Thermochimica Acta 656 (2017) 25–31

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Temperature dynamics of laser irradiated gold nanoparticles embedded in a polymer matrix

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ARTICLE INFO

Keywords:
Gold nanoparticle
Laser irradiation
Heat transfer
Temperature distribution
Polymer matrix

ABSTRACT

In this work the temperature evolution, in time and space, in two systems that consist of a single gold nanoparticle and an ensemble of gold nanoparticles, both embedded in a polystyrene sulfonic acid matrix, is numerically modeled. The heat accumulated by the gold nanoparticles is estimated considering the system irradiation with a nanosecond laser at 532 nm. The distribution of the temperature in time and space is calculated by solving the heat diffusion equations with appropriate initial and boundary conditions. The rise of nanoparticle size determined the temperature increase of the gold nanoparticle and implicitly of the entire system but also the increase of the necessary time for reaching the thermal equilibrium of the system related to the surrounding polymer volume. The temperature evolution and the dynamics of the system towards reaching the thermal equilibrium are influenced by the gold nanoparticles distribution in the polymer matrix.

1. Introduction

An increased interest for gold nanoparticles has been recorded since 1990′s because of their potential applications to photo-chemistry, nonlinear optics, electronic devices and molecular recognition [1–3]. Also, gold nanoparticles (AuNPs) exhibit a non-optic response reflected in applications such as temperature distribution control [4], material growth [5], cancer treatment [6,7], controlled drug release [8–10] and different chemical reactions [11]. In this view, one of the AuNPs properties that attracted interest in the past several years is their possibility to absorb energy from the visible light [12]. This behavior is significantly reflected in the gold micro- and nanostructures fabrication process using direct laser writing in polymer doped thin films. For instance, when gold ions in polystyrene sulfonic acid (PSS) matrix are photo-reduced by pulsed laser irradiation, continuous double nanowire shape rather than single nanowire shape metallic structures were obtained [13]. The difference between these patterns comes from the existence of a deep hole located at the center of the laser beam path [13,14], which is created by the thermal effect generated at the laser spot area [14]. Therefore, two processes exist in competition: gold fabrication, initiated by laser irradiation which generates the metallic structures onto the substrate surface through photo-reduction, and ablation, which is destructive [14]. The starting point originates at the focal point, where gold nanoparticles are generated, and then these particles strongly absorb the laser energy. Thus, when irradiated with laser radiation, AuNPs exhibit a sharp and brief increase of the temperature [12].

As can be seen this effect of AuNPs is developed in well determined volume systems. The heat generated by the AuNPs after laser irradiation is localized inside and near the particle and because of their reduced sizes it is difficult to be measured. Thus, the temperature is indirectly determined and can be done generally by mathematical modeling but also, experimentally. The different models proposed by the scientists differ as approach and simplifications. For example, Letfullin determined the particle temperature in terms of energy accumulation from the incident laser radiation and energy loss due to heat diffusion into the surrounding medium [15]. Smirnov studied laser irradiated AuNPs by monitoring the changes suffered by the surrounding medium [16]. Sassaroli numerically investigated the heating and vapor formation around a nanosecond irradiated AuNP having water as surrounding medium. In this article the conductivity, specific heat and density of water and gold were considered as a function of temperature [17]. Plech used x-ray scattering to resolve lattice changes in pulsed laser irradiated AuNPs embedded in water. It was also considered a

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http://dx.doi.org/10.1016/j.tca.2017.08.008
Received 15 March 2017; Received in revised form 1 August 2017; Accepted 16 August 2017
Available online 22 August 2017

non-perfect contact between the AuNP and the surrounding medium, and the interface thermal conductance was calculated [18]. Pustovalov studied the heating, phase changes and cooling of a pulsed laser AuNP in different media. A nonlinear temperature dependence of heat conduction coefficient was taken into account and a solution for quasi-stationary distributions of temperature inside and around the AuNP was obtained [19]. Bauffou and Rigneault studied the temperature distribution in a spherical AuNP immersed in water and irradiated with femtosecond laser pulses [12]. Both a continuous and femtosecond pulsed laser illumination were considered and the influence of different AuNP sizes, gold-water interface and the pulse repetition rate were studied. Finally, the model was extended to non-spherical nanoparticles [12]. Rashidi-Huyeh and Palpant modeled the temperature dynamics in a nanosecond and femtosecond laser irradiated spherical AuNP embedded in different surrounding medium (SiO_2, Al_2O_3). As time as in femtosecond regime, the electron–electron collisions and the hot Fermi distribution cannot be neglected, this work describes the electron, lattice and matrix temperature variation with time. The importance of the metal NP diameter among the heat generation was studied and the temperature dynamics of Au:SiO_2 materials with varying metal concentration was modeled.

The most studied application related to the heat generated by the AuNPs after laser irradiation is the hyperthermia therapy of cancer. Thus, Y. Ren calculated the heat generated by laser irradiated media (tissue that contains AuNPs) using Monte Carlo method and Beer's law. The heat generation was introduced as a volumetric heat source in Pennes bioheat equation. The influence of period heating, AuNPs volume fraction, laser irradiated area and tumor aspect ratio is tackled [20]. Another interesting approach for this subject is proposed by Lamien [21]. They treated the laser induced hyperthermia cancer therapy as a state estimation problem that was solved with the Auxiliary Sampling Importance Resampling algorithm. For this model, continuous laser irradiated AuNPs embedded in a non-homogeneous medium were used [21].

In case of the experimental methods, Gogorov used Raman spectroscopy to determine the temperature on the surface of ice embedded AuNPs. Also, they tried to determine the AuNP surface temperature using a polymer that binds to the AuNP and changes its size with the temperature increase [22]. Additional CdTe nanoparticles (CdTeNPs) were attached to this polymer, thus forming an AuNP-polymer-CdTeNP complex. Taking into account that the CdTeNP emission depends on the distance to the nanoparticle, the AuNP temperature was determined measuring the emission intensity [22]. Other methods for determining the AuNPs temperature are photoacoustic imaging [23] or white light scattering spectroscopy [24].

As it can be seen the temperature control is vital in all the above-mentioned applications and can be done by changing the AuNP size and shape, the surrounding medium or the laser parameters − laser pulse wavelength, pulse energy and pulse duration [12,25–27].

Most mathematical models that study laser irradiated AuNPs take into account various NP sizes, temperature varying material parameters, a non-perfect contact between the AuNP and the surrounding medium. It is worth emphasizing that they do not address the issue of heat transfer in case of more than one AuNP and the influence of the various geometries in which the metallic nanoparticles exist in the surrounding matrix. Also, the problem of simulating a large (infinite) system is not tackled.

The aim of our research is to evaluate the thermal effect caused by the interaction of the laser radiation with the gold nanoparticles by numerical modeling of the temperature evolution, in time and space, in two systems: i) a single AuNP embedded in a polymer matrix (System I), and ii) an ensemble of AuNPs embedded in a polymer matrix (System II). The second system is assumed to extend infinitely and therefore simulate a more realistic problem. Also, the influence of the AuNPs size and particles distribution inside the system as factors that influence the amount of heat generated is studied.

Table 1
Polymeric matrix properties at 20 °C and atmospheric pressure.

Density ρ/(kg m^{-3})	1071.5
Heat capacity Cp/(J kg^{-1} K^{-1})	3043.77
Thermal conductivity k/(W m^{-1} K^{-1})	0.45

2. Material and methods

Within this work two types of systems were studied. System I consists of a single gold nanoparticle embedded in polystyrene sulfonic acid matrix (PSS) as surrounding medium. System II consists of 100 gold nanoparticles embedded in the same polystyrene sulfonic acid matrix. In this system, by imposing periodic heat boundary conditions in both x and y directions, we are able to simulate heat diffusion in a medium which can be considered to extend infinitely in these directions. In both cases the simulations start from 293 K as initial condition.

The polymeric matrix properties (thermal conductivity, density and specific heat) were experimentally determined and the values were used as received. A photopyroelectric technique is used to detect the thermal diffusivity (α) and thermal effusivity (e), respectively. The static volume specific heat (C) and the thermal conductivity (k) are related to the other two parameters through the following relations: $k = C\alpha$ and $e = (Ck)^{1/2}$ [28]. Thus, the density, heat capacity and thermal conductivity of the polymeric matrix are experimentally determined and presented in Table 1.

To be able to simulate the AuNP and the surrounding medium temperature it was assumed that: the system is isolated, and in the AuNP the electron and lattice temperature are equalized due to the fast heat transfer from electrons to phonons. Thus, the nanoparticles are heated uniformly and the heat loss is due to heat conduction from the AuNP to the surrounding medium. It is also assumed that all the parameters that describe the system remain constant in the studied temperature range and the polymeric matrix is optically transparent to the laser light.

The heat accumulated by the AuNP is estimated considering the system irradiation with a Nd:YAG laser at 532 nm and a Gaussian pulse duration τ = 12 ns FWHM [15]. The laser pulse time profile is described by a gaussian:

$$f(t) = \exp(-(t - t_0)^2/\tau^2), \tag{1}$$

where t_0 is the position of the center of the peak.

Taking into account that the nanosecond laser irradiation of Au is responsible for the heat accumulated in the metal nanoparticle, the AuNPs were defined as heat sources. We assume that the nanoparticles heat uniformly (the heat does not have a radial distribution), and so the heat generated by the particles is calculated using the following equation:

$$Q = \frac{3K_{abs}If(t)}{4r}, \tag{2}$$

where K_{abs} is the absorption efficiency, I/(W/cm^2) is the intensity, r/(m) is the nanoparticle radius and f(t) is the laser pulse time profile [15]. In System II it is assumed that all the AuNPs absorb the light in the same time, and mutual interferences are not considered as affecting the absorbed energy. Also, the polymer matrix that surrounds the AuNPs contains a large amount of water (18 %wt. PSS) which can efficiently absorb the heat generated in the proximity of the particles and can overcome the potential changes inside the system due to heat propagation. Moreover, the polymer presence ensures a stable distribution of the embedded particles.

The heat transfer equation for our systems is described by equations

$$\rho_{AuNP} C_{p_{AuNP}} \frac{\partial T_{AuNP}}{\partial t} = k_{AuNP} \nabla^2 T_{AuNP} + Q \tag{3}$$