. One can view the spatial confinement of the near-field photoacoustic distribution as the spatial resolution of the nanoparticle, where the near-field photoacoustic signal interacts with the nanoparticle’s immediate medium, such as a cell. We show that there is an optimized near-field photoacoustic signal intensity. The destructive acoustic interference undermines the near-field photoacoustic intensity for short laser pulses, and thermal non-confinement reduces the photoacoustic intensity for long laser pulse.

For most localized interaction, one should choose the laser pulse width according to Eq. (7) and Eq. (8). The nanorod’s size influences the near-field intensity. The absorption power density is higher for a smaller nanorod, on the other hand, the loss of thermal energy to the media is lower for a bigger nanorod. Due to the two effects, there is an optimal nanorod’s size with certain laser pulse width described by Eq. (10). A thermally isolative coating can reduce the thermal dissipation, however, will also increase the separation between the nanorod and the targeting receptor. The optimal coating thickness is linear to the pulse width, as shown in Eq. (11). We further give an optimal pulse width-to-nanorod size region for both good photoacoustic confinement and photoacoustic amplitude, with a nanorod’s length of 32 nm to 75.8 nm, a laser pulse width of 0.011 ns to 4.6 ns, and a coating thickness of 8.5 nm to 25.6 nm.

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Fig. 1 | Schematics of photoacoustic pressure generated by a single gold nanorod showing anisotropy in the near-field and spatial confinement. a, The nanorod absorbs energy from a pulsed laser and generates a confined acoustic pressure. b, Attenuation of the acoustic amplitude over distance with different laser pulse width. c, Distribution of the photoacoustic pressure at different laser pulse width. All pulses are centered at two times of the pulse width, and the photoacoustic pressure is measured at four times of the pulse width.
Fig. 2 | Calculated anisotropic photoacoustic near-field spatial distribution generated by a gold nanorod. 

**a**, Optical absorption spectrum. The laser is circularly polarized to excite both the longitudinal and transverse modes of the nanorod. Note that the particular handedness (left or right) is not critical regarding the nanorod’s absorption. The inset shows the electric field distribution on resonance (at 1100 nm). The absorption spectrum and the electric field distribution are simulated with a finite element solver (COMSOL Multiphysics 5.5, Electromagnetic Wave, Frequency domain module). 

**b**, Absorption and second derivative of temperature as a function of time. The temperature profile is simulated using a finite element solver (COMSOL Multiphysics 5.5, Heat Transfer Module). 

**c**, Numerical simulation of the acoustic wave using the partial differential Eq. (1), simulated using a finite element solver (COMSOL Multiphysics 5.5, PDE Module). The time frames are marked as the red dots in **b**.
Fig. 3 | Influence of nanoparticle orientation on the near-field photoacoustic amplitude. 

- **a,** The near-field acoustic amplitude of a nanorod calculated by Green’s function method. The field inside the nanorod is set as zero.
- **b,** The acoustic amplitude of a spherical wave given by Eq. (4). The source of the spherical wave locates at the center of the nanorod.
- **c,** 2D map of the $R_p$ coefficient, which is the ratio between the near-field amplitude in **a** to the spherical wave in **b.**
- **d,** Photoacoustic amplitude of both the near-field and spherical wave at the two cut lines. The pressures are calculated by multi-physical simulation, Green’s function method (Eq. (3)), and spherical wave approximation (Eq. (4)). T-line: cut line along the transverse direction, L-line: cut line along the longitudinal direction. The distance starts from the surface of the nanorod, as marked in the insets.
- **e,** $R_p$ calculated by simulation and Green’s function at the cut lines.
Fig. 4 | Tuning the near-field photoacoustic amplitude with laser pulse widths. **a**, The second time derivative of the nanorod’s thermal energy, $Q$, with different pulse widths. **b**, $R_p$ distribution at different pulse widths. **c**, $R_p$ on the surface of the nanorod versus the pulse width. The analytical solution is calculated with Green’s function method (Eq. (3)) and condition of thermal confinement (Eq. (2)).
Fig. 5 | Near-field photoacoustic amplitude decays over distance showing spatial confinement. a, 2D map of the acoustic pressure over acoustic pressure at 1 \( \mu m \) along the transverse direction. b, Acoustic pressure versus distance with different pulse width.
Fig. 6 | Optimize photoacoustic near-field amplitude by tuning nanorod dimensions. 

(a) The spectrum of the acoustic efficiency with a different scaling factor. 

(b) $Q_{\text{ac}} / a$, being related to the photoacoustic power density, versus scaling factor. 

(c) The normalized photoacoustic amplitude at different scaling factors. The PA amplitude is measured at the transverse (T) location. 

(d) Optimal nanorod’s size versus logarithm of the laser pulse width.
Fig. 7 | Tuning the near-field photoacoustic amplitude by lipid or dielectric coating. a, The second time derivative of the nanorod’s thermal power, $Q$, and the input power, $H$, with different coating thicknesses. The nanorod has a length of 160 nm, being same as Fig. 2, 3, and 4. b, Photoacoustic amplitude versus shell thickness. The PA amplitude is measured at the H spot. The density, thermal conductivity, and heat capacity of lipid are $1.2 \text{g/cm}^3$, $0.2 \text{W/(m·K)}$, $2348 \text{J/(kg·K)}$. The absorption of the nanorod is taken as a constant. d, Optimal nanorod’s size versus logarithm of the laser pulse width.
Fig. 8 | Design criteria of the laser pulse widths, nanorod materials and dimensions for optimizing near-field photoacoustic amplitude. The three curves are given by conditions in Eq. (7), Eq. (8), Eq. (10), and Eq. (11) respectively. The green region between the black and red curves provides the highest attenuation rate of the photoacoustic field, and the blue curve provides the highest photoacoustic intensity. The blue curve between the two green arrows marks the optimal condition considering both the attenuation rate and the photoacoustic intensity. The x-distance between the blue and the green curve shows the optimal coating thickness of a lipid shell. The green region illustrates the more confined photoacoustic field, yielding $R_p$ over 70% of its peak value.
Supplementary information for Understanding the Spatiotemporal Resolution of Near-Field Photoacoustics from Nanostructures

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**Note 1. Normalization of nanorod’s thermal energy under different laser’s pulse width**

With a Gaussian pulse with a fixed fluence, the optical absorption of the nanorod is

$$H(t) = \frac{F \sigma_{abs}}{\sqrt{2\pi w}} \exp\left(-\frac{1}{2} \frac{(t-t_0)^2}{\sigma^2}\right).$$  \hspace{1cm} (S1)

The time derivative of the optical absorption is

$$H'(t) = -2.3548 \frac{F \sigma_{abs}(t-t_0)}{\sqrt{2\pi w^3}} \exp\left(-\frac{1}{2} \frac{(t-t_0)^2}{\sigma^2}\right).$$  \hspace{1cm} (S2)

Using $t/w$ as variable, the parameter $H'(t)w^2$,

$$H'(t)w^2 = -2.3548 \frac{F \sigma_{abs}(t/w-t_0/w)}{\sqrt{2\pi}} \exp\left(-\frac{1}{2} \frac{1}{2.3548^2(t/w-t_0/w)^2}\right)$$ \hspace{1cm} (S3)

is unrelated to the pulse width. Therefore, we choose $H'w^2$ and $Q''w^2$ as normalized thermal energy of the nanorod.

**Note 2. Rescaling of the thermal equation and photoacoustic equation**

The heat transfer equation of the nanorod is

$$\rho C \frac{dT(r,t)}{dt} = k \nabla^2 T(r,t) + H(r,t),$$ \hspace{1cm} (S4)

where $\rho$, $C$, and $k$ are density, heat capacitance, and thermal conductivity of the model (for gold in nanorod and for water in the media), and $H$ is the absorption power density. When the nanorod is
rescaled by a factor of \( a \), equivalently, the spatial variable is rescaled by \( 1/a \), and the temporal domain is equivalently to be rescaled by \( a \).

\[
\rho C \frac{dT(r_2, t_2)}{dt'} = k \nabla^2 T(r_2, t_2) + H(r_2, t_2),
\]

(S5)

where \( t_2 = at \), and \( r_2 = \frac{1}{a} r \). For example, if the nanorod is reduced to half of its original size, \( a = 0.5 \).

Instead of changing the nanorod’s size, we define the new dependent variables as \( t' = 0.5t \) and \( r_2 = 2r \).

In other words, the space is stretched to twice of its original size, and the heat transfer process is speed up by two times, so the solution of the heat transfer equation remains the same.

The thermal relaxation time is therefore proportional to the scaling coefficient, \( \tau_t = a\tau_{t_0} \), where \( \tau_{t_0} \) is the thermal relaxation time of the nanorod with a length of 160 nm, \( \tau_{t_0} = 0.0633\text{ns} \). By choosing the normalized pulse width, \( W_n \), as used in Fig. 4c, the thermal profile with respect to the normalized position, \( r/a \), remains consistence regardless of the scaling factor.

Similarly, the photoacoustic equation (Eq. (1)) remains unchanged with the normalized position

\[
(\nabla^2 - \frac{1}{v_z^2} \frac{\partial}{\partial t^2})p(r/\alpha,t) = -\frac{\beta}{\kappa v_z^2} \frac{\partial^2 T(r/\alpha, t)}{\partial t^2}.
\]

(S6)

The photoacoustic pressure measured at the surface of the nanorod at the fixed normalized time \( \alpha t \) remains the same per unit absorption power density.

Note 3. Thermal relaxation time

The thermal relaxation time is defined as the time required to cool to \( 1 - e^{-1} \) (63.2%) of its initial thermal
energy. We simulate the decay of the nanorod’s temperature started from a uniform temperature distribution. As shown in Figure S1, the nanorod reach 63.2% of its initial temperature at 0.0633 ns.

**Fig. S1** Cooling of the gold nanorod. The nanorod starts with a uniformed temperature distribution and cool to 63.2% of its initial temperature at 0.0633 ns.

**Note 4. Spectrum of the photoacoustic pulses**

The Fourier transform of the temporal profile of the photoacoustic pulse under thermal confinement (Eq. (2) in the main text) is

\[ |F(p(t))| \sim \sigma f \exp\left(-\frac{1}{2} \sigma^2 f^2\right), \]  

(S7)

where \( f \) is frequency. The peak frequency of the spectrum (i.e., central frequency of the pulse’s spectrum) is \( f_{\text{peak}} = \frac{1}{\sigma} \). Therefore, the peak frequency is reciprocal to the laser pulse width. A shorter laser pulse leads to a higher central frequency of the photoacoustic pulse. As the simulation shown in Fig. S2b, the simulated spectra of the photoacoustic pulses are similar to the analytical solutions, and the central frequency decreases with the laser pulse width. The differences are led by the thermal non-
confinement and acoustic interference.

**Fig. S2** Photoacoustic pulse in the time domain and the frequency domain. (a), Photoacoustic pulse in the time domain. The temporal profile with laser pulse widths, w, being below or equals to 0.1 ns are simulated with multi-physical simulation, and higher than 0.1 ns are calculated with Eq. (1) in the main text with the simulated temperature profile. The analytical solution is given by Eq. (2) in the main text. (b), Spectra of the photoacoustic pulse in (a) and the analytical solution. The analytical solutions are calculated by Eq. S7. Sim. denotes numerical simulations; Anal. denotes analytical calculations.

**Note 5. Anisotropic photoacoustic near field created by isotropic nanoparticles**

The anisotropic photoacoustic distribution can not only be created by anisotropic nanoparticles, such as nanorods illustrated in the main text, but also isotropic nanoparticles with anisotropic arrangement. For example, as shown in Fig. S3b, the photoacoustic amplitude created by three nanospheres is also anisotropic, and the distribution is very similar to the one created by the nanorod (Fig. 3a in the main text). Similar to the nanorod’s photoacoustic field, the photoacoustic wave created by the three nanospheres shows anisotropic distribution in the near field and converges to a spherical wave in the far field (Fig. S3c).
**Fig. S3** Anisotropic photoacoustic near-field created by three isotropic nanospheres. 

**a,** Simulated second time derivative of the nanosphere’s temperature. The nanospheres have a radius of 15 nm and separation of 65 nm. The laser pulse width is 0.1 ns. The absorption power density of the nanospheres is taken same as the gold nanorod. **b,** Distribution of the photoacoustic amplitude along the transverse and longitudinal cutlines. The positions of the cutlines are marked in the inset. **c,** Simulated photoacoustic pressure at different time frames. The time frames are marked with the solid dots in **a.**