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Effects of particle size and laser wavelength on heating of silver nanoparticles under laser irradiation in liquid

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Abstract. Laser energy absorption results in significant heating of metallic nanoparticles and controlling the heating of nanoparticles is one of the essential stages of selective cell targeting. It is necessary to note that the laser action should be done by laser pulses with a wavelength that is strongly absorbed by the particles and it is important to select wavelengths that are not absorbed by the medium. Laser pulse duration must be chosen sufficiently short to minimize heat flow emitted from absorbing particles. Numerical calculations based on Mie theory were used to obtain the effect of laser wavelength and particle size on absorption factor for colloidal silver nanoparticles with radii between 5 and 50 nm. Calculations for acquiring temperatures under irradiations of pulsed KrF laser and pulsed Nd:YAG laser were performed. We showed that for low wavelengths of the laser, smaller nanoparticles have larger absorption efficiency compared to larger nanoparticles and in high wavelengths, temperature of all particles increased in the same way.

Keywords. Nanoparticles; pulsed laser; heating; absorbance.

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1. Introduction

Knowledge of size-dependent optical properties of nanoparticles is important for these nanoparticles to be used in various areas such as nanomedicine, nanomaterials, nanoelectronics, and plasmonics [1–5]. The most important applications of nanoparticle size-dependent optical absorption are the cell targeting process in nanomedicine and thermally controlled release of drugs. Nanomaterial processing such as size reduction, size modification, change of dimension and plasmonic melting in nanoelectromechanics devices and ways to improve the performance of thin-film solar cells are among the other important applications of nanoparticle size-dependent optical absorption [6–8]. Heating of nanoparticles in liquid environments causes the nanoparticle's temperature to increase considerably. Knowledge of localized heating effect due to laser irradiation on the nanoparticles are required to prevent unintentional thermal effects [9]. Various metals such as gold, silver and copper can be used for heating. The antimicrobial properties of silver have been known since time immemorial [10–12]. Recently, silver nanoparticles have gained more attention because of their antimicrobial activity which offers the possibility of using them for medical and hygienic purposes. Silver nanoparticles in different formulations and with different shapes and sizes exhibit various antimicrobial activities [13–15]. Silver nanoparticles were used in the studies here because of these features. Nanoparticles contain large optical field enhancements, resulting in strong scattering and absorption of light. The enhancement in the optical and photothermal properties of noble metal nanoparticles arises from resonant oscillation of their free electrons in the presence of light [16,17], also known as localized surface plasmon resonance. It has been proved that laser irradiation of silver nanoparticles which were attached to gene markers can be delivered to specific cells and this feature can be used for selectively destroying cancerous cells or bacteria. Similar approach has been designed for biological imaging, when optoacoustic signals generated by nanoparticles help to differentiate tumors from normal tissue. Doping the walls of the microcapsules with metal nanoparticles is a new method to remote release the encapsulated drugs into specific cells by targeting metal nanoparticles using laser beams [18–22]. The plasmonic resonance of noble metal nanoparticles makes them effective as bright optical tags for molecular-specific biological imaging and optical microscopy [23]. In the past several years, the interaction between laser radiation and metal nanoparticles has caused a considerable interest and become one of the increasingly important topics [24]. Experiments were done by special laser pulses that are only absorbed by the nanoparticles, but not by the medium. Laser energy absorption results in significant heating of metallic nanoparticles. Controlling the temperature of nanoparticles is one of the essential stages of selective targeting of the cells for laser photothermal therapy of cancer [23,25].

The calculations of optical absorption and temperature of spherical silver nanoparticles with radii between 5 and 50 nm under irradiations of pulsed KrF laser and pulsed Nd:YAG laser are performed in the current study. First, optical absorbance of the nanoparticles was obtained by considering the dependence of dielectric function on size. Then, by considering the radiant energy absorbed, the maximum temperature of silver nanoparticles in aqueous was calculated. The calculations show that final temperature of the nanoparticles in definite time duration depends on the size of the nanoparticles and wavelength of the laser. Shorter wavelengths provide suitable conditions for heating control which depends on the size of nanoparticles. The results can be used for determining the threshold laser intensity and optimal size of the nanoparticles.

2. Computational methods

Interactions of lasers and nanoparticles and the effects can be studied by investigating the properties of an individual nanoparticle. The first step is to determine the absorption of laser radiation by a single metal nanoparticle. Optical absorption of colloidal silver nanoparticles was estimated using Mie theory. The size of the sphere was optimized to give the highest possible absorption efficiency at any wavelength.

Absorption of electromagnetic waves of a spherical particle of defined radius and refractive index can be solved exactly [26]. Electromagnetic field in a homogeneous and isotropic environment should satisfy wave equation. Internal and scattered field can be expressed in a simpler way by introducing Ricatti–Bessel functions. The functions used are as follows:

$$a_n = \frac{m\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{m\psi_n(mx)\xi_n'(x) - \xi_n(x)\psi_n'(mx)}, \tag{1}$$

$$b_n = \frac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi_n'(x) - m\xi_n(x)\psi_n'(mx)}. \tag{2}$$

In the above equations, $m = k/k_m$, $x = k_m r_0$, $\psi_n(x) = x j_n(x)$, $\xi_n(x) = x h_n^{(1)}(x)$, r_0 is the radius of the nanoparticles and k_m is the wavenumber in the environment. All particles are considered as spherical and optical properties of particles are defined by the efficiency factor of absorption $k_{\mathrm{abs}}(r_0, \lambda)$ of the incoming radiation with wavelength λ by a spherical particle. Coefficient of absorption α_{abs}, of radiation by a single particle is determined by the following expression [24]:

$$\alpha_{\mathrm{abs}} = \pi r_0^2 k_{\mathrm{abs}}. \tag{3}$$

So, the absorption efficiency of a metal nanoparticle which has smaller diameter than the laser wavelength is

$$k_{\mathrm{abs}} = \frac{24\pi^2 r^2 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2(\omega)}{(\varepsilon_1(\omega) + 2\varepsilon_m)^2 + \varepsilon_2^2(\omega)}. \tag{4}$$

ε_m is the dielectric constant of the surrounding medium, $\varepsilon_1(\omega)$ is the real part and $\varepsilon_2(\omega)$ is the imaginary part of the dielectric function of the metal. Its maximum absorption occurs when $\varepsilon_1(\omega) = 2\varepsilon_m$ is satisfied [6]. The calculation of optical absorption of spherical silver nanoparticles with radii between 5 and 50 nm is performed and shown in figure 1.

As shown in figure 1, for each radius, absorption peak occurs in a specific the wavelength and larger nanoparticles absorbed more energy. The absorbed energy is different for various radii in the wavelength range from 350 to 500 nm. For wavelengths less than 350 nm or more than 500 nm, values of absorption for all particles are almost different. As the absorption is the same in these wavelength ranges, it is expected that increasing the temperature of particles does not make much difference.

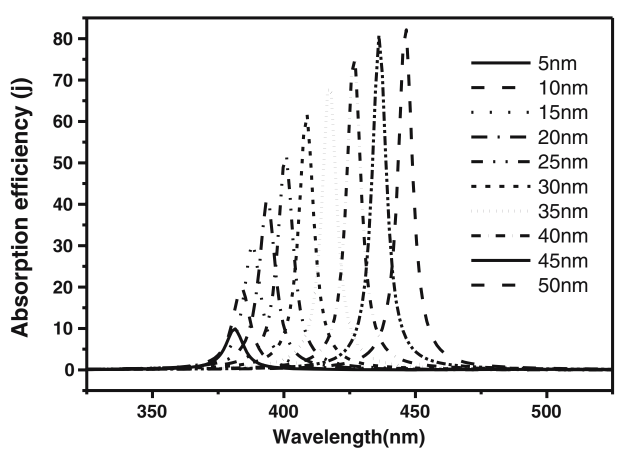

Figure 1. Absorption spectra for spherical silver nanoparticles with radii between 5 and 50 nm.

Another important issue is the integral of the energy that particles absorbed by laser radiating which should be calculated.

$Q_{\rm abs}$, the absorbed energy when the particle is irridiated from $t = 0$ to t can be calculated as

$$Q_{\rm abs} = \pi r_0^2 \int_t^0 I_0(t) k_{\rm abs} {\rm d}t \quad (5)$$

and, the thermal energy absorbed by the particle is

$$E_{\rm T} = \rho_0 c_0 V_0 T_0, \quad (6)$$

where ρ_0 and c_0 are the density and the specific heat capacity of the particles and T_0 is the temperature. All particles were considered to be spherical and $V_0 = (4/3)\pi r_0^3$ is the volume of the spherical particles [27].

The laser beam is perfectly uniform and the radius of the laser beam is set at 1 mm. Time intensity function of pulsed laser is 30 ns. As heating includes melting, the total thermal energy is calculated after the particle reaches evaporation point.

$$Q = Q_1 + Q_2 + Q_3. \quad (7)$$

Q_1 is the amount of energy required to increase the temperature of a particle to melting point, Q_2 is the latent heat required to convert unit mass of the solid into the liquid without change in temperature and Q_3 is the amount of heat energy the particles require to change the temperature in liquid state.

The energy conservation law for particles is described by the equation

$$Q_{\rm abs} = E_{\rm T} - E_{\rm T\infty} - Q_m, \quad (8)$$

where $E_{\rm T} = \rho_0 c_0 V_0 T_0$ is the initial value of the thermal energy of the particle, T_∞ is the initial particle temperature and $Q_m = \rho_0 V_0 l_{\rm m}$ is the energy spent for particle melting [27]. Q_m is applicable only if the particle reaches a temperature higher than the melting temperature.

The final temperature of the particles is directly proportional to the initial temperature and the amount of absorbed heat energy and inversely proportional to the density, specific heat capacity and the radius of the particles.

It has been established experimentally and theoretically that nanoparticles have some special properties due to their very high surface area to volume ratio. Melting temperature, cohesive energy, surface melting, Deby temperature, specific heat capacity and solubility are some of these special properties [28–33]. Melting point of the metal particles is less than the bulk mode. Besides, by reducing the particle size, it will be decreased further [34–39]. The new thermal behaviour of nanomaterials, leads to development of new properties with various applications in materials. Many of the properties of nanomaterials depend on their coordination number. However, by changing the size and shape of the particles, the coordination number will be changed too [40–42]. The coordination number also affects the cohesive energy and directly affects the melting point of nanoparticles. In short, melting temperature decreases when the bulk size decreases [28,38]. In addition, effect of size in the value of melting point is accounted in the calculations as well.

Nanoparticles have radii between 5 and 50 nm. The laser beam with wavelengths of 248, 266, 355, 532 and 1064 nm are generated from excimer lasers, fourth harmonic of Nd:YAG laser, third harmonic of Nd:YAG laser, second harmonic of Nd:YAG laser and Nd:YAG laser, respectively. The initial temperature of the particles is 0°C and the laser pulse duration is 30 ns with a width of 1 mm.

3. Results and discussion

According to the absorbed energy, the temperature of the colloidal silver nanoparticles was calculated for different radii. In this work, we focus on studying the optical absorption and heating of colloidal silver nanoparticles under pulsed KrF laser and pulsed Nd:YAG laser irradiations. In the current study, optical absorption and temperature of spherical silver nanoparticles having radii between 5 and 50 nm has been calculated. The particle size range was chosen in such a way that the absorption spectra were dominated by the dipole plasmon resonance. Moreover, in order to gain the highest possible absorption efficiency at any wavelength, sphere size was optimized.

Figure 2 shows the temperature of particles under pulsed excimer laser irradiation at a wavelelength of

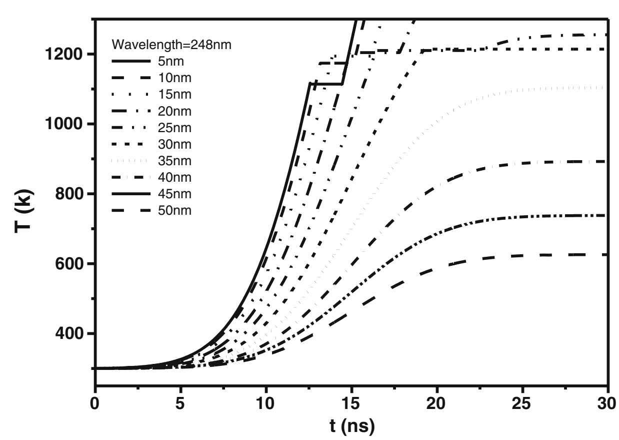

Figure 2. Temperature of silver nanoparticles under the irradiation of excimer laser at a wavelength of 248 nm with respect to the effect of size on the melting temperature of the nanoparticles.

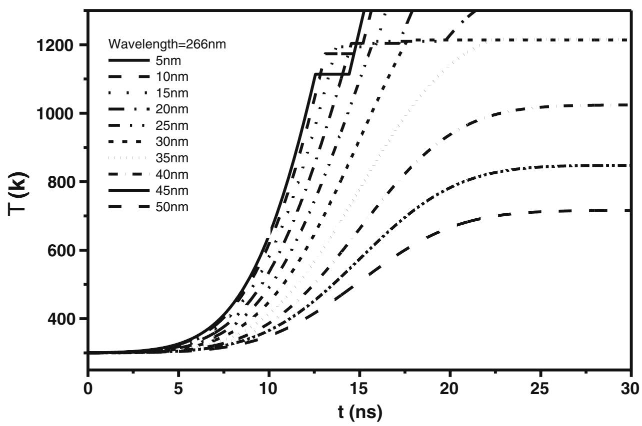

Figure 3. Temperature of silver nanoparticles under fourth harmonic of Nd:YAG laser irradiation at 266 nm wavelength with respect to effect of size on the melting temperature of the nanoparticles.

248 nm. As illustrated in figure 2, the final temperature of nanoparticles at different times during the laser pulse irradiations depends on the size of the particle. Moreover, smaller particles undergo a greater increase in their temperature.

Figure 3 depicts temperature changes under the irradiation of fourth harmonic of Nd:YAG laser at a wavelength of 266 nm. It can be clearly seen that particles with 5 nm radius had the maximum absorption, and the maximum value of temperature equals 1234 K, whereas particles with 30 nm radius only received latent heat of melting point. At the same time, 50 nm particles did not even reach melting stage and their maximum temperature is 715 K. As pulsed laser was used, in both figures 2 and 3, at the end of the absorption time, rate of temperature increase for all particles is the same. Figure 4 shows the changes in temperature in third

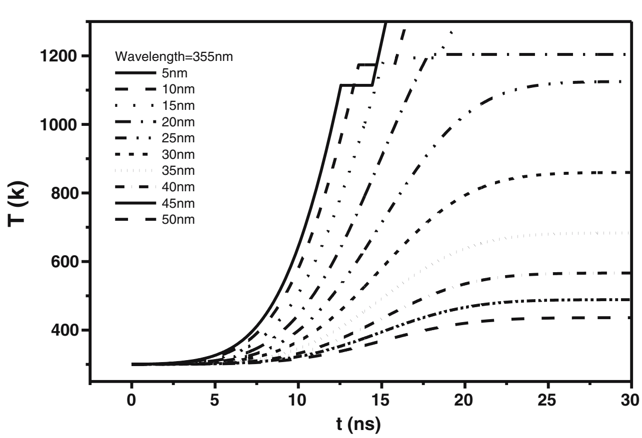

Figure 4. Temperature of silver nanoparticles under low intensity irradiation of third harmonic of Nd:YAG laser at 355 nm wavelength with respect to the effect of size on the melting temperature of the nanoparticles.

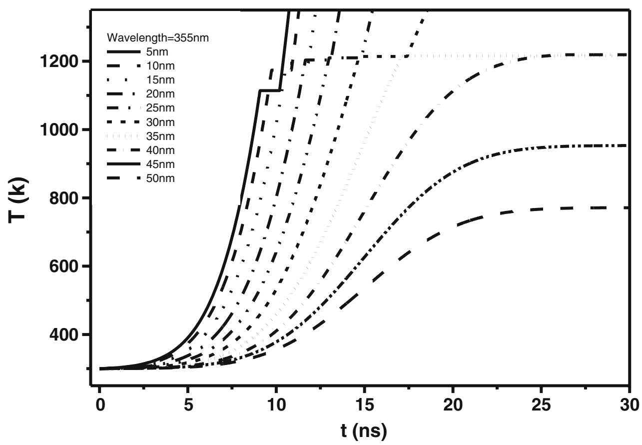

Figure 5. Temperature of silver nanoparticles under intermediate intensity irradiation of third harmonic of Nd:YAG laser at 355 nm wavelength with respect to the effect of size on the melting temperature of the nanoparticles.

harmonic of Nd:YAG laser irradiation with a wavelength of 355 nm. As yet, the laser intensity was adjusted to 5 nm particles, but this time it was adjusted to particles with 25 nm radius. Indeed, the laser intensity was increased. By increasing the laser intensity, which is shown in figure 5, temperature of all particles increased sharply. Accordingly, it is clearly seen that the final temperature of 5 nm particles in this stage is high, up to the melting point and only particles with 45 and 50 nm radii are not in the melting phase. By using high-intensity laser, for 50 nm particles, the temperature of the particles increased much more, and the time taken by 5 nm particles to reach the melting stage is about 6.5 s (see figure 6). The noticeable difference between figures 7 and 6 is that, for all particles, final temperature is extremely

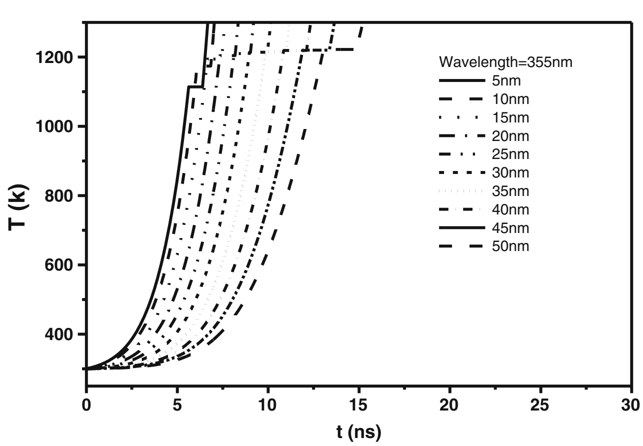

Figure 6. Temperature of silver nanoparticles under high intensity irradiation of third harmonic of Nd:YAG laser at 355 nm wavelength with respect to the effect of size on the melting temperature of the nanoparticles.

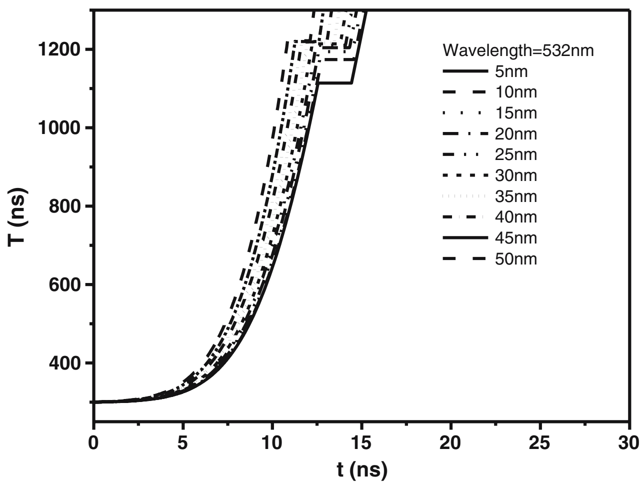

Figure 7. Temperature of silver nanoparticles under irradiation of second harmonic of Nd:YAG laser at 532 nm wavelength with respect to the effect of size on the melting temperature of the nanoparticles.

high and all of them have reached the melting stage. What should be noted here is that, unlike previous wavelengths, at this time, the largest particles have the highest temperature at the end and the same is also expected from the absorption figure (figure 1). Moreover, in figure 7, the difference between temperatures is less and curves are getting closer.

According to calculations made in 1064 nm wavelength, absorption efficiency does not depend much on the size of the nanoparticles in this wavelength. Figure 8 displays the temperature changes of 5–50 nm particles under irradiation of Nd:YAG laser with

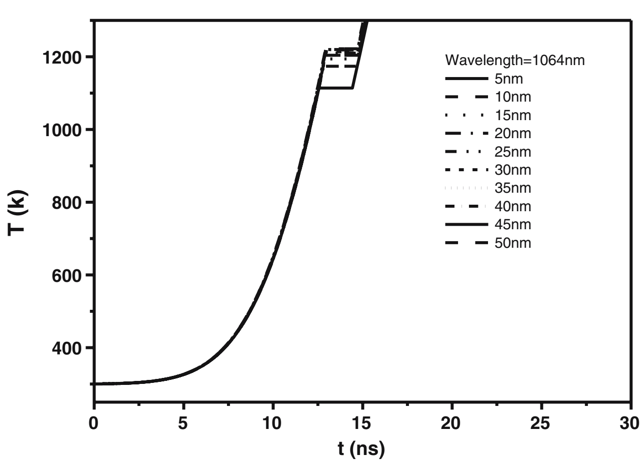

Figure 8. Temperature of silver nanoparticles under irradiation of Nd:YAG laser at 1064 nm wavelength with respect to the effectof size on the melting temperature of nanoparticles.

a wavelength of 1064 nm. It is clearly seen that the temperature of the nanoparticles at different times during laser pulse irradiation does not depend much on the particle size. The increase in temperature is the same for almost all particles and separating the particles, especially at low temperatures, is difficult at this wavelength. All particles reach the melting point and higher and the highest temperature is for 50 nm particles. Final temperature difference between 5 and 50 nm particles is about 77 K.

After all, in the case of short-wavelength radiations, smaller particles can achieve high temperatures only by low-intensity laser irradiation. For larger nanoparticles, time duration for the temperature rise is short. Besides, for more uniform heating, larger nanoparticles are more effective, as they have more controllable heating. In contrast, for high-wavelength radiations, rise in temperature is the same for all particles and there is very little difference in final temperature and also in the heating in all the stages.

On the whole, shorter wavelengths, where absorption efficiency depends on the particle size, are suitable in cell targeting. By contrast, at higher wavelengths, temperature of nanoparticles with different dimensions increases in the same way. In addition, at lower wavelengths, larger nanoparticles are preferred for large area damage at lower temperatures, while small nanoparticles are more useful in destroying a small area of cells completely. For heating nanoparticles using laser radiation with higher wavelengths, more intensive radiations are needed. To put it in another way, these wavelengths are appropriate for uniform heating in large areas that contain nanoparticles of different sizes as rise in temperature is the same for all particles. Heating with this wavelength is useful for destroying a large area completely; however it may have some thermal effects.

According to the calculation results, as the absorbing efficiency of nanoparticles at high wavelengths decreases, low intensity and high wavelengths in low temperatures can be used for purposes such as drug delivery. By using these calculations, the threshold intensity of the laser and also optimal size of the nanoparticles on laser wavelength can be determined. The calculation shows that the particle temperature can increase only via adjusting the particle size without increasing the laser pulse energy. The results are applicable in cell targeting below the tissue damage threshold energy. The theoretical results can be directly used in experimental researches of pulsed laser action on metal nanoparticles and also can be applied to estimate the experimental results of selective killing of cancerous cells or bacteria, remote release of encapsulated material into specific cells and biolabelling.

4. Summary

In this study, optical properties of spherical silver nanoparticles at laser radiation wavelengths have been examined for some laser applications in nanomedicine and nanotechnology by using Mie theory. Calculation of absorption factors and their maximal temperatures when the radii of the nanoparticles are between 5 and 50 nm is performed under pulsed KrF laser and pulsed Nd:YAG laser irradiations. The final temperatures for all particles have been obtained. It has been inferred that at short wavelength, temperature of small particles rises rapidly, while at high wavelengths, temperature rise is the same for all particles.

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