Synthesis of stable silver colloids by laser ablation in water

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ABSTRACT
The stable colloid with silver nanoparticles has been produced by irradiation of metal target in deionized water by pulse 1064 nm laser. The dependences of the nanoparticle size and colloid stability on fluence, ablation time, surface conditions of the target, and thickness of the water layer have been studied. The sizes and shape of nanoparticles have been measured by dynamic light scattering and by scanning electron microscopy. It has been shown that decrease of the water layer thickness above the target surface leads to increase of the colloid stability. The proper number of treatment cycles allowed to prepare the target surface for production of the nanoparticles with average size about 34 nm obtained by statistical analysis of the scanning electron microscope images. Several methods have been used to increase the colloid stability: (1) increase of the laser fluence, (2) decrease of the water layer thickness above the target surface, (3) the treatment of the target surface by laser beam scanning. The subsequent increase of the colloid concentration by partial drying slightly enhanced the nanoparticle size. The optimized synthesis conditions and drying parameters allowed to produce the pure colloid with concentration about 0.5 g/l and stability over a month of almost spherical silver nanoparticles with typical size 45±5 nm.

Keywords: silver nanoparticles, pulse laser ablation, silver colloid, laser fluence, colloid concentrating

1. INTRODUCTION
In the last decade, there has been increased interest both in basic and applied sciences to the synthesis of silver nanoparticles and study of their properties for practical use. The rise in this field is primarily due to wide usage of these nanoparticles in microelectronics, optics, catalysis, medicine, biotechnology, sensory analysis, and other areas. Silver nanoparticles have got a rare combination of physical and chemical properties such as unique optical characteristics, highly developed surface and catalytic activity. Possible applications of nanoparticles for diagnostics and treatment of various diseases as well as for immunochemical analysis and production of biosensors are actively studied. In particular, it is shown that silver nanoparticles can be used for production of various antibacterial materials. In this regard, the development of simple and effective physical and chemical methods for the synthesis of the stable silver nanoparticle colloids is important.

By chemical methods, the silver nanoparticles are generally formed by reduction of salt solutions. The main disadvantage of these methods is the presence of impurities and reaction products in the solution, which are almost impossible to remove. This makes chemical methods unsuitable for the synthesis of pure metal nanoparticles. Pulsed laser ablation is one of the most effective physical methods of metal nanoparticles production. This universal method allows synthesizing a variety nanoparticles can be obtained of almost all solid materials.

Laser ablation can be performed both in gas and liquid. The nanoparticles synthesized in the gas are often agglomerated into micropowder, which is difficult to disperse. In contrast, the nanoparticles during produced by laser ablation in liquid can be easily collected. Moreover, ablation in liquid allows to create the stable colloidal solutions. The high stability of the colloidal solutions is caused by charging of nanoparticles as far as part of their surface atoms is oxidized. It should be noted that the laser ablation of nanoparticles in liquids is produced by the interaction of the liquid vapor with the molten metal on the target surface; therefore, the colloid are absolutely pure. This method allows to control the colloid stability and nanoparticle size by choosing the technological conditions such as laser wavelength, frequency, fluence, pulse duration, ablation time, mixing intensity, light focusing and target surface.

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The disadvantage of this method is the low concentration of nanoparticles in the colloid caused by absorption and scattering of the laser irradiation by suspension. The problem of concentration increase has been discussed only in several articles.

The ablation by pulsed Nd:YAG laser (wavelength 1064 nm) results usually in production of the silver colloids with very low concentration about 0.0004 g/l and 0.03 g/l. Even the long-time ablation during 2 hours by second harmonic of pulsed Nd:YAG laser (wavelength 532 nm) allowed to produce the silver colloid with concentration 0.06 g/l only.

The various important applications, such as the study of nanoparticle toxicity on biological cells require colloidal solution with concentration of nanoparticles above 0.1 g/l. Therefore, the development of the colloid synthesis methods with high concentration is of great practical importance.

In this paper we have investigated the dependence of the nanoparticle size and the stability of the colloidal solution on the laser fluence, ablation time, the target surface condition, and the thickness of the water layer. It was shown that optimization of the ablation parameters allowed to concentrate the colloidal solution without essential increasing of the nanoparticle size. The synthesis of the stable colloidal solutions of high purity silver nanoparticles with concentration up to 0.5 g/l using fiber laser with wavelength of 1064 nm and pulse duration of 100 ns has been demonstrated.

2. EXPERIMENT

The silver nanoparticles colloids were produced by laser ablation of the silver target (99.99 % purity, thickness 1 mm) placed on the bottom of glass vessel with 5-30 ml of pure deionized water. Laser system Fmark-20RL (LTC, Russia) based on Yb fiber laser with wavelength of 1064 nm, pulse duration of 100 ns, pulse energy of 1 mJ, and repetition rate of 21 kHz was used for synthesis. The laser beam has been focused on the target surface with the fixed spot diameter 40 μm and fluence ranged from 15 to 80 J/cm².

The thickness of the water layer above the target ranged from 2 to 10 mm. The target was cleaned by deionized water in an ultrasonic bath before laser ablation. The scanning by the focused laser beam was carried out on the target surface along the area ranged from 25 to 300 mm² with velocity about 270 mm/s. The motor-driven stirrer was used to reduce the scattering of the laser beam on cavitation bubbles and to remove the ablated nanoparticles cloud from the radiation area during synthesis. The duration of the ablation experiments ranged from 1 to 60 min. The value of ablated mass was determined by weighting the target before and after ablation using an analytical balance ME 235 S (Sartorius).

The colloid concentration was increased by partial water evaporation at 50°C on a heat plate. The concentration of 0.5 g/l of the stable suspension has been achieved.

The size distribution function of the nanoparticles has been measured by dynamic light scattering (DLS) at an angle of 173° using particle size analyzer Zetasizer Nano ZS (Malvern) and by statistical analysis of the high resolution images obtained by scanning electron microscope (SEM) CrossBeam Workstation Auriga (Carl Zeiss).

The average size and shape of nanoparticles has been estimated by analysis of the absorption spectrum of the colloidal solution measured in a spectral range from 200 to 700 nm using a spectrophotometer Helios Alpha (TermoSpectronic).

The phase composition of the nanoparticles has been determined by X-ray diffraction analysis using a diffractometer D8 Advance (Bruker).

Zeta potential of silver colloid has been measured by electrophoretic light scattering using analyzer Zetasizer Nano ZS (Malvern).

The relief of the target surface has been visualized by scanning electron microscopy and its average roughness Ra has been measured by optical profiling system WYKO NT1100 (Veeco).

3. RESULTS AND DISCUSSION

In order to select the optimal parameters of synthesis, the dependence of the nanoparticle size and colloid stability on the laser fluence, ablation time, the target surface condition, and the thickness of the water layer was studied.
3.1 Influence of laser fluence

The influence of the laser fluence and ablation time on the silver colloid parameters has been studied by removing for analysis the small part (about 10%) of the colloid after each scanning cycle and restoration of the liquid volume by adding the appropriate volume of the deionized water. It allows to measure the dependence of the nanoparticle size and absorption spectra on the laser fluence and ablation time. All scanning cycles have been done at the same target region.

The observation of the single peak of the intensity-weighted distribution function was observed by DLS for all studied colloids allowed to determine the mean diameter $d_N$ as the position of a peak of the number-weighted distribution function. It was shown that $d_N$ of nanoparticles increases with increase of the laser fluence. The typical dependence of $d_N$ on laser fluence for laser ablation during 60 s is presented on Figure 1a.

![Figure 1. (a) Dependence of mean diameter $d_N$ on laser fluence for laser ablation during 60 s; (b) absorption spectra of silver colloid produced by laser ablation during 60 s for different laser fluence.](http://example.com)

The measurements of the absorption spectra of the colloid (Fig. 1b) allowed to reveal the absorbance resonance around 400 nm, which is typical for surface plasmon resonance (SPR) of silver nanoparticles. The existence of the single SPR peak maintains that the shape of the synthesized nanoparticles is close to spherical. The revealed decrease in the wavelength corresponding to SPR maximum with decreasing of the laser fluence can be attributed to formation of silver nanoparticles with smaller sizes. Moreover, the rise of the SPR peak intensity can be attributed to increase of the nanoparticle concentration.

The mechanism of nanoparticles formation during laser ablation represents not only nucleation and growth of particles in a dense plasma cloud, but also ejection of metal drops or solid fragments from the target (“explosive boiling”). This is the reason to increase the agglomeration probability with increase of the laser fluence, as it increases the melting depth of the target surface and amount of target material simultaneously appeared in liquid. As a result, the smallest and the most homogeneous nanoparticles have been produced at low laser fluence. However, the decrease of the ablation efficiency with reduction of the laser fluence imposes restriction on nanoparticle synthesis by low laser energy.

3.2 Influence of laser ablation time

Single peak of the intensity-weighted distribution function observed by DLS for all studied colloids allowed to use the mean diameter $d_N$ as the averaged size of nanoparticles. The time dependence of the nanoparticle size and concentration for laser fluence 30 J/cm$^2$ in the time range from 5 to 60 min is presented on Figure 2. The essential size decrease obtained during the first 30 minutes (Fig. 2a) can be attributed to two mechanisms. First, decrease of the fluence due to “screening effect” representing absorption of laser irradiation by colloid solution with increasing concentration of nanoparticles. Second, change of the target relief as a result of evaporation during scanning. The size stabilization for longer ablation time is caused by decreasing of the fluence below the threshold value.

The obtained change of the nanoparticle size with ablation time was confirmed also by decrease of the SPR maximum wavelength with ablation time for the first 30 min and absence of any change for longer ablation time (Fig. 2b). Increase of the SPR peak intensity with ablation time indicates an increase of the colloid concentration. The observed narrowing of SPR band for long ablation time indicates an increase of the colloid monodispersity.
It was shown that the colloids produced at laser fluence 30 J/cm² and ablation time from 15 to 60 min with mean value of zeta potential above 35 mV have been stable over month.

### 3.3 Influence of target surface condition

The dependence of the nanoparticle size on the target surface relief has been studied by comparison of the nanoparticles produced at the subsequent scanning of the target, which was milled and polished to roughness (Ra) about 10 nm before the experiment. The change of the target surface relief was measured for 30 cycles of laser beam scanning (fluence 80 J/cm², duration of scanning cycle 1.4 min, water layer thickness 5 mm). The colloid was completely removed from the cuvette for analysis after each laser irradiation cycle. The cuvette was cleaned and filled with deionized water to exclude the impact of concentration increase. It has been found that the nanoparticle size decreases essentially with increasing the number of scanning cycles to the tenth cycle and does not change after subsequent cycles (Fig. 3a).

![Figure 3](image_url)

Figure 3. Dependences on the number of scanning cycles of: (a) nanoparticle mean diameter $d_N$, (b) target roughness Ra. Laser fluence 80 J/cm².

![Figure 4](image_url)

Figure 4. SEM images of the silver target surface after various number of scanning cycles: a) 1, b) 3, c) 15.
SEM visualization of target surface demonstrated essential relief change with increasing of the cycle number (Fig. 4). It was shown also that the average surface roughness of the target surface increased (Fig. 3b). Moreover the DLS measurements demonstrated existence of two peaks of the intensity-weighted distribution function (5-8 nm and 80 nm) after ten laser scanings. Nevertheless the nanoparticles with sizes below 10 nm have not revealed by direct SEM visualization (Fig. 6d).

The obtained facts can be attributed to change of the spherical nanoparticle shape after number of scanning cycles. It has been shown that nonsphericalness of nanoparticles leads to appearance of a false minor peak in the DLS distribution function\(^{13}\). In this case the correlation function measured at a 13-degree scattering angle with two relaxation modes corresponding to the rotational and translational Brownian diffusions have been detected\(^{13}\). The same behavior of the correlation function has been revealed by us for studied suspensions obtained after ten scanning cycles. In order to remove the false peak induced by rotational diffusion, the minimum size cut-off was applied. The position of maximum of the number-weighted distribution function obtained after cut-off is in good agreement with the nanoparticle size obtained by analysis of the SEM images (Fig. 6a). The obtained results allowed us to use ten scanning cycles for preparation of the target surface for production of the stable colloid with uniform sizes of nanoparticles.

The revealed influence of the target surface relief on the nanoparticle parameters can be attributed to change of the target absorbance as a result of multiple light reflections by the complicated surface relief. The alternative mechanism can be attributed to specific surface layer which has been appeared as a result of target polishing and removed during scanning. The calculated average thickness of the surface layer removed after 10 laser cycles was about 1.2 µm.

**3.4 Influence of the thickness of the water layer**

The dependence of the nanoparticle size and colloid stability on the thickness of the water layer above the target surface has been studied at laser fluence 80 J/cm\(^2\) and ablation time 1.4 min. The target surface was prepared by laser scanning. It was shown that reducing the water layer thickness leads to increase of the absolute value of zeta potential (Fig. 5). This fact can be related to the increasing of the laser radiation which come down to the target surface and more intense photoionization of nanoparticles due to increasing the number of oxidized surface atoms. At the same time no significant change of nanoparticle size was observed while varying the water layer thickness from 5 mm to 2 mm. Moreover, the reduction of the water layer thickness led to an increase of the achieved colloid concentration due to decreasing of the absorption of the laser radiation by previously synthesized nanoparticles.

Figure 5. The dependence of colloid zeta potential on the thickness of the water layer above the target surface. Fluence 80 J/cm\(^2\).

In order to achieve the maximum the colloid stability, the 2 mm-thick water layer has been used. The smaller thickness of the water layer can lead to ablation of the target material in the air due to cavitation effect during the laser beam scanning on the target surface.
3.5 The size of nanoparticles produced by laser ablation in water

The maximum concentration of the silver colloid about 0.12 g/l has been produced for the following optimal parameters for the pulse laser ablation in water with wavelength of 1064 nm and pulse duration of 100 ns: (1) laser fluence 80 J/cm², (2) the thickness of the water layer above the target surface 2 mm.

![Graph showing size distribution of nanoparticles](image)

Figure 6. Comparison of the results of size measurements of silver nanoparticles produced by laser ablation in water at laser fluence 80 J/cm²: (a) DLS: before (dash line) and after (solid line) cut-off, (b) SEM. (c) The absorption spectrum of the silver colloid synthesized by laser ablation at laser fluence 80 J/cm² during one scanning cycle. (d) Visualization of the silver nanoparticles by SEM.

X-ray diffraction analysis determined that the silver nanoparticles produced by laser ablation at laser fluence 80 J/cm² had a face-centered lattice structure. The average size of silver nanoparticles obtained by analysis of SEM images was about 34±5 nm (Fig. 6b) and by DLS in the number-weighted distribution function – about 44 ± 4 nm (Fig. 6a).

3.6 Influence of fragmentation time

It was shown that fragmentation of silver colloid (fluence of 80 J/cm²) prepared with polished target surface and with surface after number of scanning led to aggregation of silver nanoparticles and change of the colloid color from yellow to pale grey. After synthesis the zeta potential value of silver colloid was about - 30 mV corresponding to stable colloid, but after fragmentation during 6 min zeta potential is reduced to 19 mV (in absolute value). The longer colloid fragmentation leads to further decreasing of zeta potential.
3.7 Colloid concentrating

The further increasing of the nanoparticle concentration in stable aqueous colloid can be achieved by various methods including centrifugation, lyophilization and evaporation single without addition of the sorbents\(^1\). Disadvantages of lyophilization are necessity of careful preparation of a dried product, creating a high vacuum, long drying time and high-energy. The disadvantage of centrifugation is the difficulty of selection of the speed and time parameters of centrifuges. Thus we have used the partial evaporation of the water (“partial drying”) for colloid concentrating. However the stable colloid must be used for partial drying as the concentrating processes are commonly associated with formation of aggregates.

After concentrating up to 0.5 g/l the nanoparticle size has been measured by statistical analysis of 850 SEM images (Fig. 7c,d). The obtained average size of silver nanoparticles was about 49±5 nm (Fig. 7b). This value is close to the size revealed by DLS in the number-weighted distribution function after cut-off – about 57±10 nm (Fig. 7a).

![Figure 7. Comparison of the results of size measurements of silver nanoparticles produced by laser ablation in water at laser fluence 80 J/cm\(^2\) and concentrating: (a) DLS, (b) SEM. (c, d) Visualization of the silver nanoparticles by SEM.](http://proceedings.spiedigitallibrary.org/)

**4. CONCLUSION**

For the first time the stable colloid of silver nanoparticles with concentration of 0.5 g/l were obtained without any surfactant by laser ablation in water using a fiber laser with a wavelength of 1064 nm and a pulse duration of 100 ns. The decrease of the nanoparticle size with decreasing of the laser fluence and increasing of the ablation time has been demonstrated. The silver colloid stability has been achieved by reducing the thickness of the water layer above the target surface. The preparation of the target surface by laser scanning, the stirring of the liquid during synthesis and using of the optimal values of laser fluence, duration of the synthesis and the thickness of the water layer allowed to produce the stable enough colloid for further concentrating by partial drying without essential increasing of the nanoparticle size. The obtained synthesis of the stable colloids with high concentration of silver nanoparticles opens the new possibilities for their application.
5. ACKNOWLEDGEMENTS

The equipment of the Ural Center for Shared Use “Modern Nanotechnology,” Institute of Natural Sciences, Ural Federal University was used. The research was made possible in part by RFBR and the Government of Sverdlovsk region (Grant No. 13-02-96041-r-Ural-a), by RFBR (Grant No. 13-02-01391-a), by OPTEC LLC and with the financial support of young scientists in terms of Ural Federal University development program.

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