Thermoplasmonic Generation of Gold Nanorods Based on Size and Structure

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Abstract: Thermoplasmonic phenomena have emerged as a key area in plasmonic research because of their ability to utilise metallic nanostructures for generating nanoscale heat. Gold nanorods (GNRs) are particularly promising in this field due to their unique geometry, which enables dual plasmonic resonance modes – longitudinal and transverse. These modes allow efficient absorption of light at different wavelengths, which enhances their thermoplasmonic capabilities. GNRs serve as efficient nanoscale heat sources by converting absorbed light into heat through electron–phonon and phonon–phonon interactions. The versatility of plasmonic GNRs has led to widespread applications in biomedical fields, such as photothermal cancer therapy, drug and gene delivery and photoacoustic imaging. However, challenges persists in optimising the control of heat distribution and minimising dependence on costly photothermal agents and devices. Recent developments in photosensitising materials and laser technologies, including diode lasers, have considerably expanded the potential of thermoplasmonic applications in medicine. This study focuses on the impact of size, structure and the surrounding medium on the plasmonic and thermoplasmonic performance of GNRs. The aim is to enhance the efficiency of GNRs in therapeutic and diagnostic applications.

1 INTRODUCTION

Thermoplasmonics has attracted wide interest within the nano-photonics and plasmonics research community due to its immense technological potential. This field utilises metallic nanostructures to generate heat at the nanoscale [1]. Thermoplasmonics combines two fields: nano-thermodynamics and nano-optics. Thermoplasmonics also focuses on controlling heat generation in nanoparticles through light absorption. This absorption is improved and confined close to the nanoparticle surface, which then heats up and acts as a nanoscale heat source [2]-[4]. In contrast to bulk metallic materials, noble metal nanoparticles can control and confine light within nanoscale volumes due to surface plasmin resonance (SPR).

When plasmatic nanoparticles (Au) are exposed to laser light, they oscillate with their resonant surface plasmon oscillation; this oscillation enables them to strongly absorb the light and rapidly convert it into heat through multiple photophysical processes [5]. We have chosen to work with nanorods due to their double absorption bands, which are exhibited by surface plasmons associated with oscillations along the two main axes of nanomaterials [6]. The two characteristic lengths of the nanorod's geometry are intrinsically linked to the excitation of surface plasmons at two different wavelengths. The presence of the two modes provides an advantage over other nanoparticle shapes: one is the longitudinal SPR, and the other is the transverse SPR. Throughout this process, oscillating electrons convey their kinetic energy to the particle lattice via electron-phonon interactions, subsequently followed by phonon-phonon interactions with the surrounding medium [7], [8].

Gaining a predictive understanding of how nanoparticles distribute incident optical energy has been a longstanding challenge, which is difficult to address experimentally with a high degree of certainty [9]. The use of metallic nanoparticles as essential building blocks for sophisticated electronic systems and gadgets is growing

Gold nanorods (GNRs) have extensive biomedical applications due to their unique surface chemistry and electronic and optical properties; these properties depend on the size and shape of the object and the type of surrounding medium [10].

An important step forward is the implementation of selective photothermal analysis in medicine [11]. Over the past decade, efforts have been made to develop novel approaches for cancer treatment. Hyperthermia provides adequate external energy to generate heat in target tissues. Nowadays, hyperthermia is used to destroy tumours [12]. Thermoplasmonics has resulted in significant applications, particularly in biology and medicine, including photothermal cancer therapy, photothermal imaging, drug and gene delivery, and photoacoustic imaging [13].

In recent years, numerous studies have focused on using metallic nanostructures to delivery heat in photothermal applications. Tissue temperature control has been widely used for therapeutic applications in various medical fields, such as oncology, physiotherapy, urology, cardiology, ophthalmology and photothermal therapy [14].

The photothermal effect is attracting great interest due to developments in new photosensitising materials and improved light sources. However, studies are often limited by the need to utilise exogenous photothermal agents and costly irradiation devices [15]. Therefore, a nanoscale heat source that works under laser illumination by generating heat is needed in medical treatments. For example, a diode laser is a monolithic semiconductor device that directly converts electrical energy into laser light. It offers unique levels of power and wavelength scalability, which support a wide range of medical applications. Different semiconductor compositions enable selected wavelengths; for example, GNRs can have output wavelengths in the blue, green, red or near and mid infrared ranges [15]-[18].

Diode lasers for medical applications underscores their exceptional role in revolutionising medical treatments. These lasers offer a compact, efficient and scalable light source suitable for numerous biomedical applications, such as thermoplasmonic therapies. Their ability to deliver precise wavelength outputs tailored for GNRs optimises light absorption, which improves heat generation at the nanoscale. Moreover, the integration of diode lasers with advanced nanoparticle systems such as GNRs opens new possibilities for minimally invasive and highly targeted treatments, particularly in oncology and physiotherapy [19]. Thermoplasmonic applications, specifically those using GNRs, have transformative potential across various fields. By optimising the size, shape and environmental parameters of these nanoparticles, they can enhance the efficiency of targeted hyperthermia, improve drug delivery mechanisms and enable highly precise photoacoustic imaging. Recent research focuses on integrating GNRs with other materials, such as high refractive index coatings (e.g. SiO_2) to further increase their absorption and heat generation efficiency. Developments in laser technology will also play a crucial role in expanding the applications of GNRs in medicine, particularly in oncology and minimally invasive therapies [20].

In this investigation, the finite element approach with COMSOL Multiphysics is used. It is based on the Mie theory and heat transport models. The investigation focuses on the thermoplasmonic generation of GNRs with different lengths in air and water environments. This analysis is conducted under the illumination of an 810 nm laser diode.

2 MANUSCRIPT PREPARATION

The cylindrical symmetry structure represented GNRs of different lengths (D) and a constant radius (d) immersed in air, followed by homogeneous deionised water at room temperature. The GNRs were irradiated using an 810 nm laser.

Optical part: COMSOL Multiphysics 6.1 software is used to design the correct settings for GNRs of different lengths, as shown in Figure 1. The electromagnetic wave frequency domain model is employed to examine the numerical computation of the absorption cross section (ACS) for the GNRs in various mediums, as calculated numerically and displayed
in (1) [21]:

$$\delta_{abs} = k\,\mathrm{Im}(\alpha) - k^4 / 6\pi\, |\alpha|^2. \quad (1)$$

where k denotes the wave number and α is the polarizability.

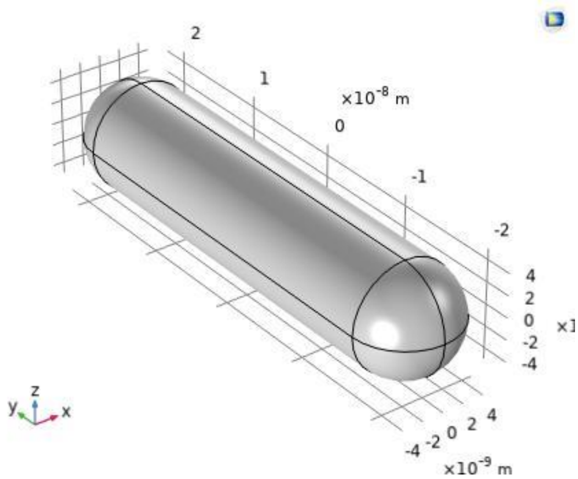

Figure 1: Diagram showing nanorod structure.

Table 1. Physical properties of materials used in this study.

Parameters	Au	Water	Air	SiO_2	Unit
Thermal Conductivity K	317	0.6	0.02	1.38	W/(m.k)
Specific heat Capacity c	128.5	4187	1000	703	J/(Kg.K)
Mass Density ρ	19320	1000	2.9	2203	Kg/m^3

High quality can be achieved by using λ/6 as the mesh in this particular model. All materials' real and imaginary components of their refractive indices of all materials are interpolated.

Thermal analysis: The photothermal response of GNRs, which arise from the absorption of incident light energy, is investigated using (2) [22]:

$$\Delta T = \frac{\delta_{abs}\, I}{4\pi\, R_{eq}\, \beta\, K_m}. \qquad (2)$$

Where I is the light irradiance, E is the electric field amplitude of the incoming light, n is the refractive index, K_m is the thermal conductivity of the surrounding medium and R_{eq} is the equivalent radius:

$$R_{eq} = \left[(3D - d)\,\frac{d^2}{16}\right]^{\frac{1}{3}}. \qquad (3)$$

Here, D and d represent the length and diameter of the gold nanorods (GNRs), respectively, and a corrective factor is applied to account for deviations from idealized geometries or assumptions in the analytical model:

$$\beta \simeq 1 + 0.096587\, ln^2\left(\frac{D}{d}\right). \qquad (4)$$

The heat transfer model is used with the same boundary conditions that were utilized to ascertain the optical properties are applied to the heat transfer model. Table 1 lists the characteristics of the materials employed in this investigation.

In (1): Au [23], Water [24], Air [25], SiO_2 [26].

3 RESULTS AND DISCUSSION

To gain deeper insights into the thermoplasmonic behaviour of GNRs, exploring the interplay among their geometric parameters, optical properties and the surrounding medium is necessary. The results demonstrate a clear correlation between the length of GNRs and the red shift in SPR [19].

Figure 2 displays the ACS for several GNRs as a function of wavelength (400–1,400 nm). For different GNR lengths and constant diameters in air and water.

In air, the SPR characteristics show a red shift and an increase in the ACS magnitude as the length of GNRs extends. In water, the SPR characteristics exhibit a larger red shift and a decrease in the ACS magnitude compared with those in air. The shift is due to that higher refractive index of water (1.33) causes more light to bend and scatter, which decreases the light available for absorption by the GNRs [27].

The proposed GNR is considered to lie in a horizontal direction, which makes an angle ($\Theta = 90^o$) with respect to the normal incident of the plain background field (and laser illumination) to achieve maximum absorption, as discussed in [28].

The orientation of GNRs is pivotal in optimising their thermal efficiency. As demonstrated, aligning the nanorods at an angle of 90° to the incident light improves the excitation of longitudinal plasmon resonance modes, which results in maximum heat generation. This characteristic is particularly advantageous for targeted therapies. Precise control of heat localisation is crucial to minimising damage to surrounding tissues.

Figure 3 presents the absorption cross section (ACS) as a function of wavelength (500–800 nm) for various orientation angles of the gold nanorods (GNRs), specifically at 0°, 30°, 60°, and 90°. When ϴ = 0°, the incident light is aligned with the nanorod axis, effectively exciting longitudinal oscillations of the free electrons along the rod's length. As the orientation angle increases, the alignment between the incident electric field and the nanorod axis diminishes, resulting in a progressive decrease in the ACS. This demonstrates that maximum absorption occurs when the incident field is parallel to the nanorod axis, and it gradually declines as the angle deviates from this alignment [29].

The temperature elevation of GNRs corresponding to laser irradiation is shown in Figure 4. The proposed laser source is a diode laser with a power of 1 mW/μm² and a wavelength of 810 nm, with normal incidence.

Figure 5 illustrates the temperature elevation of gold nanorods (GNRs) under laser irradiation. The proposed laser source is a diode laser operating at a wavelength of 810 nm, with a power density of 1 mW/μm² and normal incidence. This configuration is designed to effectively excite the longitudinal plasmon resonance of the GNRs, leading to localized photothermal heating.

In an air environment, the maximum opto-heat generation of GNRs occurs at length of 70 nm due to its higher ACS magnitude, followed by 60 and 80 nm, as indicated by (2). In a water environment, the maximum opto-heat generation of GNRs occurs at length of 50 nm due to its higher ACS magnitude, followed by 45 nm, as explained previously. This result is due to the decrease in the collective refractive index.

In certain experimental conditions, the lengths of gold nanorods (GNRs) may be constrained to values shorter than 60 nm. Under such conditions, the absorption cross section (ACS) is significantly reduced, resulting in minimal temperature elevation. To enhance the photothermal efficiency of these short nanorods, one effective strategy is to coat them with a material possessing a high refractive index, such as silicon dioxide (SiO_2). This coating enhances the local electromagnetic field around the nanorods, thereby increasing their light absorption and subsequent heat generation.

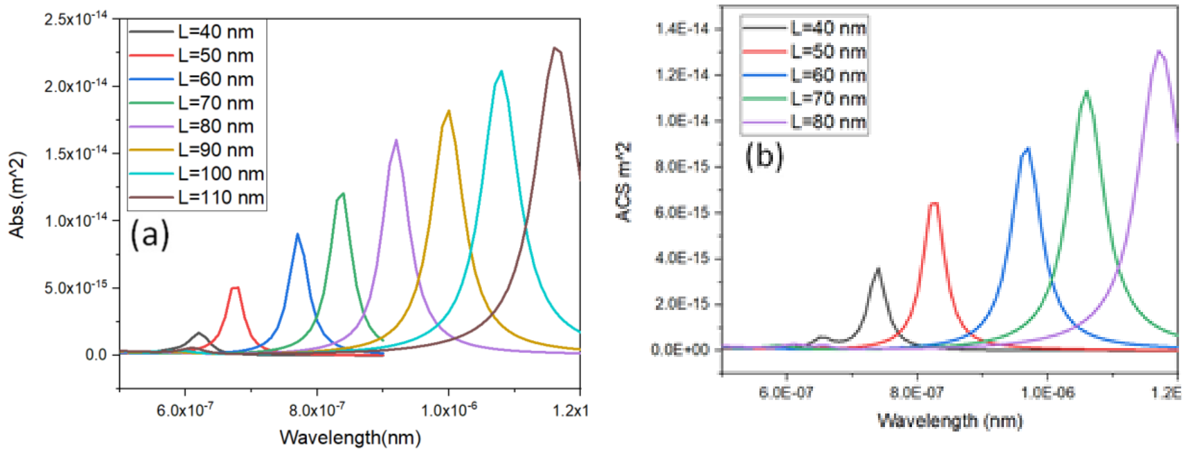

Figure 2: ACS of different nanorod lengths in a) air and b) water.

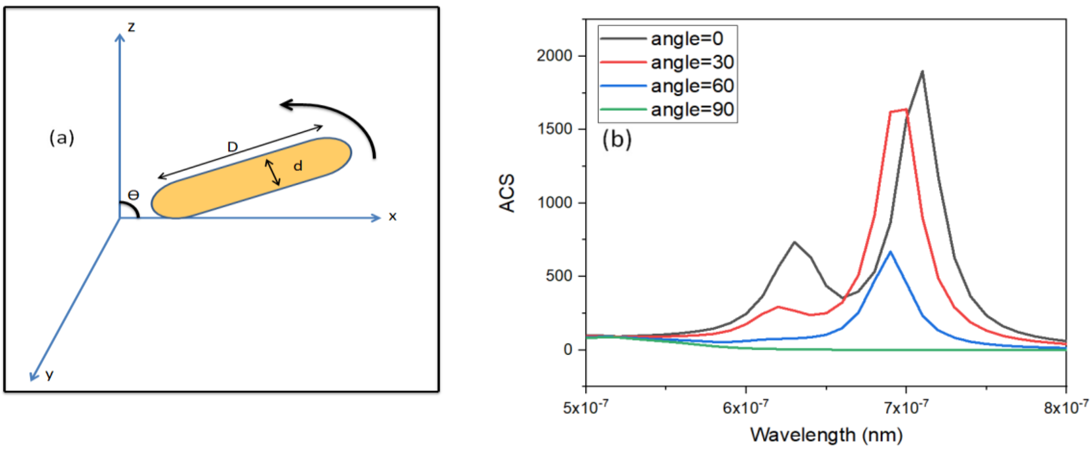

Figure 3: Schematic of GNR orientation a) and b) absorbance of GNRs at different angles

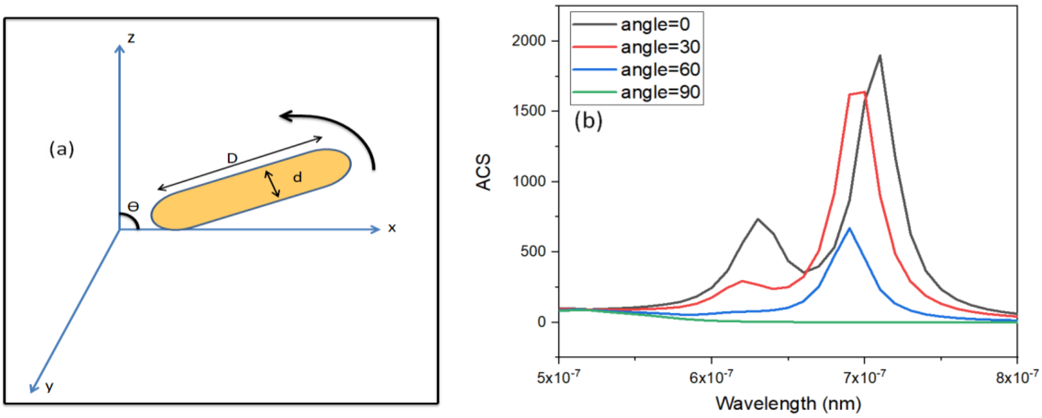

Figure 4: Heat elevation of GNRs in a) air media and b) water media.

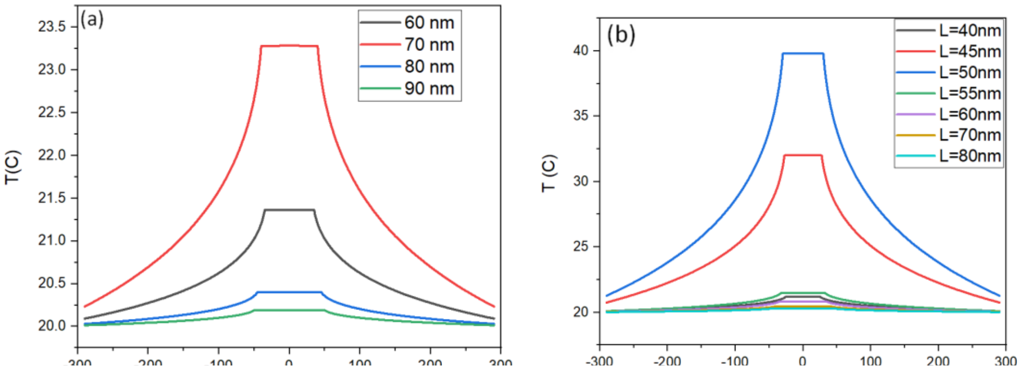

Figure 5: Heat elevation of GNRs in a) air media and b) water media.

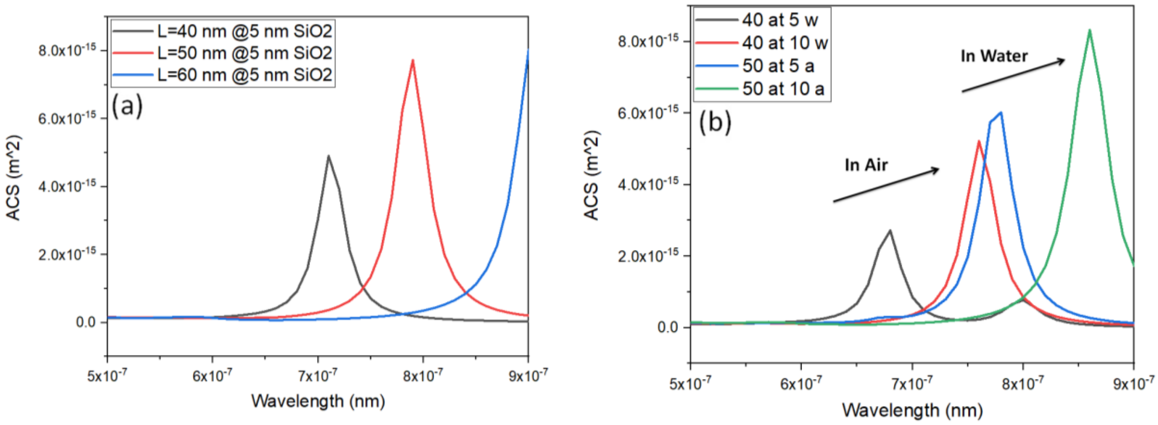

Figure 6: Absorption cross section (ACS) of gold nanorods (GNRs): a) for varying GNR lengths at a fixed SiO_2 shell thickness, and b) for a fixed GNR length with varying SiO_2 shell thicknesses, in both air and water environments.

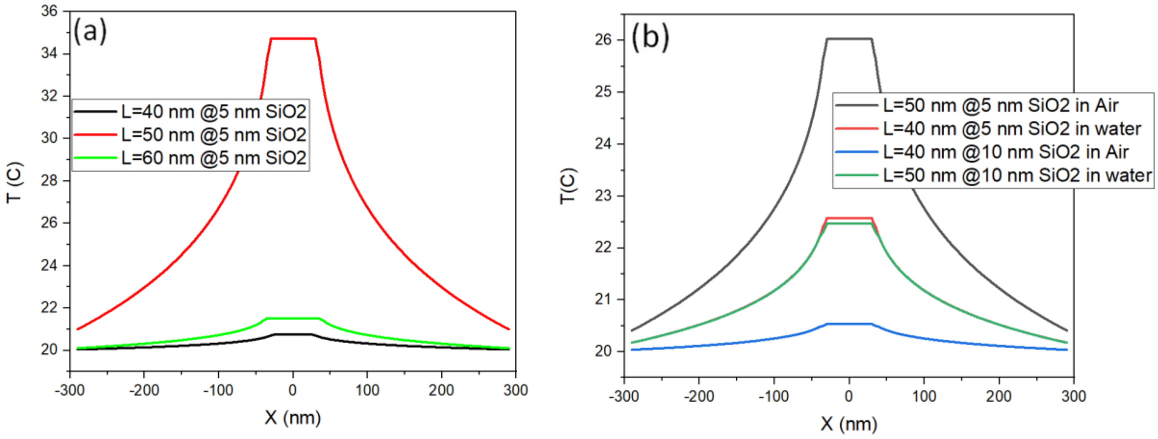

Figure: 7: Heat elevation of GNRs for (a) different GNR lengths @ fixed SiO_2 shell thickness and (b) different GNR lengths @ different SiO_2 shell thicknesses.

Figure 6 show the ACS for various GNR as a function of wavelength (500–900 nm) for two scenarios: varying gold nanorod (GNR) lengths at a fixed SiO_2 shell thickness, and a fixed GNR length with varying SiO_2 shell thicknesses.

Utilizing high-refractive-index materials such as silicon dioxide (SiO_2) as coatings is crucial for enhancing the optical and thermal performance of gold nanorods (GNRs). The application of a SiO_2 shell not only improves the structural stability of the nanorods but also significantly increases their ability to absorb and retain incident light, as evidenced by the elevated absorption cross section (ACS) and enhanced thermal response. These dielectric coatings enable precise tuning of the surface plasmon resonance (SPR) characteristics, thereby optimizing the photothermal conversion efficiency. As illustrated in Figure 6, variations in the SiO_2 shell thickness directly influence heat generation across different wavelengths. This tunability renders SiO_2-coated GNRs highly suitable for advanced applications such as controlled hyperthermia and high-resolution optical imaging [30].

A red shift in the surface plasmon resonance (SPR) wavelength is observed with increasing gold nanorod (GNR) length, primarily due to the enhanced sensitivity of the plasmonic response to the refractive index of the surrounding medium [31].

A red shift is also observed when the gold nanorod (GNR) length is held constant and the thickness of the SiO_2 shell is varied. As the SiO_2 shell thickness increases, the absorption cross section (ACS) correspondingly increases, indicating enhanced light absorption and plasmonic coupling due to the higher effective refractive index surrounding the GNRs [28]. (Fig. 7). Heat elevation profiles of gold nanorods (GNRs) as a function of distance (*x*, in nanometres): (a) for varying GNR lengths at a fixed SiO_2 shell Figure 7a shows that the maximum heat elevation occurs for gold nanorods (GNRs) with a length of 50 nm and a SiO_2 shell thickness of 5 nm, which corresponds to the highest absorption cross section (ACS) observed in Figure 6a. Concurrently, Figure 7b illustrates the influence of increasing shell thickness on opto-thermal heat generation, highlighting the tunability of the ACS through dielectric coating. This observation is consistent with prior studies that demonstrate enhanced photothermal performance resulting from modifications in the surrounding refractive index [32].

4 CONCLUSIONS

This paper proves that the thermoplasmonic performance of gold nanorods (GNRs) can be expressively improved by regulating their length and orientation, and the adjacent medium. Longer GNRs aligned at 90° to the incident light proved enhanced longitudinal surface plasmon resonance and better heat generation. The adjacent medium likewise plays an important role. GNRs in water exhibit a red shift in absorption but reduced heating compared to those in air. The findings demonstrate that engineering GNR properties, including length, orientation, surrounding media and coating thickness, provides exceptional flexibility in customising their thermoplasmonic performance. These results pave the way for integrating GNRs into advanced biomedical devices for cancer therapy, drug delivery and high-resolution imaging. Future research should concentrate on optimising the interaction between

GNRs and their environment to unlock their full potential in real-world applications, such as industrial heat management and minimally invasive medical treatments.

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