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Photothermal response of hollow gold nanoshell to laser irradiation: Continuous wave, short and ultrashort pulse

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ABSTRACT

This paper is to investigate numerically the photothermal response of the most common size of gold nanoshell (AuNS) in an aqueous medium for biomedical applications. Three types of laser light irradiate the particle; a continuous-wave (CW), short (nanosecond) and ultrashort (femtosecond) pulse laser. The spatiotemporal evolution of the temperature profile inside and around the AuNS is computed using a numerical framework based on the finite element method (FEM). For CW and nanosecond (ns) pulse laser where the AuNS's electrons and lattice are at thermal equilibrium, the ordinary heat diffusion equation is used to describe the heat transfer to the surrounding water. For femtosecond (fs) pulse laser, due to the inexistence of the thermal equilibrium, a two-temperature model (TTM) is used to describe the heat transfer processes occurring in the AuNS and the normal heat diffusion equation is used for the heat flux calculation at the particle/water interface. For each case, the influence of laser intensity on the maximum temperature reached at the particle/water interface is studied. The aim of this study is to provide a description for the fundamentals of heat release of AuNSs and useful insights for the development of these particles for biomedical applications such as drug delivery, photothermal cancer therapy and optoporation of cells.

1. Introduction

Gold nanoparticles (AuNPs) are well known for their capabilities to support localized surface plasmon resonance (LSPR) due to collective and coherent oscillations of free electrons at the surface of the particle. In resonance with an external electromagnetic wave, occurring at a specific wavelength range, the AuNPs show unique optical and thermal properties [1,2]. Illumination of the AuNPs at or close to LSPR wavelength results in a near field enhancement, scattering and conversion of absorbed light energy to heat [3]. In addition, the surface of AuNPs can be routinely functionalized with active ligands, monoclonal antibodies and thiolated molecules due to the strong Au-S bond [4,5]. These novel properties of AuNPs provide a highly localized functional and multifunctional platform in biomedical applications, particularly in photothermal therapy, optoporation of cells and selective or targeted drug delivery. At low temperatures, this process can be exploited for thermally induced release of drugs attached to AuNPs, which allows precise, on-demand delivery into the intracellular environment [6–8]. However, at higher temperature, AuNPs temperature raises killing tumour cells that can be furfure exploited for cancer therapy [9–13].

Among all AuNPs, the ultra-thin hollow gold nanoshells (AuNSs) exhibits a unique combination of small size, strong, narrow and tunable absorption band in the near infrared (NIR) tissue window (wavelength: 700–900 nm). These particles consist of a spherical gold shell filled with its embedding aqueous medium [14]. For biomedical applications, smaller size (outer diameter, 30–50 nm) allows prolonged blood circulation time and better chance in crossing the tumour vessel wall. The strong and tunable absorption band in NIR regime enables a large penetration depth, even at low laser intensities, that ranges from a few millimeters to several centimeters depending on tissue type [15–17]. The hollow core allows higher drug loading capacity, easier synthesis, and the pure gold composition reduces toxicity [18,19]. AuNSs are usually synthesized using cobalt (Co) nanoparticles as sacrificial templates, the gold shells being grown via a galvanic reaction with Au ions [14,19–21].

Photothermal response of AuNSs strongly depends on the irradiation regime (CW, ns and fs) that can be selected based on the requirement of a specific biological application. For instance, irradiation of AuNSs by a CW laser is best suited for applications that

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require an enduring, moderate increase in temperature, such as hyperthermia and photothermal release of molecules. In this case, AuNSs dissipate the absorbed energy into their surrounding environment without a substantial increase of their temperature [22,23]. Some applications such as photoacoustic imaging of cells and gene silencing by transfection, necessitate a much higher energy density in the vicinity of the AuNSs [24]. Further reducing of the pulse width up to fs regime enables a very high-localized temperature increase, more efficient energy deposition allowing the cleavage of bonds to link molecules to the AuNS surface [25].

In recent years, there has been few research interests to advance fundamental understanding of plasmon-assisted photothermal phenomena around AuNS [26,27]. The main objective of this paper is to investigate the spatiotemporal photothermal response of the most common size of AuNS (40 nm diameter and 3 nm shell thickness) for biomedical applications [28]. The particle is irradiated by CW, ns and fs laser pulses in water medium at a wavelength of 800 nm where scattering in biological tissue is very low. It has been found that such a AuNS around this size anneals into solid particles within hours at 523 K [29], therefore, we restrict the maximum temperature increase calculation to be in the same range. For each irradiation regime we show the maximum temperature increase dependency and rate to laser intensity. It is worth to mention here that although we performed the calculations for a particular sized AuNS, however, upon request the developed tools are capable of doing the same calculation for any metallic configuration and shape.

2. Methods

The modeled system consists of AuNS with water core of radius of 17 nm and a gold layer with a thickness of 3 nm. The AuNS is immersed in water since this medium has proven to be adequate for the modeling of laser processes occurring in a cellular medium. The time-dependent distribution of the electromagnetic field and thermal response of the AuNS is modeled by a system of partial differential equations (PDE). The system is solved in three-dimensional (3D) using the finite element method (FEM) provided by the commercial software COMSOL 4.3 (www.comsol.com).

2.1. Electromagnetic field distribution

Assuming time-harmonic electric field, the electric field distribution $\vec{E}(r,t)$ is computed using the Helmholtz equation [13]:

$$\nabla \times (\mu_r^{-1} \nabla \times \vec{E}) - k_0^2 \left(\varepsilon_r - j \frac{\sigma}{\omega \varepsilon_0} \right) \vec{E} = 0 \tag{1}$$

where ε_r is relative permittivity. For gold shell this quantity is a complex, frequency dependant number and interpolated from Johnson and Christy [30]. For water ε_r is set to be 1.77. The relative permeability μ_r is taken as unity and k_0 is the wave number. The other parameters in Eq. (1) are given in the reference [13]. This equation is solved in a spherical domain 10 times larger than the AuNS with an outer perfectly matched layers (PML) shell and a scattering type boundary condition that emulates an infinite domain.

Assuming a non-dissipative host medium, the absorbed and scattered energies by the AuNS are obtained as [31]:

$$Q_{scat} = \frac{1}{2} \mathrm{Re} \left[\iint_s \vec{E}_{scat} \times \vec{H}_{scat} \cdot \vec{n} ds \right] \tag{2-a}$$

$$Q_{abs} = \frac{1}{2} \mathrm{Re} \left[\iint_s \vec{E}_{tot} \times \vec{H}_{tot} \cdot \vec{n} ds \right] \tag{2-b}$$

where $\vec{E}$ and $\vec{H}$ represent the electric and magnetic field vectors, respectively. $\vec{n}$ is an outward-pointing unit vector normal to the surface of the AuNS. The absorption, scattering and extinction cross-section are defined as $\sigma_{abs} = Q_{abs}/I_0$, $\sigma_{scatt} = Q_{scatt}/I_0$ and $\sigma_{ext} = \sigma_{abs} + \sigma_{scatt}$, respectively. Here, $I_0 = (1/2)\varepsilon_0 n_w E_0^2$ represents the intensity of the incident laser beam of amplitude E_0 in the surrounding medium.

2.2. Thermal evolution

The equation governs the thermal evolution of the AuNS and surrounding water strongly depends on the irradiation time-regime. Comparison the pulse laser time width to the electron-lattice thermalization time ~0.5–1 ps [32] plays a key role to choose thermal evolutional equations. For CW irradiation and ns pulses, the pulse width is much longer than electron-lattice thermalization time, therefore, the gold electrons and lattice are heated in relative equilibrium. In this case the AuNS and water temperature evolution are calculated from the usual heat diffusion equation [33]:

$$\rho(r) c(r) \frac{\partial T(r,t)}{\partial t} = \nabla \cdot (k(r) \nabla T(r,t)) + Q(r,t), \tag{3}$$

in above equation, $T(r,t)$ is the local temperature, r is the position with the origin fixed at the particle center and t is the time. Three material parameters: $c(r)$, $\rho(r)$ and $k(r)$ are the heat capacity, mass density and thermal conductivity, respectively. $Q(r,t) = \langle \vec{j}(r,t) \cdot \vec{E}(r,t) \rangle_t$ is the local heat generation density resulting from the electric current density $\vec{j}(r,t)$ in the shell. In the case of pulse laser, the local field intensity calculated in Eq. (1) is modulated by the Gaussian time profile of the incident laser pulse. The intensity of the ns and fs pulse lasers are modeled by a Gaussian curve, as following:

$$I(t) = \frac{F_L}{\sqrt{2\pi} t_\sigma} \exp \left(\frac{-[t - t_0]^2}{2 t_\sigma^2} \right) \tag{4}$$

in the above equation, $t_\sigma = t_l / 2\sqrt{2 \ln 2}$ is the pulse width, where t_l is the laser pulse width defined as the full with at half maximum of the Gaussian temporal profile, t_0 is the position of the center of the peak and F_L is the incident laser energy density (fluence). Absorption of radiation in the core and in the surrounding medium is neglected. In our calculations, the following thermal characteristics of water and gold are used: $c_w = 4182\ \mathrm{J\ kg^{-1}\ K^{-1}}$, $\rho_w = 10^3\ \mathrm{kg\ m^{-3}}$, $k_w = 0.6\ \mathrm{W\ K^{-1}\ m^{-1}}$, $c_{Au} = 130\ \mathrm{J\ kg^{-1}\ K^{-1}}$, $\rho_{Au} = 19.3 \times 10^3\ \mathrm{kg\ m^{-3}}$ and $k_{Au} = 300\ \mathrm{W\ K^{-1}\ m^{-1}}$.

To study fs pulsed laser and AuNS interaction mechanisms, we consider the case where t_l is much smaller than the characteristic time constants of the transient non-equilibrium photothermal effects. These characters are electron–lattice interactions and phonon–phonon interactions at the surface of the particle. For this time regime the TTM can be used in which the electrons and lattice remain at different temperatures (T_e and T_l). This is due to the fact that the heat conduction in the lattice is small compared to that in the electrons. Also the electron relaxation time is shorter than tens of fs for gold. In the water, considering laser fluences well below the optical breakdown, direct absorption is neglected and the usual one temperature heat diffusion equation applies. However, because of the phonon mismatch factor, discontinuity between the water and shell temperature appears at the interface. We solve the following set of thermal evolutional equations for the electrons and the lattice for AuNS and water [34]:

$$C_e(T_e) \frac{\partial T_e(r,t)}{\partial t} = \nabla \cdot (k_e \cdot \nabla T(r,t)) - G \cdot [T_e(r,t) - T_l(r,t)] + S(t) \tag{5-a}$$