

Local nanoheating and substrate nanomodification based on enhanced absorption and near-field properties of gold nanoparticles

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In this paper a theoretical and experimental investigation on the local heating and near field properties of gold nanoparticles placed on a substrate is presented. The system under consideration consists of single gold nanoparticles with diameters of 80 and 200 nm deposited on substrate and irradiated by ultrashort laser pulse at wavelength of 800 nm. The heating of the nanoparticle is described by two-temperature heat model as the input optical properties of the nanoparticles are evaluated on the basis of Mie theory. The properties of the local field enhancement in the vicinity of nanoparticles are also discussed on the basis of Finite Difference Time Domain simulation results. The near field properties and the effect of nanoparticle heating predicted by the theory are confirmed by experiments on substrate modification mediated by gold nanoparticles. In the case of silicon substrate the produced nanoholes express clear dependence on the near field properties, while for dielectric substrate the particle heating is the main mechanism for substrate modification. The conducted research is directed toward the application of noble metal nanoparticles in photothermal therapeutic treatment of living cells at the optical transparency window (600-1300 nm) of the tissues.

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1. Introduction

The research field of characterization and utilizing the properties of nanosized objects of different materials attracts a growing interest in recent years [1-5]. The interest in this field is not only related to the common tendency of miniaturization of the new photonic, biophotonic and data storage devices, but also to the specific physical properties that these structures show. Reducing the material dimensions in nanometer spatial range results in strong change of the electronic properties as the density of states and the electron motion scale becomes material's size dependent [6]. The existence of discrete energy levels in these structures opens a new way in fabrication of photonic devices and development of efficient energy conversion technologies.

From the point of view of practical applications some specific properties of noble metal nanoparticles are believed to be a basis of fundamentally new technologies [7]. Due to the effective coupling of electromagnetic radiation to the plasmon oscillation in these structures a significant enhancement of the field intensity in their near field zone can be produced. The intensity can exceed melting or ablation threshold of the substrate placed near the metal structure and this can result in permanent modification of the substrate surface. Since the induced near electromagnetic field has properties of an evanescent wave, its amplitude decreases rapidly with the distance from the metal surface. Thus, the size of the field

enhanced zone is governed not by the wavelength of the incident radiation, but by the size of the illuminated metal structure. The efficient excitation of plasmons in metal nanoparticles results also in their enhanced absorption and scattering cross sections [8] which is used for cell processing [9-11] and cell imaging [10,12]. In the field of particle mediated cell processing applications the enhanced absorption of the particle leads to its strong heating that can result in triggering of irreversible chemical effects, or bubble formation in the material in its vicinity. In addition to the high efficiency, the application of nanoparticles can ensure strong localization of the processing area when the wavelength of the incident irradiation falls in the transparency window of the surrounding material.

In this work two effects of the interaction of electromagnetic field with gold nanoparticles are considered. The first one is related to the localization and enhancement of the electromagnetic field intensity in near field zone of the nanoparticles. In addition, the enhanced absorption and subsequent nanoparticles heating is described by theoretical modeling. The described effects can result in a permanent surface modification when the particles are deposited on a substrate. Such modifications are demonstrated in different materials and used to define the role and domination of the near field enhancement effect and particle heating. The incident irradiation in the presented study is ultrashort laser pulses at wavelength of 800 nm. The use of ultrashort pulses ensures high temporal

and spatial localization of the laser-matter interaction which leads to minimization of the heat diffusion and ensures processing with high precision. The used wavelength falls into the tissue transparency window (600 – 1300 nm), and the obtained results can be used in designing of applications of nanoparticles in in-vivo biophotonics. The parallel study of the presented mechanisms shown here that has not been presented up to now is important for the better understanding of laser radiation – nanoparticle interaction and designing of practice applications.

2. Simulation model

The electromagnetic field distribution and the optical near field enhancement in the vicinity of nanoparticles when they interact with electromagnetic field are calculated by Finite Difference Time Domain (FDTD) method [13]. The method is a numerical algorithm for solving Maxwell's equation and it can be used for description of the electromagnetic distributions for complex geometries and inhomogeneous systems. In the present work the simulated system consists of gold nanoparticle in vacuum or deposited on substrate surface. The simulation system is divided into elementary cells, where the electric and magnetic field components are calculated at each time step by "leap-frog" scheme [13]. The dielectric function of the gold particles is described by Drude model as the input parameters are taken from [14, 15]. Simulations are made for system that consists of gold nanoparticle with diameter of 80 and 200 nm placed on PMMA and silicon substrates. The dielectric functions of the materials are taken from [16]. The electric field intensity which is an input parameter for FDTD simulation is assumed to be 1 (V/m)² in all simulations.

The temperature evolution of the particle during and after the interaction with the laser pulse is described by one-dimensional two-temperature model:

$$C_e \frac{\partial T_e}{\partial t} = -\gamma(T_e - T_i) + \frac{IC_{abs}}{V_p} \quad (1)$$

$$C_i \frac{\partial T_i}{\partial t} = \gamma(T_e - T_i) \quad (2)$$

In system (1)-(2) T_e and T_i are the temperatures of the electron and lattice systems, I is the laser intensity, respectively. $V_p = 4/3\pi R^3$ is the particle volume. C_{abs} is the absorption cross section of the particle. C_i , C_e , are the lattice and electron system heat capacities, and γ is the electron-lattice coupling constant, respectively. In the presented model the spatial distribution in the particle heating is neglected and it is assumed to be homogeneous. The system (1)-(2) is solved using a classical finite difference scheme and taking into account the temperature dependence of the electron heat capacity according to the relation $C_e = A_e T_e$, where $A_e = 70 \text{ J/m}^3\text{K}^2$, and the

temperature dependence of C_i [17]. The value of the coupling coefficient used is $\gamma = 3.10^{16} \text{ W/m}^3\text{K}$.

Since the optical properties of nanoparticles, generally depends on their properties, the absorption cross section C_{abs} is obtained on the base of Mie scattering theory using the equation:

$$C_{abs} = C_{ext} - C_{sca}, \quad (3)$$

where the extinction C_{ext} and scattering C_{sca} cross sections are given by [18]:

$$C_{ext} = \frac{4\pi R^2 \epsilon_m^{3/2}}{\lambda a^3} \sum_l (2l+1) \text{Re}(A_l + B_l) \quad (4)$$

$$C_{sca} = \frac{4\pi R^3 \epsilon_m^{1/2}}{\lambda a^3} \sum_l (2l+1) (|A_l|^2 + |B_l|^2) \quad (5)$$

here, λ is the wavelength of the incident irradiation, ϵ_m is the dielectric function of the surrounding medium, $a = (2\pi R \epsilon_m^{1/2})/\lambda$, R is the particle radius, and A_l and B_l are electric and magnetic partial oscillation coefficients. The optical parameters for gold used in the calculation are taken from Ref. 14.

3. Experimental details

In order to estimate the effect of interaction of nanoparticles with electromagnetic radiation, gold nanoparticles are deposited on different substrates and irradiated by ultrashort laser pulses delivered by Ti:sapphire chirped pulse amplification system that produces 1 mJ pulses at a repetition rate of 1 kHz, and center wavelength of 800 nm. The laser pulse duration is 100 fs FWHM. The laser radiation is directed normally to the surface and it is focused by a lens with a focal length of 250 mm. The pulse energy is adjusted by a variable attenuator. The experiments are done on a single shot basis, as the shot number is controlled by a high speed mechanical shutter. Gold colloids with particles having diameter, D , of 80 and 200 nm (BBInternational Corp.) are used in the experiments. The particles are deposited on the substrates by spin-coating method. After deposition the particles are randomly distributed on the substrate surface.

For sensing the particle heating and the near field properties in their vicinity, PMMA and silicon substrates are used in the experiments. The roughness of the substrates is estimated as 3 nm (RMS) for PMMA, and 1 nm for Si by AFM measurement.

The irradiated samples are analyzed by SEM (Sirion 400, FEI Company).

4. Results and discussions

The excitation of plasmons in gold nanoparticles is associated with development of enhanced near field in

their vicinity. Fig. 1 shows the electric field intensity distribution in the vicinity of nanoparticles with diameter $D = 80$, and $D = 200$ nm in vacuum calculated by FDTD simulation at incident wavelength of 800 nm. The incident irradiation has circular polarization and the wave vector is in $-Z$ direction. As it seen, the field intensity in the particle vicinity has complex distribution and at the presented configuration the maximal value is localized in the vicinity of the equatorial plane of the particle with diameter of 80 nm. This distribution is related to the domination of the dipole polarization mode excited at the presented conditions. The field distribution for particle with diameter of 200 nm shows contribution of excitation of higher modes. The electric field intensity is enhanced compared to the incident one, as at the presented wavelength it is maximal for the particle with diameter of 200 nm.

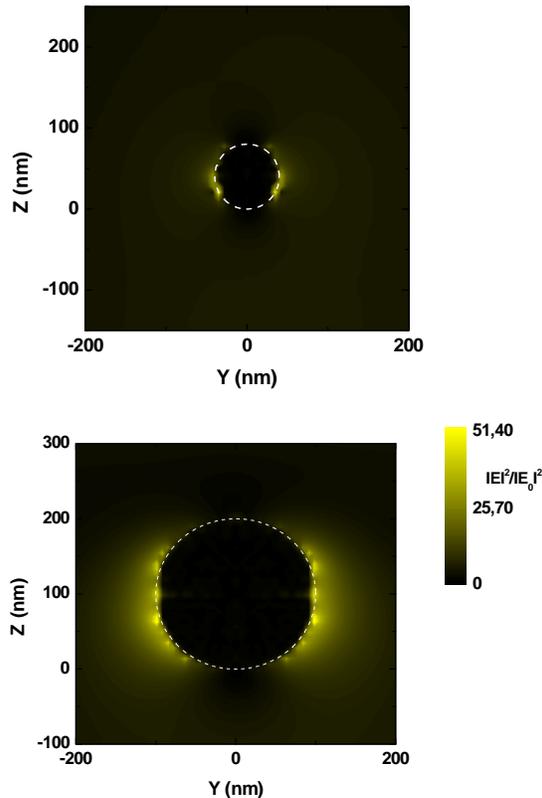


Fig. 1. Calculated electric field intensity distribution in the vicinity of gold nanoparticles with diameter 80 and 200 nm in vacuum. The incident irradiation is a plane wave directed in $-Z$ at wavelength of 800 nm. The incident electric field intensity is 1 V/m.

This effect is related to the efficient shift of plasmon excitation to the IR spectral range with increase of the particle size [19].

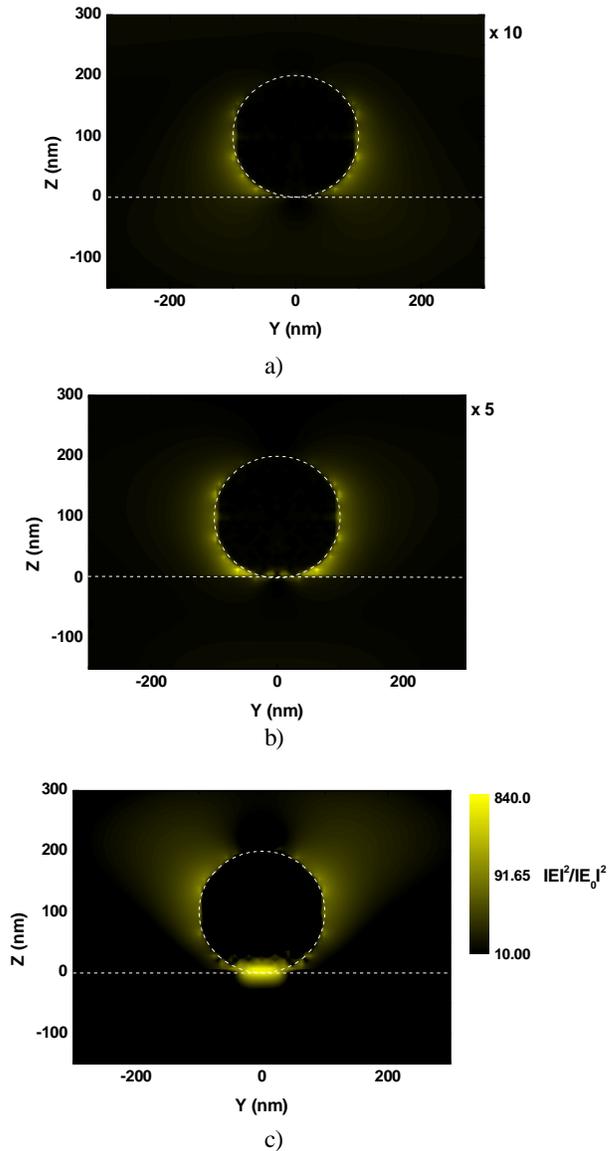


Fig. 2. Calculated electric field intensity distribution in the vicinity of gold nanoparticles with diameter 200 nm placed on different substrates. a) $n = 1.3$; b) $n = 2$; c) $n = 3.68$.

When the particle environment is not homogeneous, as in the case when particle is deposited on a substrate, the near field spatial distribution is significantly changed. Fig. 2 represents FDTD simulation results of the electric field intensity distribution where the particle with diameter of 200 nm is placed on dielectric substrates with refractive index n , of 1.3, 2, and 3.68. Due to the change of the near field scattering pattern [20] which substrate induces via contribution of excitation of higher plasmon modes and interaction between charges on the particle and image ones induced in the substrate, the zone with the highest intensity tend to localize in the vicinity of the contact point between the particle and the substrate. This effect is clearly

expressed with the increase of the substrate refractive index. The simulations made for dielectric substrates with different refractive index shows that a clear localization of the zone with the maximal field intensity on the substrate surface is observed for substrate refractive index higher than 1.7. From the viewpoint of practical applications, for example in the field of biophotonics, one should keep in mind that refractive indexes of most soft tissues are in the range of 1.35 to 1.6 (for cell membrane for example it is 1.46) [21]. In addition, if the nanoparticle-substrate system is immersed in medium, the field localization and intensity enhancement on the substrate decreases with the increase of the refractive index of the surrounding medium [22]. In such cases of low coupling with the substrate the influence of the illumination conditions on the near field properties [23] should be used for enhancement of the efficiency of nanoparticle application. Since the spatial distribution of the near field intensity is related to the polarization of the incident irradiation, the irradiation geometry (for example, at non normal irradiation) can influence the intensity properties on the substrate surface.

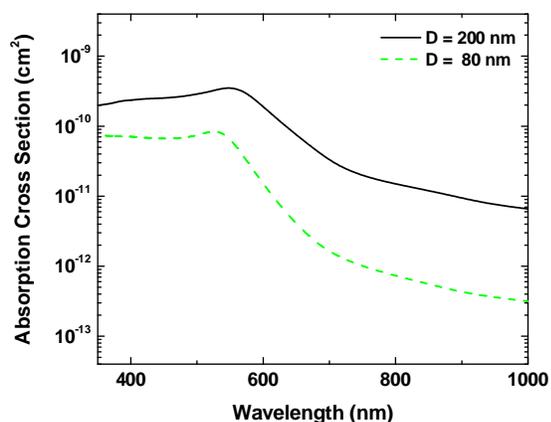


Fig. 3. Calculated absorption cross section spectra for gold nanoparticles with diameter of 80 and 200 nm in vacuum using Eqs. (3)-(5).

In addition to the localization and enhancement of the electromagnetic field in the vicinity of the nanoparticle, its absorption and consequent heating can also contribute to modification of material which is in contact with the particle. The absorption spectra of gold nanoparticles also express maxima which defines optimal wavelength that will ensure an efficient heating. Fig. 3 shows the absorption cross sections spectra for gold particles with diameters of 80 and 200 nm calculated by Eqs. (3)-(5). The resonance wavelength is in the range of 530-580 nm, as for the bigger particle the spectra is red sifted and broader. Since for practical applications in in-vivo photothermal therapy the use of wavelengths in the infrared region is crucial, we show in Fig. 4 the maximal temperatures achieved in gold nanoparticles as a function of the applied laser fluence assuming ultrashort laser pulse at wavelength of 800 nm. The presented results are

obtained by one-dimensional two-temperature model (Eqs. (1)-(2)). To have a notion about the results it should be mentioned that, in irreversible cell modification based on bubble formation (as in tumor cell killing) the necessary temperature should be at least 470 K [24, 25]. When ultrashort laser pulses are used such heating is realized in nearly isochoric conditions which leads to formation of a cavitation bubble without the need of heat accumulation i.e. after single pulse.

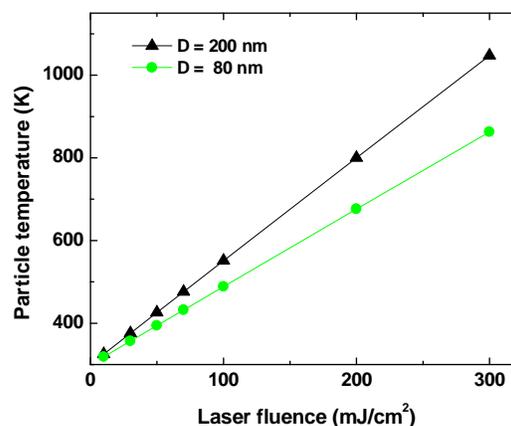


Fig. 4. Calculated dependence of the maximal temperature reached in nanoparticles with diameter of 80 and 200 nm as a function of the applied laser fluence. The incident irradiation is laser pulse with duration of 100 fs at wavelength of 800 nm.

The temperature of 470 K can be achieved in gold nanoparticles at the presented conditions after single laser pulse irradiation at fluences of about 70 mJ/cm^2 for $D = 200 \text{ nm}$ and at 100 mJ/cm^2 for particles with $D = 80 \text{ nm}$. Note also that for cell processing such temperature can be achieved using femtosecond laser pulses without nanoparticle assistance at fluences about five times higher due to the transparency of the tissue [26].

Up to now, we show theoretically that when gold nanoparticle is irradiated with ultrashort laser pulse, it can localize the electromagnetic field in its vicinity as the near field intensity is enhanced compared to the incident one. In addition, due to the energy absorption particle can be heated significantly even at moderate fluences. In order to validate the theoretical results, experiments, where the above mentioned mechanism cause modification of a substrates placed in close vicinity of the particle, are performed. The theoretical results indicate that for dielectric substrate with refractive index lower than 1.7 the near field intensity is not localized in the vicinity of the contact point between the substrate and the particle. Thus its effect in the substrate modification will be minor and the heating will have the main contribution. Fig. 5 shows modification of PMMA and silicon substrate when gold nanoparticles with diameter of 200 nm are deposited on it and the system is irradiated by a single ultrashort laser pulse with fluence of 60 mJ/cm^2 and 200 mJ/cm^2 ,

respectively. Note that the applied laser fluence is lower than the ablation threshold of the substrates, and the area only under the gold particle is modified. The incident irradiation here has linear polarization. The insert in Fig. 5 a) shows the calculated electric field intensity distribution on the PMMA substrate surface under the gold nanoparticle. The spatial distribution of the intensity on the Si substrate shows similar features. It is clearly seen that in the case of PMMA substrate the observed modification has a high radial symmetry, while in the case of Si substrate the shape of formed structure is elongated in direction of the polarization. The shape of the modifications observed in silicon is in excellent agreement with the near field intensity distribution calculated by FDTD. Note that the PMMA and Si have refractive indexes of 1.488 and $3.68 + i 0.006$ respectively at the used wavelength.

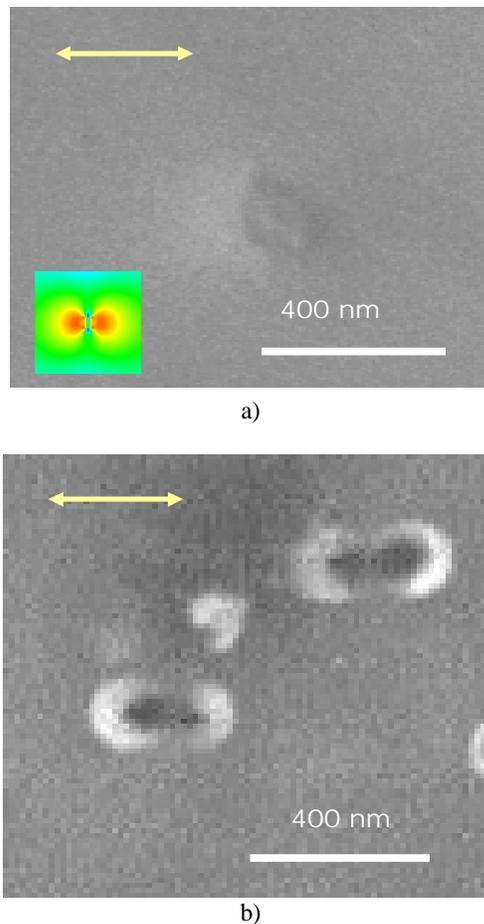


Fig. 5. SEM images of a) PMMA and b) silicon substrate when gold nanoparticles with diameter of 200 nm are deposited on it and the system is irradiated by a single ultrashort laser pulse with fluence of 60 mJ/cm^2 and 200 mJ/cm^2 , respectively. The insert in Fig. 5 a) shows the calculated electric field intensity distribution on the PMMA substrate surface under the gold nanoparticle. The arrow shows polarization direction of the incident irradiation.

The correspondence between the hole shape observed in Fig. 5 b) and FDTD results for the near field intensity distribution shows that in the case of silicon the near field intensity localization and enhancement induced by the gold particle is the dominant mechanism for substrate modification. The absence of clear relation between the near field intensity distribution and the shape of the observed modification in the case of PMMA indicates that here the heating of the particle is responsible for substrate processing. According to the numerical model the maximal temperature achieved with the presented fluence is about the melting temperature of the PMMA substrate (440 K).

The definition of the two mechanisms of particle assisted surface modification is important due to the fact that the maximum in the absorption spectra, which is related to particle efficient heating, generally does not coincide with the near field scattering efficiency maximum. This is especially valid for particles with sizes beyond the dipole approximation [19]. Furthermore, the near field intensity spatial distribution is strongly influenced by the irradiation geometry and this can alter the contribution of the near field localization and enhancement in the processing of a substrate.

5. Conclusions

Theoretical and experimental study on the effects arising when of gold nanoparticle interact with ultrashort laser pulses at wavelength of 800 nm are presented. It is found that the electromagnetic field in the near field zone around the particle can be localized and the field intensity enhanced compared to the incident one. When the particle is deposited on a substrate, the spatial distribution of the field intensity is strongly influenced by the dielectric properties of the substrate. In the case of substrates with refractive index higher than 1.7 the near field intensity is localized in the vicinity of the contact point between the particle and the substrate.

The model combining optical properties calculation using Mie theory and two-temperature diffusion model shows that the heating of the nanoparticle can be significant for applications in biophotonics at wavelengths within the tissue transparency window.

The experimental results confirm the theoretical predictions. Irradiation of substrates with deposited nanoparticles results in formation of permanent substrate modifications under the gold particles. In the case of silicon substrate the shape of the observed modifications shows direct relation to the spatial distribution of the calculated near field intensity. When linear polarization is used the observed nanohole shape is elongated in the polarization direction. The surface modification of PMMA substrate does not show direct relation to the near field distribution. The modification process in this case is related mainly to the particle heating.

The obtained results can be a basis of designing applications of nanoparticles is biophotonics and near field optics. Further study is needed to clarify the substrate

modification mechanism, especially when it is related to the efficient localization of the electromagnetic field and intensity enhancement in the particle vicinity. Such investigation is under way.

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