Gold nanoparticles as nanoheaters and nanolenses in the processing of different substrate surfaces

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Abstract. We present results of our recent study on the heating process and near field localization arising when gold nanoparticles are irradiated by ultrashort laser pulses at wavelength of 800 nm. The system under consideration consists of Au nanoparticles with diameter of 40, 80, or 200 nm in vacuum or deposited on different substrates. Substrate materials with different dielectric properties are used in order to sense and visualize the nanoparticle heating and near field electromagnetic distribution. The theoretical analysis is based on the optical properties obtained by the Mie scattering theory. The absorption coefficients calculations are implemented in a two-temperature heat model for estimation of the nanoparticle temperature. The near field distribution in the vicinity of the particles is calculated by the finite difference time domain (FDTD) method. It is found that at even moderate laser fluences the temperature of the particle can reach a value sufficient for bubble formation in biological tissues. The analysis of the near field distribution shows that when the particle is deposited on a substrate surface, the dielectric properties of the substrate define the spatial distribution and the enhancement of the near field intensity. The observed localization and field enhancement may result in a precise modification of the substrate with a resolution defined only by the nanoparticle size. Such modifications are experimentally observed in different substrates.

1. Introduction

Being an object of the fundamental modern physics as materials with “unusual” properties related to size dependent electron energy states, metal nanostructures found a practical application four centuries ago [1,2]. The specific extinction spectra that for gold structures have a strong peak in the visible region give the brilliant ruby color used to decorate glasses in cathedrals in the 17th century. About a hundred years ago, in 1908, Gustav Mie explained the phenomena describing the absorption and scattering of the electromagnetic radiation by spherical particles. It became clear that the decrease of the particle size to dimensions smaller than the illuminating wavelength can contribute to the possibility of a resonant excitation of collective electron oscillations (plasmons) in these structures.

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The plasmon excitation influences their far field optical properties, giving sharp resonances in the absorption and scattering spectra [3, 4] which are not present in bulk material. In 1985, B. Messinger et al. [5] applied the Mie theory to describe the scattering properties of metal nanoparticles in the near field zone. They showed that the power scattered in the vicinity of the particle can be orders of magnitude higher than the incident one for a given geometrical cross-section. It can be shown [6, 7] that this enhancement is related to the charge distribution on the metallic surface and the properties of the near field are evanescent; i.e. they are present in the very close vicinity of the particle. Thus, the size of the metallic structure defines the zone of the near field localization and the influence of the incident wavelength as a limiting parameter for the smallest spatial resolution (an effect related to the diffraction limit) vanishes.

The narrow absorption band and the existence of the enhanced near field that are characteristic of the noble nanoparticles - electromagnetic radiation interaction open new trends in many aspects in the modern technologies: in biological applications as biomedical diagnostics [8], targeted drug delivery [9], photo thermal therapy [10], surface-enhanced Raman spectroscopy (SERS) [11], near field scanning optical microscopy [6], tip enhanced Raman spectroscopy [12] with a resolution on a nanometer scale. The enhanced field in the vicinity of the metal nanoparticle can also result in a permanent modification of the surface in the near field zone [7, 13-17].

However, the physics of the plasmon properties and the near field characteristics need further clarification. While for a single isolated particle the properties of the local enhanced field depend on the particle parameters, and on the properties of the incident irradiation and surrounding medium, for a nanoparticle array they can be additionally modified and influenced by the inter-particle coupling [17-20]. These mechanisms are still not fully understood.

In this work we estimate the heating of gold nanoparticles when they interact with ultrashort laser pulses and define some of the main features of the electromagnetic field in the particle vicinity. The effects of particle heating and near field intensity enhancement are demonstrated experimentally as nanosized modifications of different substrates are shown. The incident irradiation is assumed to consist of ultrashort laser pulses at wavelength of 800 nm. The application of ultrashort laser pulses limits the heat affected zone which is crucial for many applications. The use of radiation at wavelength falling in the tissue transparency window (600 - 1300 nm) gives an opportunity of designing techniques for application of nanoparticles in medicine.

2. Theoretical model
In order to describe adequately the nanoparticle heating process, its optical parameters should be obtained. In this study the absorption cross-section is obtained on the basis of Mie scattering theory using the following equations:

\[ C_{\text{abs}} = C_{\text{ext}} - C_{\text{sca}}, \] (1)

where \( C_{\text{ext}} \) and \( C_{\text{sca}} \) are the extinction and scattering cross sections given by [4]:

\[ C_{\text{ext}} = \frac{4\pi R^2 \varepsilon_m^{3/2}}{\lambda a^3} \sum_I (2I + 1) \text{Re}(A_I + B_I), \] (2)

\[ C_{\text{sca}} = \frac{4\pi R^3 \varepsilon_m^{1/2}}{\lambda a^3} \sum_I (2I + 1)(|A_I|^2 + |B_I|^2). \] (3)

Here, \( \lambda \) is the wavelength of the incident irradiation, \( \varepsilon_m \) is the dielectric function of the surrounding medium, \( a = (2\pi\varepsilon_m^{1/2})/\lambda \) is the particle radius, and \( A_I \) and \( B_I \) are the electric and magnetic partial oscillation coefficients. The optical parameters for gold used in the calculation are taken from [21].

The temperature evolution of the particle during and after the interaction with the laser pulse is traced by the one-dimensional two-temperature diffusion model:
$$C_e \frac{\partial T_e}{\partial t} = -\gamma (T_e - T_l) + S,$$

$$C_l \frac{\partial T_l}{\partial t} = \gamma (T_e - T_l),$$

$$S = IC_{abs} \frac{V}{V_p}.$$  

Here, $T_e$ and $T_l$ are the electron and lattice temperatures, $S$ and $I$ are the laser energy source and laser intensity (time dependent), respectively. $V_p = 4/3 \pi R^3$ is the particle volume. $C_l$, $C_e$, and $\gamma$ are the lattice and electron system heat capacities and the electron-lattice coupling constant, respectively. In the present model the spatial characteristics of the particle heating are neglected and the heating is assumed to be homogeneous.

The coupled equations (4)-(6) are solved using a classical finite difference scheme and by taking into account the temperature dependence of the electron heat capacity according to the formula $C_e = A_e T_e$, where $A_e = 70$ J/m$^3$K$^2$, and the temperature dependence of $C_l$ [22]. The electron heat conductivity of gold is assumed to be constant, as the value of $2 \times 10^3$ W/mK is used as an average obtained from the expression $k_e = k_{eo}(T_e/T_l)$, for the electron temperature range from 300 K to 9000 K, and $k_{eo} = 318$ W/mK [23]. The lattice heat conductivity of gold is $318$ W/mK [23]. The value of the coupling constant, $\gamma = 3 \times 10^{16}$ W/m$^3$K is taken from [24].

FDTD simulation [25] is applied in order to study the near field properties around the irradiated nanoparticles. The method is based on the numerical solution of Maxwell’s equations and can be used to obtain adequate picture of the electromagnetic field properties in the near and far field zone around structures with arbitrary shapes [26-28]. The simulation system consists of a gold nanoparticle or a 2D nanoparticle array placed on different substrates. Absorbing boundary conditions are applied to the boundary of the simulation cell. For the simulations of nanoparticle arrays, a hexagonal arrangement of the particles is assumed because this arrangement is predominantly obtained by the existing chemical methods for deposition. Simulations with circular and linear polarization of the incident irradiation are performed. The electric field strength of the incident wave is set at 1 V/m.

3. Experimental setup

The gold spherical particles used in the experiments have diameter of 40, 80 and 200 nm, with a standard diameter deviation of less than 8% (BBInternational Corp.). The particles are deposited as a colloid on polished silicon and PMMA substrates by spin-coating. Under these conditions all the substrate surfaces are covered by randomly distributed gold particles. The roughness of the substrates (without particle deposition) is in the order of few nanometers. The samples are irradiated by laser pulses delivered by a Ti: sapphire chirped pulse amplification system that produces pulses with energy of 1 mJ at a repetition rate of 1 kHz, and center wavelength of 800 nm. The laser pulse duration used is 100 fs FWHM. The laser radiation is incident normally to the substrate surface and is focused by a lens with a focal length of 200 mm. The pulse energy is adjusted by a variable attenuator. The experiments are done in air, on a single shot basis. Linear and circular polarization of the incident irradiation is used. The irradiated samples are analyzed by SEM and AFM. The substrate surface is not chemically cleaned after the laser irradiation.

4. Results

4.1. Gold nanoparticles as nanoheaters

Figure 1 presents the absorption cross-section spectra of single gold nanoparticles with radius of 20, 40 and 100 nm calculated by (1)-(3). The clearly expressed peaks in the absorption cross sections are related to the plasmon excitation in the nanoparticles. The maximal values are observed in the range of about
525 to 550 nm for particles with radius R = 20 and 100 nm, respectively. The values of the absorption cross-sections at wavelength of 800 nm are about two orders of magnitude lower than the optimal ones for particles with R = 40 and 80 nm. Although the increase of the particle dimensions results in a broadening of the plasmon absorption band and a shift of the maxima to the longer wavelengths, the value of the cross-section for a particle with radius of 100 nm is about 5 times lower than the peak value. Using the calculated absorption cross-sections the temperature of the particles is obtained using the two-temperature diffusion model. The values of the maximal temperature reached in the nanoparticles when they are irradiated by a 100 fs laser pulse as a function of the incident laser fluence are shown in figure 2.

It should be noted that for biophotonics applications, such as cell membrane modification and when irreversible cell modification is based on bubble formation (as in tumor cell killing) the necessary temperature increase should be at least 170 K [29, 30]. When ultrashort laser pulses are used such heating is realized in nearly isochoric conditions which will result in the development of significant tensile stress [31] in the vicinity of the heating point. This will lead to the formation of a cavitation bubble without the need of heat accumulation, i.e. after a single pulse. As is seen in figure 2, a temperature increase of 170 K can be obtained in gold nanoparticles after a single laser pulse at fluences of about 70 mJ/cm$^2$ for R = 100 nm and at 100 mJ/cm$^2$ for particles with R = 40 and 80 nm. It should also be mentioned that the experimentally obtained threshold for biological cell modification (the example is for human breast MDA-MB cells [32]) using direct femtosecond laser pulses irradiation (without nanoparticle mediation) is estimated to be about 500 mJ/cm$^2$, i.e. five times higher.

4.2. Near field localization
Figure 3 presents the calculated distributions of the electric field around a gold particle with radius of 100 nm – (a) in vacuum, and (b) placed on a Si surface. The incident laser radiation has circular polarization in both cases. The electric field distributions are shown in a cross-sectional plane of the system, (a) - through the center of the sphere and parallel to the incident wave propagation and (b) – through the center of the sphere and the point of contact between the particle and the substrate.
In the case of isotropic vacuum environment and a small particle (when dipole excitation is dominant) the charge oscillation direction follows the direction of the incident electric field. The induced near electric field on the particle surface has a maximal value in the vicinity of the equator and approaches the incident field amplitude on the poles. Although for a particle with the dimensions chosen higher modes can dominate the near field distribution, at the wavelength used of 800 nm only dipole mode can be efficiently excited [7]. When the particle is placed on the substrate surface (figure 3 (b)) the near electric field distribution becomes quite different. As it is seen in figure 3 (b), the field is localized in the vicinity of the point of contact on the Si surface. In the present case, the strong field on the gold particle surface produced by charge accumulation induces image charges in the substrate material. The field distribution both on the gold sphere surface and in the substrate is related to the existence of a component in the direction of the incident electric field and a z-component, which appear due to the interaction between the particle and substrate charges. Due to this component, the induced charge density in the bottom of the sphere is significantly higher than that in the upper hemisphere. Since the near electric field amplitude decreases rapidly with the distance, the density of the induced image charges on the substrate surface increases in the direction to the point of contact.

The properties of the near field for a system consisting of a particle deposited on a substrate will depend on the charge density induced on the substrate surface [7]. In its turn, this density depends on the dielectric properties of the substrate material and one should expect different characteristics of the near field for different substrate materials. The simulations made for dielectric substrates with different refractive indices show that the effect of near field localization in the vicinity of the contact point between the particle and the substrate becomes more pronounced (and therefore the value of the field intensity on the substrate surface increases) with the increase of the refractive index of the substrate [7, 17]. A clear localization of the zone with maximal intensity on the substrate surface is observed for substrates with a refractive index higher than 1.7.

In order to validate the theoretical results, experiments on modification of substrates with assistance of nanoparticles are performed. The theoretical results indicate that for a dielectric substrate with a refractive index of 1.488, the near field intensity is not localized in the vicinity of the contact point between the substrate and the particle. A possible modification of the underlying substrate could be related only to the particle heating. Figure 4 shows modification of PMMA and silicon substrates when gold nanoparticles with radius of 100 nm are deposited on them and the systems are irradiated by a single ultrashort laser pulse with fluence of 60 mJ/cm² and 200 mJ/cm², respectively. The polarization of the incident irradiation is linear (shown by an arrow). In the case of a PMMA substrate, the nanohole shape has radial symmetry and there is no observable influence of the incident irradiation polarization on the hole shape.
Figure 4. SEM images of nanomodification when gold nanoparticles with radius of 100 nm are deposited on (a) PMMA and (b) Si substrate and irradiated by single laser pulse with fluence of 60 mJ/cm² and 200 mJ/cm², respectively. The inset in (a) shows the distribution of the near field intensity on the substrate surface predicted by FDTD simulation. The arrow shows the polarization of the incident irradiation.

Such dependence is not seen in the fluence range up to the modification threshold of the native substrate. Furthermore, the rest of the substrate remains unchanged which confirms the idea of local interaction under the particle only. According to the numerical model, the maximal temperature achieved with this fluence is near the melting temperature of the PMMA substrate (440 K). These results indicate that heating has the main contribution to the substrate modification in this case. In the case of a Si substrate, the shape of the modified area corresponds to the field intensity distribution and the nanoholes formed have a shape elongated along the polarization direction. This shows that at these conditions the enhancement of the near field under the gold particle is the governing mechanism for surface modification rather than particle heating. When circular polarization of the incident irradiation is used the hole shape formed shows good radial symmetry [7].

The characteristics of the nanoholes produced depend also on the nanoparticle dimensions [16]. Figure 5 shows SEM images of holes produced when a 0.185 J/cm² laser pulse irradiates a Si surface with gold particles with (a) R = 100 nm, (b) R = 40 nm, and (c) R = 20 nm deposited on it. The polarization of the incident radiation is circular. The maximal depths of the holes are 30 nm, 15 nm, and 7 nm, respectively.

Figure 5. SEM images of holes produced when a 0.185 J/cm² laser pulse irradiates a Si surface with gold particles with radius of (a) 100 nm, (b) 40 nm, and (c) 20 nm deposited on it.
4.3. Nanoparticle array

Figure 6 shows experimentally obtained absorption spectrum of gold nanoparticles with radius of 100 nm deposited on glass substrate. The inset shows a SEM image of the deposited particles. The dashed line shows the absorption spectrum of an isolated nanoparticle calculated by Mie theory. It is seen that the absorption of the nanoparticle cluster is efficient in the wavelength range from 550 to about 850 nm in the case of the structure presented. The near field distribution in the vicinity of the nanoparticle array is also different compared to the case of single particle [17, 20]. Figure 7 a) shows the calculated distribution of the electric field intensity on a Si substrate when closely packed nanoparticle array is placed on it.

A cross sectional view of the field intensity distribution in a nanoparticle chain within the array is shown in figure 7 b). Due to plasmon coupling, the zone with the maximal field intensity in a nanoparticle array is localized between particles, where its value is about two orders of magnitude higher than that on the substrate surface.

Thus, for surface modification applications the cluster heating will be dominant mechanism rather than the direct near field localization and enhancement as it is in the case of single particle.

5. Conclusions

We present experimental and theoretical results on two effects when laser pulse interacts with gold nanoparticles. On the basis of Mie theory, the particle absorption cross-section is estimated and the maximal nanoparticle temperature is calculated. It is shown that at laser fluences lower than human tissue modification, the nanoparticle can be heated to temperatures that may induce local cell damage. In addition to the particle heating, the properties of the near electromagnetic field are also investigated. It is shown that the field intensity can be strongly enhanced as the enhancement value depends on the properties of the environment. This dependence is used to distinguish between the domination of the two mechanisms studied in the modification of different substrates. In the case of a substrate with a refractive index higher than approximately 1.7, the near field intensity is localized in the vicinity of the contact point between the particle and the substrate. In such a case the near field intensity...
enhancement plays a dominant role in the substrate modification. When the substrate has a lower refractive index, the heating of the particle has the main contribution. In all cases, the laser irradiation of the samples at fluences lower than the modification threshold of the native surface results in the formation of nanoholes with a size smaller than the gold nanoparticle diameter. When a 2D nanoparticle array is considered, the absorption spectra and near field intensity distribution are found to be different than the case of single particle. For such a structure the interparticle plasmon coupling defines the optical response.

The results obtained can form the basis for the development of techniques for nanomodification of different materials. The heating of nanoparticles can be used in photothermal therapy of biological samples. Furthermore, the present analyses can be used for the appropriate selection of efficient substrates for SERS technique.

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