Numerical modeling and analytical evaluation of light absorption by gold nanostars

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ABSTRACT

In this paper, the regularity of local light absorption by gold nanostars (AuNSts) model is studied by method of numerical simulation. The mutual diffraction influence of individual geometric fragments of AuNSts is analyzed. A comparison is made with an approximate analytical approach for estimating the average bulk density of absorbed power and total absorbed power by individual geometric fragments of AuNSts. It is shown that the results of the approximate analytical estimate are in qualitative agreement with the numerical calculations of the light absorption by AuNSts.

Keywords: Plasmonic nanoparticles, gold nanostars, laser hyperthermia, transfection, finite element modeling

1. INTRODUCTION

Systems and methods based on plasmon-resonant gold nanoparticles (AuNPs) represent a perspective approaches favorable for biophotonics and laser medicine.[1,2] AuNPs unique optical properties relate to the localized surface plasmon resonance (PR)[3,4] described as a collective oscillation of electrons at the surface of nanoparticles in resonance with an electromagnetic wave of a specific wavelength PR dramatically enhances laser absorption leading to photothermal and related phenomena such as acoustic shockwaves generation, microbubble formation, and heating. Therefore, the efficiency of laser-based applications of AuNPs is strongly depended on their thermal interaction with laser light pulses or continuous waves, which can be described by melting and evaporation from the particle surface and particle fragmentation. For theranostics (including cell optoporation) of AuNSts an important point is to select the optimum mode of the photothermal effect of laser radiation on tissues and cells induced by AuNSts. Thus, it is necessary to know the AuNSts light absorption features, which are the purpose of this study.

2. NUMERICAL MODELING OF AuNSts LOCAL LIGHT ABSORPTION

Mathematically rigorous calculation of the arbitrary polarized light absorption by AuNSt is an extremely complicated mathematical problem. The real geometric form of AuNSt is very complex, but in the first approximation it can be approximated in the form of a spherical core with tips.[5,6] To estimate the AuNSt absorption value, a numerical simulation was performed of the scattering of a plane linearly polarized monochromatic light wave in the software product Comsol Multiphysics 5.1 (the Wave Optics module) on it. This approach takes into account the mutual diffraction effect of the components of the AuNSt model. The simulation was performed for a nanostar model, which is a spherical core with a diameter D=24 nm with attached six elongated semi-spheroids attached to it with a major semi-axis a=17 nm and small $b=a/10$. The axes of these semi-spheroids were directed along three axes of the Cartesian coordinate system. The light field with a wavelength of λ=1064 nm propagated along the x-axis and was linearly polarized along the z-axis. The

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amplitude of the field E_z was assumed to be 1 V/m. The refractive index for the AuNSt material was set equal to N=0.3-7.2i (gold), for the surrounding medium N_m=1.3 (water). The surface distribution of the bulk density of the absorbed power is shown in Fig. 1 (a). The distribution of the bulk density of the absorbed power along the x, y and z coordinate axes is shown in Fig. 2.

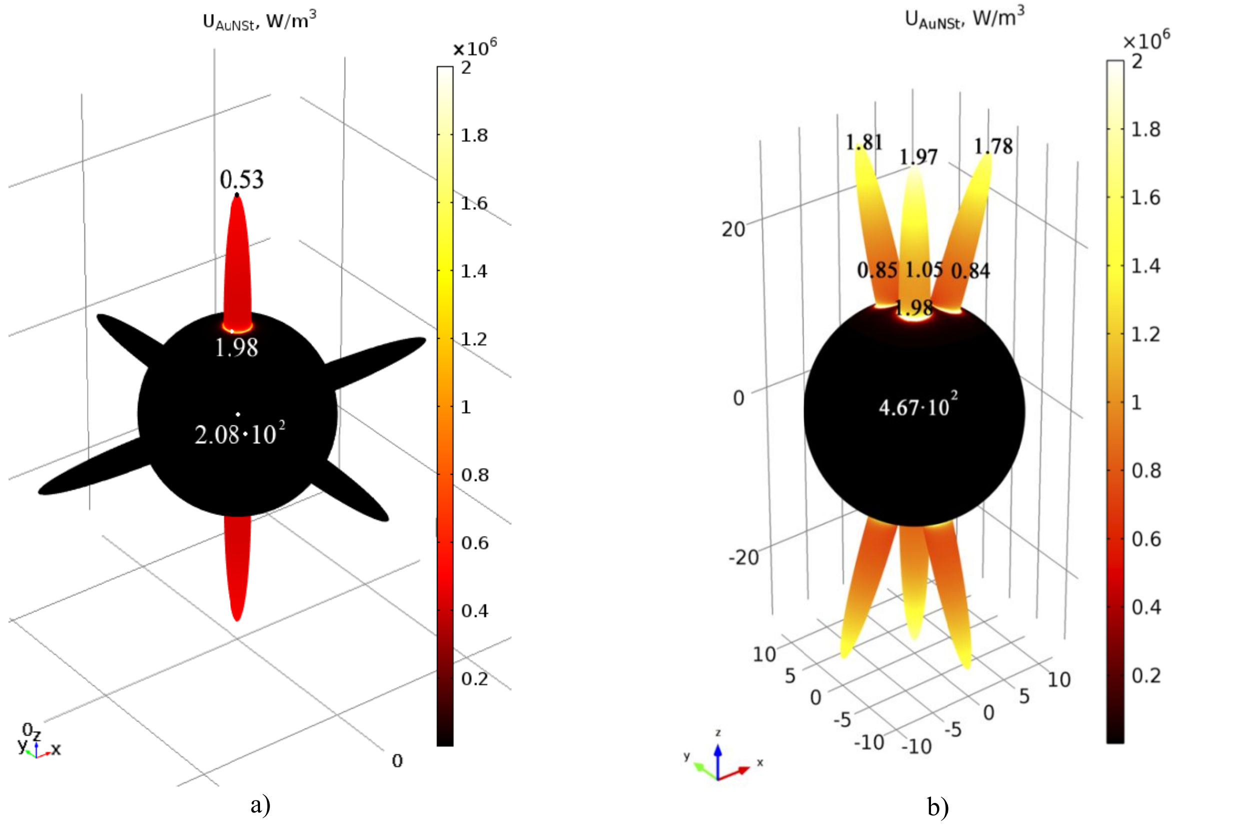
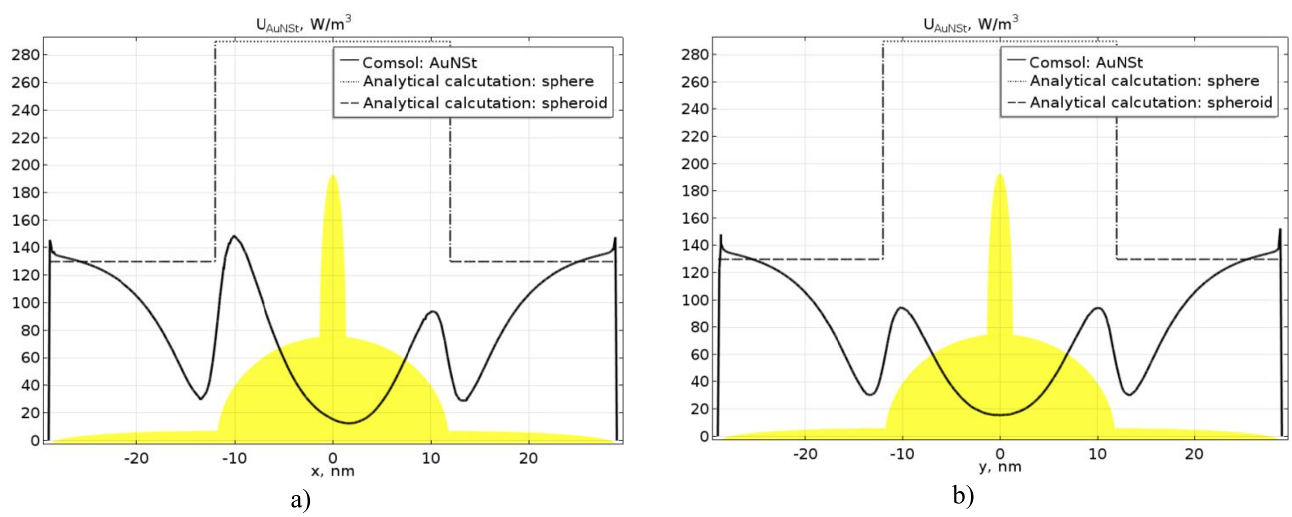
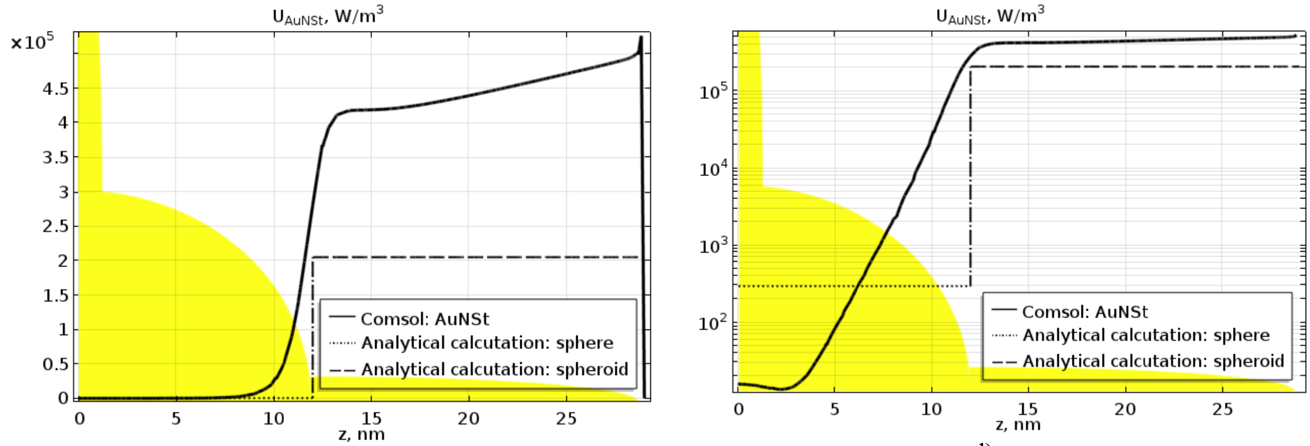


Figure 1. Surface distribution of the bulk density of absorbed power (U_{AuNSt}) for two models of nanostars with dimensions D=24 nm, l=17 nm, illuminated by a light wave propagated in the positive direction of the x-axis and linearly polarized along the z-axis : a – a model with semi-spheroid large axes oriented along three axes of a Cartesian coordinate system, b – model with two semi-spheroid oriented along the z-axis and four semi-spheroids oriented at an angle of 20° to the z-axis and lying in the planes yz and xz. The digits indicate the characteristic values of the specific absorption.





c) d)

Figure 2. Distribution of the bulk density of the absorbed power (U_{AuNSt}) for the nanostar model in Fig. (1a): a and b – along the *x*-axis and the *y*-axis; c and d – long the *z*-axis (along the polarization vector of the incident field) in linear and logarithmic scale, respectively. The points and the dotted line represent the distribution of U_{AuNSt} according to an approximate analytical estimate.

The asymmetry in the distribution U_{AuNSt} relatively to the center of AuNSt (x=y=z=0) in Fig. 2a is due to a relatively small but non-zero change in phase of the incident wave inside AuNSt. This asymmetry is absent in the distributions U_{AuNSt} along the *y*-axis (Fig. 2b) and the *z*-axis. Therefore, in Fig. 2 c, d distributions of U_{AuNSt} are presented on half of considered interval of changing *z*-coordinate. As can be seen from the figures, the bulk density of light absorption in the nanostar tips directed along the *z*-axis is several orders of magnitude greater than the absorption in the core and tips directed orthogonally to this axis. Real nanostars have a large number of tips (of the order of fifty pieces) and an important problem is clarification of the amount of laser power absorbed by them. This is relevant, for example, for the subsequent calculation of the distribution of the temperature field in the problem of laser heating of a medium with nanoparticles[7,8,9]. An important point here is to take into account the nature of the joint diffraction interaction of components of such a complex geometric structure. To this end, a symmetric AuNSt model was constructed with the same dimensions (D=24 nm, l=17 nm) with six semi-spheroid tips: two main ones directed along the polarization vector of the electric field directed along the *z*-axis and four additional, located at an angle of 20º to the *z*-axis and lying in the planes *yz* and *xz*. The surface distribution of the bulk density of light absorption by a nanostar (U_{AuNSt}) for it is shown in Fig. 1 (b). From the analysis of the results in Fig. 1 and Fig. 2, it can be concluded that U_{AuNSt} in tips parallel to the polarization vector of the irradiating light and close to this direction exceeds by several orders of magnitude the corresponding absorption in the core and tips located orthogonally to it.

3. APPROXIMATE ANALYTICAL EVALUATION OF THE AuNSt LOCAL LIGHT ABSORPTION AND DISCUSSION OF THE RESULTS

Each nanostar tip is characterized by a certain angle θ between the tip axis and the polarization vector of laser beam. This leads to the fact that the absorbing power of each nanostar tip depends on this angle. Using the ellipsoid of rotation with the ratio of the semi-axes lengths $a/(b=c)=10$ (elongated spheroid) to approximate the real shape of the nanostar tips, the absorbed power density U [W/m^3] in the quasi-electrostatic approximation can be calculated analytically by the formula[10]

$$U = G\cos^2(\theta) + Q\sin^2(\theta), \tag{1}$$

where

$$G = A\left|1 + L\left(\frac{N^2}{{N_m}^2} - 1\right)\right|^{-2},\ Q = A\left|1 + \frac{1-L}{2}\left(\frac{N^2}{{N_m}^2} - 1\right)\right|^{-2} \tag{2}$$

and

$$A = \frac{2\pi\, \mathrm{Im}(N^2) I}{\lambda N_m},$$
$$L = (1 - e^{-2})\left(\frac{1}{2e}\ln\frac{1+e}{1-e} - 1\right),$$
$$e = \left(1 - \frac{b^2}{a^2}\right)^{\frac{1}{2}}, \tag{3}$$

where I is the light intensity at the location of AuNSt. In the case $a = b + 0$ formulas (1)-(3) determine the intensity of light absorption by the sphere of radius a. Based on numerical simulation, we also calculated the total absorbed power and the average value of its bulk density in individual geometric fragments of nanostar models (in a spherical core and semi-spheroid tips). These data and corresponding values according to formulas (1)-(3) for AuNSt of two sizes are given in Tables 1-2.

Table 1. Values of bulk density of absorbed power and total absorbed power in the different components of gold nanostar (D=24 nm, l=17 nm) model and comparison that with values of absorption of spheroid and sphere with equivalent sizes.

Calculation method	Along polarization vector of electric field		Orthogonal to polarization vector of electric field		Core	Sphere
	Tip	Spheroid	Tip	Spheroid		
Average bulk density of absorbed power ($U, W/m^3$)						
Analytical	-	$2.05\cdot10^{5}$	-	$0.13\cdot10^{3}$	-	$0.29\cdot10^{3}$
Comsol	$4.40\cdot10^{5}$	$2.07\cdot10^{5}$	$0.08\cdot10^{3}$	$0.13\cdot10^{3}$	$1.39\cdot10^{3}$	$0.33\cdot10^{3}$
Total absorbed power (W)						
Analytical	-	$4.22\cdot10^{-20}$	-	$2.62\cdot10^{-23}$	-	$2.12\cdot10^{-21}$
Comsol	$4.55\cdot10^{-20}$	$4.26\cdot10^{-20}$	$8.51\cdot10^{-24}$	$2.76\cdot10^{-23}$	$1.00\cdot10^{-20}$	$2.41\cdot10^{-21}$

Table 2. Values of bulk density of absorbed power and total absorbed power in the different components of gold nanostar (D=28 nm, l=22 nm) model and comparison that with values of absorption of spheroid and sphere with equivalent sizes.

Calculation method	Along polarization vector of electric field		Orthogonal to polarization vector of electric field		Core	Sphere
	Tip	Spheroid	Tip	Spheroid		
Average bulk density of absorbed power ($U, W/m^3$)						
Analytical	-	$2.05\cdot10^{5}$	-	$0.13\cdot10^{3}$	-	$0.29\cdot10^{3}$
Comsol	$4.32\cdot10^{5}$	$2.05\cdot10^{5}$	$0.10\cdot10^{3}$	$0.14\cdot10^{3}$	$1.80\cdot10^{3}$	$0.34\cdot10^{3}$
Total absorbed power (W)						
Analytical	-	$9.15\cdot10^{-20}$	-	$5.68\cdot10^{-23}$	-	$3.37\cdot10^{-21}$
Comsol	$9.69\cdot10^{-20}$	$9.13\cdot10^{-20}$	$2.17\cdot10^{-23}$	$6.04\cdot10^{-23}$	$2.07\cdot10^{-20}$	$3.95\cdot10^{-21}$

From these data and Fig. 2 it is seen that both methods (approximate analytical and numerical Comsol) qualitatively describe the same trend: the absorption value in the AuNSt tips directed along the electric vector of the incident light is several orders of magnitude higher than in the core and the tips located perpendicular to the electric vector. However, quantitatively, taking into account the mutual diffraction interaction of the core and the tips introduces appreciable corrections to the results obtained on the basis of a simplified approach. The absorption values for solitary spheroids and spheres calculated in Comsol are in good agreement with those calculated by formulas (1)-(3). It should be noted that the bulk density of absorbed power for spheroids with different volumes, but the same ratio of the lengths of the semi-axes, is the same and an approximate estimate of the absorption density according to formulas (1)-(3) for them gives good accuracy. However, for a sphere, the analytical calculation is more rough, because the volume distribution of the electric field in it, in contrast to the spheroid, is inhomogeneous. The magnitude of the bulk density of the absorbed power in the nanostar tips oriented along the polarization vector of the electric field is three orders of magnitude higher than the absorption in the tips oriented orthogonally to the electric vector, and the absorption density in the AuNSt tip directed along the electric vector is two orders of magnitude higher than in the core. From this, it can be concluded that the main contribution to the absorption of light and the subsequent transformation of the absorbed energy into thermal energy is made by the nanostar tips, whose direction coincides with the polarization vector of the electric field in the laser beam. Quantitatively, the magnitude of the absorption of tips and the AuNSt core due to the diffraction interaction is different, and higher than for a solitary spheroid and sphere, while the ratio is such that the core in a nanostar absorbs about four-five times more energy than a solitary sphere, and in the semi-spheroid tips directed along the field, the bulk density of the absorbed power is two times higher than in a solitary spheroid. In addition, the absorption values of AuNSt components were calculated numerically for a different number of "side" (i.e., orthogonal to the polarization vector of the electric field of the light wave) tips. It can be seen from the obtained results that the addition of "side" tips does not have a noticeable effect (the difference is observed in the third order) on the absorption of the core and tips oriented along the field. Thus, in order to reduce the cost of computing resources and reduce computation time, they can be excluded from consideration for problems requiring the determination of only full absorption. Since the absorption in them is three orders of magnitude lower compared to the tips oriented in the field and the core, their contribution to the total light absorption of AuNSt is small and in such problems it can be ignored. For a model that takes into account the joint diffraction interaction of closely spaced tips and the sphere, as follows from the results in Fig. 1b, the maximum absorption is observed at the ends of the tips and at their bases. The calculated average values of the bulk density of absorbed power are: $1.13 \cdot 10^4$ W/m^3 (core); $1.19 \cdot 10^6$ W/m^3 (tip directed along polarization vector of incident field); $1.02 \cdot 10^6$ W/m^3 (rotated tip). Total absorbed power: $8.19 \cdot 10^{-20}$ W (core); $1.23 \cdot 10^{-19}$ W (tip directed along polarization vector of incident field); $1.05 \cdot 10^{-19}$ W (rotated tip). Diffraction interaction of closely spaced tips and core leads to a significant increase in absorption in them. From a quantitative comparison of the absorption values, it can be concluded that an increase in the number of closely spaced tips leads to an increase in the electric field in the AuNSt core that gives a peculiar effect of "pumping" energy from the tips to the core. It seems interesting at what number of AuNSt tips and the angular distance between them the diffraction mutual influence of each other becomes insignificant and they can be considered as independent absorbing objects. To do this, we changed the angle θ between the electric vector of the incident wave and the axis of the tip (we call it "turned" tip). We calculated the total absorption of one of the turned the tips for three different configurations of AuNSt, shown schematically in Fig. 3.

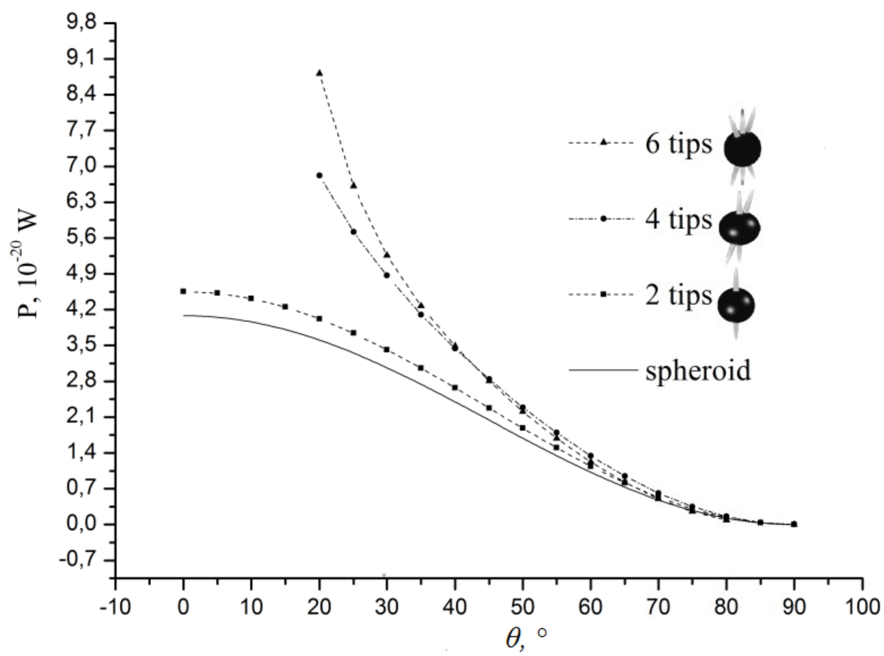


Figure 3. Dependence of the total absorption in the rotated AuNSt tip from its orientation with respect to the polarization vector of the light wave. Dashed lines show the results of Comsol calculations, solid - the dependence by the formula (1), where the volume of the spheroid multiplies *U*.

For the six tips and four tips models, the AuNst tips are in the same *xz* plane, the larger axes of the two of them are parallel to the *z*-axis, and the axes of the remaining tips are located at an angle θ to it. The magnitude of the total absorption in the turned tips is practically the same (because the size of AuNSt is much smaller than λ and the phase advance is negligible). For the two tips model the angle θ was varied in steps of 5°. For models with six tips and four tips, four and two tips, respectively, were rotated through an angle θ with the same pitch. It can be seen from the curves in Fig. 3 that for six tips and four tips AuNSt the diffraction interaction leads to increased absorption and a deviation of the angular dependence from the theoretical at a typical angular distance for real AuNSt.[9]

4. CONCLUSION

Numerical calculation of the absorption for the AuNSt model has shown that the proposed approximate analytical approach is applicable for a qualitative evaluation of the regularity in the absorption of light by various AuNSt fragments (core and tips). The magnitude of the bulk density of absorbed power in AuNSt tips, the direction of which coincides or is close to the direction of the electric vector of the incident wave, is several orders of magnitude higher than in the core and tips, the direction of which differs markedly from the direction of this vector. However, due to the diffraction interaction, which the approximate estimate does not take into account, the absorptive of the core and tips is several times higher (approximately five times for the core and two times for the tips). The close arrangement of the tips on the AuNSt surface leads to an even more significant enhancement of absorption both in them and in the core and intensifies the effect of "pumping" energy from the tips to the core.

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