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# In-flow laser modification of silver nanoparticles synthesized by spark discharge

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**Abstract.** Silver nanoparticles have unique optical properties due to surface plasmon resonance, so they are widely used in various fields of science and technology. The synthesis of aerosol nanoparticles using a spark discharge allows to obtain submicron fractal agglomerated nanoparticles. For future application there is a need to develop new methods to produce nanoparticles with different shapes and sizes to control their optical properties. The article was devoted to the study of the processes of interaction of nanosecond laser radiation of different power (0.230 and 460 MW) and wavelength (527 and 1054 nm) with the flow of aerosol agglomerates of silver nanoparticles (10-400 ml/min) synthesized in a spark discharge, and the assessment of the effect of pulsed radiation power on the morphology of silver nanoparticles. It was shown that best modification of silver nanoparticles to spherical shape was formed at the maximum laser radiation power of the wavelength of 527 nm, close to the plasmon resonance peak for silver.

**Keywords:** nanoparticles, silver, spark discharge, laser radiation, modification, plasmon resonance

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# Лазерная модификация наночастиц серебра, синтезированных в газовом разряде

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**Аннотация.** Наночастицы серебра обладают уникальными оптическими свойствами благодаря поверхностному плазмонному резонансу и широко используются в различных областях науки и техники. С помощью газового разряда можно получить аэрозоль из фрактальных агломерированных наночастиц серебра. Для дальнейшего применения интересны способы модификации их формы и размера для управления оптическими свойствами. Статья посвящена исследованию процессов взаимодействия наносекундного лазерного излучения различной мощности (0, 230 и 460 МВт) и длины волны (527 и 1054 нм) с потоком аэрозольных агломератов наночастиц серебра (10-400 мл/мин), синтезированных в газовом разряде, и оценке влияние мощности импульсного излучения на морфологию наночастиц серебра. Показано, что наилучшая модификация наночастиц серебра до сферической формы формируется при максимальной мощности лазерного излучения на длине волны 527 нм, близкой к пику плазмонного резонанса для серебра.

**Ключевые слова:** наночастицы, серебро, газовый разряд, лазерное излучение, модификация, плазмонный резонанс

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## Introduction

Silver nanoparticles (NPs) have unique optical properties due to surface plasmon resonance, which can be tuned to a specific wavelength by changing the shape and size of the nanoparticles [1]. At the moment, there are several options for manufacturing volumetric micro-sized structures from nanoparticles that are used in electronics, Raman spectroscopy, photonics, solar energetics and biomedicine [2-5]. For example, such structures are obtained by lithography, inkjet printing using nanoinks or by dry aerosol printing with nanoparticles obtained in a pulsed spark discharge. The urgency of manufacturing and modifying particles in the flow for dry aerosol printing of plasmon structures is associated with ensuring a more environmentally friendly process, in contrast to the use of nanoinks, which entails environmental pollution and requires the subsequent removal of component residues from the obtained structures from nanoparticles and cleaning the nozzles from large microdrops. Moreover, the method of producing nanoparticles in a pulsed spark discharge is economically advantageous for obtaining nanoparticles of various metals, oxides and semiconductors and is devoid of difficulties associated with the synthesis, transportation and storage of components, and provides a lower electrical resistivity of sintered lines of silver nanoparticles than when annealing particles obtained from nanoinks as well [6].

## Materials and Methods

The scheme of a setup describing the experiment principle is provided in Fig. 1. Nanoparticles synthesis was carried out in the discharge chamber that was made from glass (Duran glass, KF50, Millab) in which two hollow Ag electrodes were opposite mounted. An aerosol with silver nanoparticles was produced in a spark discharge (1.5 kV) in a flow of argon carrier gas (Ar 6.0) of 10-400 ml/min, then it was processed by laser radiation with a wavelengths' of 527 and 1054 nm at pulse energies up to 900 μJ and pulse repetition rate up to 500 Hz directly in the gas stream. The resulting aerosol was transported to a nozzle to focus it on a copper TEM-grid with carbon film for next TEM-characterization, cellulose filter and a substrate to form various plasmon nanostructures then. A more detailed description of the setup is provided in [7].

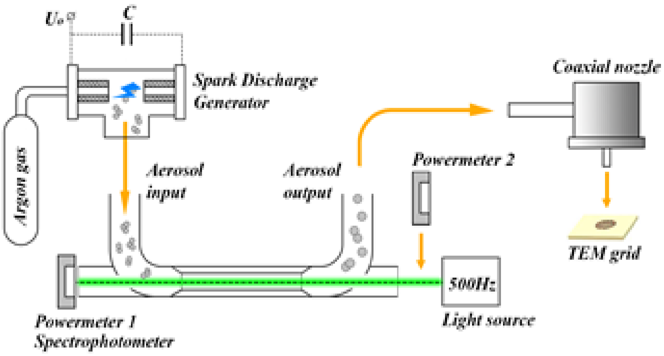



Fig. 1. Scheme of spark discharge synthesis of Ag NPs

During the project, the study of particle size parameters, morphology and phase composition was carried out using a set of methods. Transmission electron microscopy (TEM) on a JEOL JEM-2100 device with an accelerating voltage of 200 kV enforced getting images of nanoparticles and diffraction patterns for structure analyzing. Aerosol NP analyzer SMPS 3936 (TSI Inc., Shoreview, MN, USA) for measuring the particle size distribution in the flow was used. These measurements give an equivalent size of the primary nanoparticles' agglomerates. By Jasco V770 spectrophotometer extinction spectrums were obtained. ImageJ image analysis software for constructing a statistical distribution of the sizes of silver nanoparticles as well as information for analyzing diffraction patterns from the American Mineralogist Crystal Structure Database were used.

## Results and Discussion

A typical TEM image of large agglomerate of primary nanoparticles obtained in the spark discharge (gas flow 50 ml/min) without laser interaction and the corresponding electron diffraction pattern are presented on figure 2. Most of the primary NPs' sizes were detected to be from 6 to 30 nm, a few single particles with sizes of 35–43 nm were observed. The average size was 16±4.5 nm for primary silver nanoparticles, and 160±132 nm for agglomerates (TSI data). Pursuant to SAED pattern we had concluded that all of NPs were crystallized in the silver phase of the Fm3m space group.

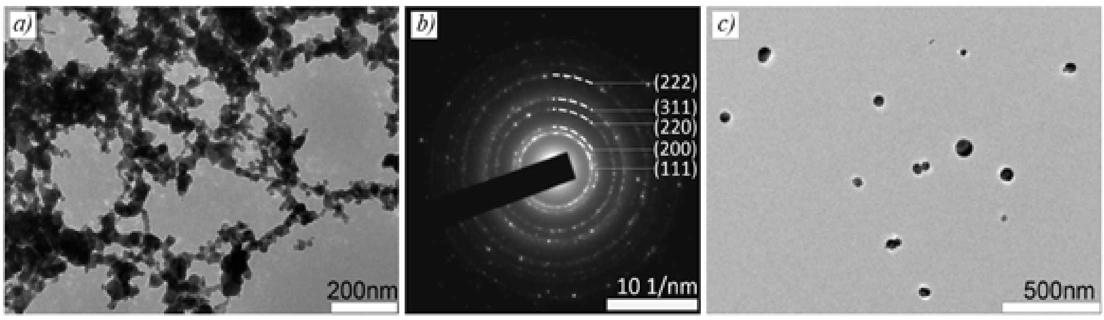



Fig. 2. TEM image of primary Ag NPs primary agglomerates (no laser) (*a*); SAED pattern taken from primary agglomerates area (*b*); TEM image of Ag NPs modified by laser radiation of wavelength of 527 nm (*c*)

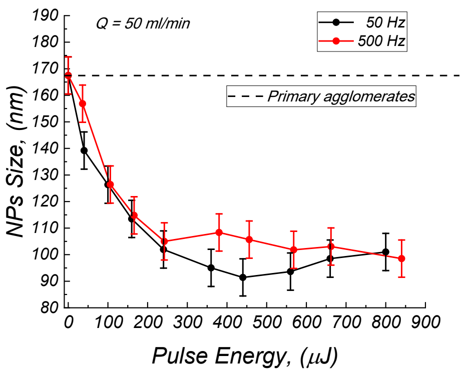
Firstly, modification of nanoparticles with radiation of wavelength of 1054 nm was investigated. As a result of the conducted research, it turned out that the power value of pulsed laser radiation affects the size of nanoparticles and the shape of their agglomerates: smaller sizes were observed for nanoparticles that did not interact with laser radiation. Half-power red laser does not provide the sintering of all nanoparticles as well as full-power radiation. But number of sintered nanoparticles is higher in the last case. Moreover, sphere-like particles with small ones on their surface were detected. According to TEM images of Ag NPs modification by laser radiation of wavelength of 1054 nm (gas flow 50 ml/min), better modification was achieved using the full laser power (460 MW).

The observed amount of remaining agglomerates of primary nanoparticles (Fig. 4, *a*) led to the assumption that not all nanoparticles have enough time to interact with laser radiation, since they can be overlapped by others that have already interacted. In this regard, it was decided to reduce the gas flow from 50 to 10 ml/min. The flow of nanoparticles decrease affects the quality of sintering: individual spherical nanoparticles and reduction of agglomerates' groups number were observed.

During pulsed laser modification of aerosol agglomerates of nanoparticles, the sizes of sintered nanoparticles in the flow were measured by their electrical mobility, depending on the energy density of the incident radiation at pulse repetition frequencies of 50 and 500 Hz (Fig. 3, *a*). In the (Fig. 3, *a*), the black dotted line corresponds to the modal distribution size of the initial agglomerates, determined by their electrical mobility. Experimental dependences of the size of agglomerates demonstrate a NPs shrinkage that is the decrease in size as the energy density of laser pulses increases was observed. With a further increase in the pulse energy density, close shrinkage values are observed in the range of pulse energy densities, the shrinkage graph reaching a horizontal region with NPs sizes close to 100 nm at energy densities from 250 to 850 μJ/cm²  and pulse repetition frequencies of 50 and 500 Hz.

The energy required for modification depends on the size, material and extinction/absorption coefficient of nanoparticles at the laser wavelength. It is known that the maximum absorption coefficient of silver at a wavelength of 400 nm, that's why better modification by green laser than red was assumed. Absorption spectra analysis of silver agglomerated nanoparticles showed the maximum intensity peak of absorption energy at 390 nm closed to the green part of visible spectrum (Fig. 3, *b*). Shape changing by green laser impact to spherical was confirmed by TEM results (Fig. 2, *c*).

*a*)




*b*)

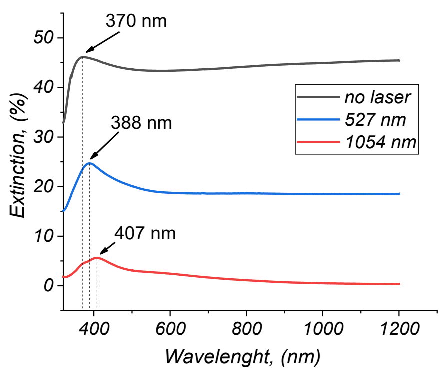



Fig. 3. Dependencies of Ag NPs size on the pulse energy density of laser radiation with the wavelength of 1054 nm at the pulse repetition rate of 50 Hz (black curve) and 500 Hz (red curve) (*a*); Absorption spectra of primary and modified NPs by laser radiation of wavelength of 1054 and 527 nm (gas flow: 50 ml/min) (*b*)

## Conclusion

The best modification was achieved using the full red and green lasers' power (460 MW). All of NPs were crystallized in the silver phase of the Fm3m space group. Longer interaction time between NPs and laser radiation by decreasing the flow of nanoparticles provides better sintering quality: individual spherical silver particles were observed. Better spherical shape was obtained by full power green laser modification than red. The maximum absorption coefficient was detected at a wavelength of ~390 nm.

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