# Nanosecond laser-induced photomodification of gold nanostars of various sizes

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## ABSTRACT

Gold nanostars are one of the new types of nanoparticles with advantages such as plasmon resonance tunability and low toxicity. Therefore, gold nanostars are promising candidates for various biomedical applications including bioimaging, cell optoporation and plasmonic photothermal therapy (PTT) in NIR I, II, and III optical transparency windows of biotissues. However, the stability and possible transformation of gold nanostars under laser irradiation still remains unexplored. In this work, we studied the photomodification of gold nanostars under the 1064-nm nanosecond pulsed laser irradiation by the transmission electron microscopy and spectrophotometry. The photostability of nanostars depends on their morphology and the plasmonic properties. Specifically, for large nanostars with a plasmon resonance at 950 nm remarkable changes occur at a threshold pulse energy of 5 µJ. At this threshold, a significant part of nanostars spikes melts and most of the nanostars start to transform into gold spheres. For higher pulse energies of about 50 µJ, all stars transform into spheres. For smaller gold stars with a plasmon resonance at 680 nm, the changes are less pronounced. Up to pulse energy of 50 µJ, they retain the shape of stars and have spikes on their surface. Moreover, the complete transformation of these stars into spheres does not occur up to pulse energy of about 150 µJ. The obtained results can be important for optimization of PTT treatment with gold nanostars and nanosecond laser irradiation.

**Keywords**: Plasmon resonance, nanostars, pulsed laser, extinction spectra, photomodification

## 1. INTRODUCTION

Gold nanoparticles are widely used in biomedicine due to their chemical and physical properties. The choice of gold as a material is due to the fact that gold has several advantages over other materials. In particular, gold is a noble metal with high chemical stability, which allows the colloid of gold nanoparticles to be stored for a long time. The most important property of gold nanoparticles is surface plasmon resonance, due to which they are used in various fields. In practice, gold nanospheres, nanorods and nanostars are most often used. Gold nanoparticles are used in medicine for diagnostics[1], photothermal and photodynamic therapy[2], as well as for drug delivery[3] and cell optoporation[4]; in photoacoustic imaging to provide increased sensitivity and detection of certain molecules[5]. The efficiency of gold nanoparticles in such applications strongly depends on the effect of laser pulses or continuous waves on them, which can lead to melting and evaporation from the particle surface, as well as to a change in the shape and fragmentation of particles. Such modifications, in turn, will cause a change in plasmon resonance properties.

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A relatively small number of studies are devoted to the study of pulsed laser irradiation of gold nanoparticles. In particular, the influence of a nanosecond pulsed laser with a wavelength of 532 nm for a wide range of laser radiation parameters on gold nanospheres with a diameter of 20 to 100 nm was studied[6]. In addition to an experimental study, a theoretical study of this effect was also performed. As a result, a photomodification threshold was experimentally determined for each size of nanoparticles. A comparison was made with the theoretical model of heat transfer of nanoparticles under the action of laser radiation. Thus, the damage threshold of nanoparticles was determined depending on the particle diameter. Photomodification of gold nanospheres on borosilicate glass substrates was also presented. The nanoparticles were radiated once[7] or repeatedly[8] by the 532 nm nanosecond laser. In both cases, laser exposure led to the formation of craters on the glass surface. With an increase in the number of pulses, the appearance of craters on the surface increased, and the number of residual gold nanoparticles decreased. Thus, it was found that photomodification of gold nanoparticles leads to the appearance of a large number of nanocraters on the substrates as a result of laser destruction of the nanoparticles and the transfer of excess energy to the substrate surface. In addition to gold nanospheres, the photomodification of gold nanorods and its effect on spectral changes in photoacoustic imaging (PAI) were also studied[5]. Photodestruction processes were evaluated using the Monte Carlo method. It was demonstrated that photomodification of gold nanorods can occur even when laser irradiation is safe for biological tissues. It was shown that during photoacoustic imaging it is necessary to take into account the possible photomodification of nanoparticles.

Gold nanoshell is another type of gold nanoparticles for which photomodification has been investigated[9]. The effect of single laser pulses on gold shells was studied. The parameters of laser irradiation for photodestruction and the formation of bubbles near the nanoshells were determined. It is shown that these phenomena can be initiated using tissue-safe energy levels of laser pulses.

However, laser damage thresholds for gold nanostars have not yet been studied. In addition to the possibility of wide tuning of PR to a given wavelength, gold nanostars have significant advantages compared to other gold particles, such as the simplicity of synthesis and the absence of toxic surfactant molecules on the surface. In addition, the presence of sharp spikes on the surface of nanostars allows to enhance the Raman signal from molecules located nearby.

In this paper, we studied the photomodification of gold nanostars of various sizes under the irradiation of a nanosecond pulsed laser with a wavelength of 1064 nm. The dependence of the photomodification of nanostars on the size and position of the plasmon resonance peak in the extinction spectrum is studied.


## 2. MATERIALS AND METHODS

### 2.1. Chemicals

Sodium hydroxide (NaOH, Sigma-Aldrich), tetrakis(hydroxymethyl)phosphonium chloride (THPC, Fluka), hydrochloric acid (HCl, 37 wt % in water, Sigma-Aldrich), hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$; 99%, Sigma-Aldrich), thiolated polyethylene glycol (PEG-SH, $M_W$=5000, Creative PEGWorks), sodium citrate tribasic dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, 99 %, Sigma–Aldrich), silver nitrate ($AgNO_3$, 99,9%, Sigma-Aldrich) and l-ascorbic acid (AA; 99.9%, Sigma–Aldrich) were used without further purification. Ultrapure MilliQ water (18 mΩ×cm; Millipore) was used in all experiments. All glassware used was cleaned with aqua regia (3:1, $HCl:HNO_3$) and was rinsed thoroughly in $H_2O$ before use.

### 2.2 Synthesis of gold seeds

Spherical gold nanoparticles were used as seeds for nanostars synthesis. For preparation of 3-nm Au seeds we used protocol, reported by Duff et al[10]. In brief, 220 μl of 1% THPC water solution and 55 μl of 2 M NaOH were added to 10 ml of MilliQ water. The solution was vigorously stirred on a magnetic stirrer at 1000 rpm, after which 420 μl of 1% hydrogen tetrachloroaurate was added. A rapid change in the color of the solution from yellow to dark brown indicated the formation of small gold nanoparticles. For preparation of 35-nm Au nanoparticles we utilized the protocol described by Frens[11]. Shortly, 0.7 ml of 1% sodium citrate were added to 50 ml of boiling 0.01% $HAuCl_4$. The solution was mixed for 20 minutes and the color changed from colorless to purple-red.

### 2.3 Synthesis of gold nanostars (AuNSts)

The synthesis of nanostars was performed by the surfactant-free method similar to the protocol[12]. In particular, 130 μl of 3-nm or 900 μl of 35-nm gold nanoparticles was added to a mixture of 10 ml of 0.75 mM hydrogen tetrachloroaurate and 30 μl of 1M HCl with stirring. 150 μl of 4 mM AgNO$_3$ and 150 μl of 100 mM ascorbic acid were added immediately and the solution was stirred for 30 seconds. In this case, the color of the solution quickly changed from light red to blue or green. A sample of nanostars synthesized on 3-nm gold seeds was designated as NST-1, and a sample synthesized on 35-nm seeds was designated as NST-2. To increase colloidal stability, 300 μl of a 1 mM PEG-SH solution was added to each sample of nanostars. Then the particles were washed by centrifugation and redispersion in MilliQ water.

### 2.4 Laser irradiation

Colloids of gold nanostars were irradiated with a 1064-nm nanosecond ytterbium fiber laser (Mini Marker 2TM, Russia) with maximum power of 20 W and beam diameter of 6 μm according to the following scheme (Fig.1). 250 μl of a colloid of gold nanostars was placed into a shortened square 10-mm cuvette. The pulsed laser was located vertically above the cuvette and focused on the upper boundary of the colloid. Then, the square section in horizontal XY plane was irradiated inside the cuvette, the laser was lowered down to 40 μm along the Z axis, and the square section inside the cell was irradiated. Thus, the entire volume of the colloid in the cuvette was irradiated. Laser pulse duration was 4 ns, repetition rate was 20 kHz, single pulse energy varied from 1 to 150 μJ. After 2h the extinction spectra of the colloids were measured and samples were deposited on TEM grids.

### 2.5. Measurements

Transmission electron microscopy (TEM) images were obtained with a Libra-120 (Carl Zeiss, Germany) microscope at the Simbioz Center for the Collective Use (CCU) of Research Equipment in the Field of Physical–Chemical Biology and Nanobiotechnology at the Russian Academy of Sciences' Institute of Biochemistry and Physiology of Plants and Microorganisms (IBPPM RAS, Saratov). Extinction spectra were measured by spectrophotometers Specord 250 and Specord S300 (Analytik Jena, Germany). For TEM statistics parameters of more than three hundred particles were measured.

## 3. RESULTS AND DISCUSSION

### 3.1 Nanoparticle characterization

Gold nanostars have a rather complex shape. For its quantitative description, we used a model of a spherical core covered with small protrusions and long conical spikes. Size parameters of synthesized gold nanostars were measured from transmission electron microscopy (TEM) images. Parameters of more than 300 nanoparticles were collected for each sample. Particularly, for as-prepared NST-1(Fig.2(a)) the average diameter of the gold core was 23.3±5.0 nm, the average length of the spikes was 49.0 ± 11.2 nm, and the average diameter of the base of the spike was 15.2 ± 2.5 nm. For initial NST-2 (Fig.2(d)) average core size was about 124.9±19.4 nm, average spike length was 50.1±20.1 nm . The average diameter of the base of the conical spike was 18.0±4.5 nm.

Under the nanosecond laser irradiation, the shape of gold nanostars changed. For the NST-1 sample, at the laser pulse energy of 4 μJ, small morphological changes occurred. In particular, for some particles the shape of the cores was rounded and approached spherical. In addition, the average core size increased. However, most particles retained their shape, as well as protrusions and long spikes on their surface unchanged (Fig.2(b)). The average diameter of the gold core was 28.2±6.8 nm, the average length of the spikes was 50.1 ± 14.1 nm, and the average diameter of the base of the spike was 15.3 ± 2.8 nm. For sample NST-2 it was found that a pulse energy of 5 μJ is a threshold value. At this pulse energy, most of the nanostars melted and transformed into nanospheres (Fig.2(e)).

With a further increase in the pulse energy, the following changes occured. In particular, at a pulse energy of 50 μJ for the NST-1 sample, the length of the spikes decreased, and the size of the core increased and even more particles had a spherical shape of the core (Fig.2(c)). The average diameter of the gold core was 36.3±7.7 nm, the average length of the spikes was 24.3±4.9 nm, and the average diameter of the base of the spike was 10.4±2.5 nm.

For the NST-2 sample, all nanostars were transformed into nanospheres of various sizes. Moreover, the change in shape occured very sharply and part of the gold flied away from the stars and formed small gold nanospheres (Fig. 2(f)).
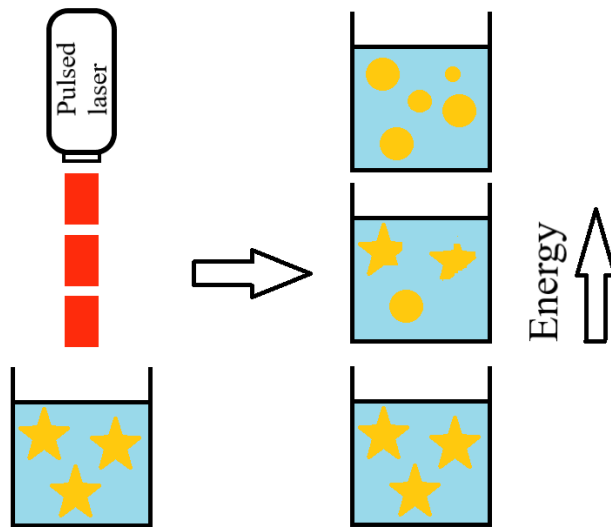
**Figure 1**. The scheme of irradiation of a colloid of gold nanostars by a nanosecond pulsed laser. An increase in the energy of laser pulses leads to photomodification of nanostars.
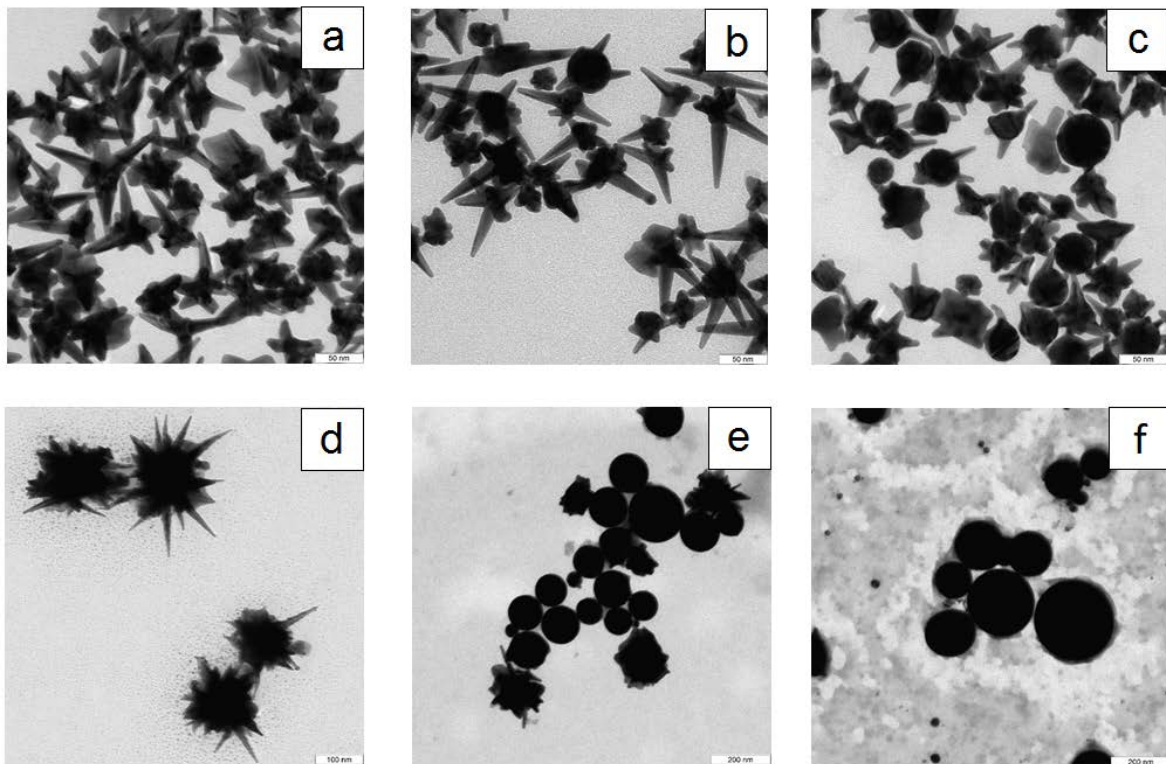


**Figure 2**. TEM images of NST-1 before (a) and after photomodification by a pulsed laser with a pulse energy of 4 (b) and 50 (c) μJ. TEM images of NST-2 before (d) and after photomodification by a pulsed laser with a pulse energy of 5 (e) and 50 (f) μJ.

### 3.2 Optical properties of initial nanoparticles

The position of the plasmon resonance peak (PRP) in the spectrum and the shape of the extinction spectrum are important characteristics for plasmon nanoparticles. From this information we can conclude about the properties of the entire ensemble of nanoparticles in a colloid. Spherical 3-nm and 35-nm gold seeds had standard extinction spectra. In particular, for gold 3-nm nanoparticles, the extinction in the range from 400 to 1100 nm is gradually reduced (Fig. 3, curve 1). For gold 35-nm seeds, a plasmon resonance peak at 530.5 nm is observed in good agreement with the known calibrations (Fig. 3, curve 2). In the extinction spectrum of NST-1 gold nanostars, a PRP is observed at a wavelength of about 680 nm, and an increase in extinction is also observed in the region of 1000-1100 nm (Fig. 3, curve 3).

Probably, the plasmon peak at 680 nm corresponds to small protrusions on the core surface. Long spikes of nanostars form a plasmon peak in the near infrared region of the spectrum. The shoulder of this peak begins to rise at 1000-1100 nm, and the peak is outside the detection limits of the spectrophotometer used. In the extinction spectrum of NST-2 gold nanostars, there is a wide extinction peak with a maximum of about 950 nm (Fig. 3, curve 4). Probably, the large width of this peak is due to the relatively wide size distributions of the cores and spikes. It should be noted that the plasmonic properties of the NST-1 and NST-2 samples were tuned so that the normalized extinction at the laser wavelength of 1064 nm was equivalent.
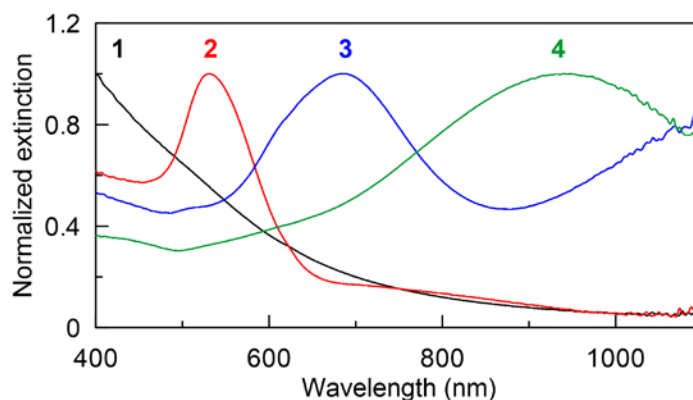


**Figure 3**. Normalized extinction spectra of of 3-nm (1), 35-nm (2) gold nanospheres, NST-1 (3) and NST-2 (4).

### 3.3 Optical properties of photomodified nanoparticles

Extinction spectroscopy is a sensitive tool for the rapid detection of changes in the shape of nanoparticles in an ensemble. Even small changes in the shape of the nanoparticles introduce changes in the spectrum. For NST-1, it can be noted that when irradiated with a pulsed laser with a pulse energy of up to 4 μJ, no noticeable changes in the spectrum occur (Fig.4(a), curve 2). However, with an increase in pulse energy up to 7 μJ, significant changes in the extinction spectrum can be observed (Fig.4(a), curve 3). The shoulder at 1100 nm decreases markedly, indicating a decrease in the number of long spikes. The peak at 680 nm shifts toward shorter wavelengths, which indicates a gradual smoothing of protrusions on the surface. A peak appears around 530 nm, which indicates that some of the stars transformed into gold spheres. At pulse energies from 10 to 50 μJ, these changes gradually turn out to be more and more pronounced (Fig. 4(a), curves 4-6). With a large increase in the pulse energy to 70 and 150 μJ, drastic changes occur in the extinction spectrum. One pronounced maximum of about 530 nm remains in the spectrum, and the main initial maximum is significantly smoothed. At lower pulse energies, a peak in the range of 900–1000 nm appeared in the extinction spectrum, and as the pulse energy increased to 70–150 μJ, this peak shifted to the left and eroded. This indicates that the spikes are getting shorter and their size distribution is expanding. However, it is worth noting that these smoothed peaks still have a noticeable intensity. This indicates that complete transformation of nanostars into nanospheres does not occur and some particles still have spikes on their surface.
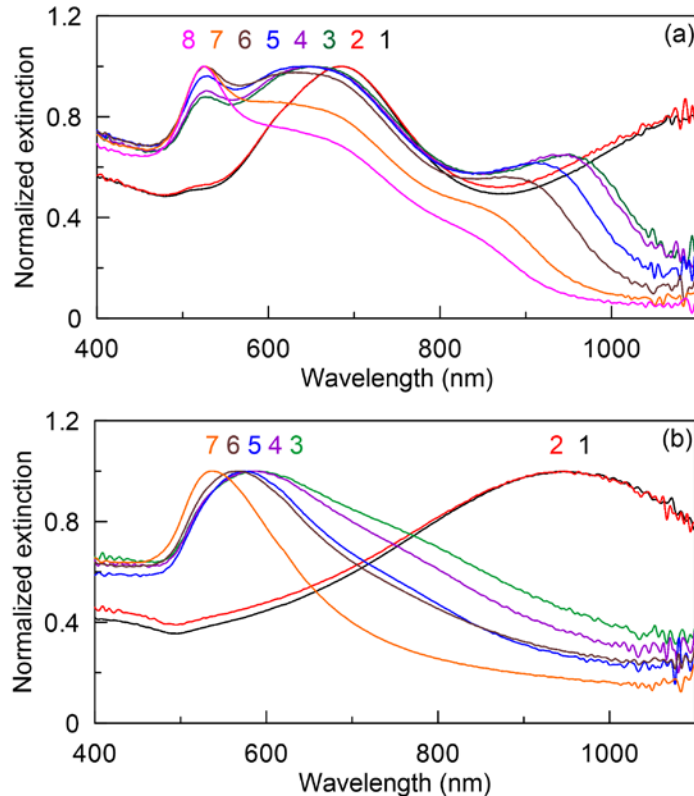
**Figure 4**. (a) Normalized extinction spectra of NST-1 before (1) and after exposure by a pulsed laser with a pulse energy of 4 (2), 7 (3), 10 (4), 30 (5), 50 (6), 70 (7) and 150 µJ (8). (b) Normalized extinction spectra of NST-2 before (1) and after exposure by a pulsed laser with a pulse energy of 4 (2), 5 (3), 10 (4), 25 (5), 50 (6) and 100 µJ (7).

For NST-2 sample, the situation looks simpler (Fig. 4(b)). At a pulse energy of 4 µJ, there are no significant changes in the spectrum (Fig. 4(b), curve 2). Stars practically do not change their shape and do not show significant statistical differences. However, at a pulse energy of 5 µJ, the extinction spectrum changes dramatically (Fig. 4(b), curve 3). The maximum at 950 nm disappears and only a gradual decline remains. A new maximum near 610 nm appears in the spectrum. As is known, a similar plasmon peak is observed in the spectrum of large gold nanospheres with an average diameter of more than 100 nm. As the pulse energy increases to 10–50 µJ, the intensity at 950 nm continues to decrease and the PRP continues to shift toward shorter wavelengths (Fig. 4(b), curves 4-6). At pulse energy of 100 µJ, NST-2 completely transform into spheres, and their extinction spectrum looks properly (Fig. 4(b), curve 7).

## 4. CONCLUSIONS

In this work we report on synthesis of gold nanostars of various sizes with plasmon resonance peak at 680 and 950 nm. We studied their photomodification under the nanosecond pulsed laser irradiation. It was found that with an increase in the energy of laser pulses, gold nanostars change shape and transform into spheres. It was determined that the photomodification threshold of gold nanostars depends on the position of their plasmon resonance in the extinction spectrum. For nanostars with a plasmon resonance at 950 nm, a pulse energy of 5 µJ is threshold. At this energy, a significant part of nanostars spikes melts. At a higher pulse energy of 50 µJ, almost all of these stars were transformed into spheres. For nanostars with a plasmon resonance of 680 at a pulse energy of 4 µJ, a small fraction of the stars are rounded. However, they still retain spikes on their surface. At a pulse energy of 50 µJ, a significant part of these nanostars is rounded, but also has shortened spikes on its surface. However, the complete transformation of these nanostars into spheres and the destruction of spikes at pulse energies up to 150 µJ do not occur. Thus, it was found that the morphology and plasmonic properties of gold nanostars have a significant effect on their photostability under the

nanosecond pulsed laser irradiation. Obtained results can be important for optimization of laser-induced treatment with gold nanostars.

## ACKNOWLEDGEMENTS

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