Investigation of laser and thermal sintering processes of silver nanoparticles agglomerates synthesized by spark discharge

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Abstract. Changes in the shape and size of silver nanoparticles (NPs) during their laser and thermal sintering have been studied experimentally and theoretically. Aerosol silver NPs forming dendriledagglomerates 180 nm in size were synthesized by spark discharge and exposed to laser radiation and high temperature of 750 °C. The shape and size of the NPs were investigated depending on the power of the laser radiation and the temperature of the gas. It is estimated that, at a power density of laser radiation of the order of $10^3 - 10^4$ W/cm², the formation of spherical NPs with an average size of 140 nm is expected. Such particles turn out to be similar to NPs thermally heated in a gas flow at 750 °C for 6 seconds.

1. Introduction
Nanoparticles (NPs) are an interesting and important object for study, due to their high demand for research problems and their promising potential in many technological industries. With their help, point delivery of drugs, detection of hazardous substances, change in the optical and electronic properties of materials is carried out [1-3]. Currently, there are many methods for producing NPs: lithography, synthesis from colloidal solutions, laser ablation, and others [4-6]. However, one of the most effective ways to obtain NPs in terms of mass productivity and synthesis capabilities is their synthesis in a gas discharge. [7,8]. This method makes it possible to control the delivery of NPs and their agglomerates, composition and morphology directly in the aerosol flow using external influences [9].

In this work, we study the effect of continuous laser radiation with wavelengths of 527 and 980 nm and high temperatures on agglomerates of aerosol silver NPs synthesized in a spark discharge in order to obtain non-agglomerated spherical NPs.

2. Experiment setup and research method
The synthesis of NPs was carried out by the method of a spark gas discharge in an argon flow (99.99998%) between coaxially arranged silver cylindrical electrodes. Primary silver NPs with an average size of 10 nm in an aerosol flow agglomerated and formed dendrild-like nanostructures, which were studied in an aerosol NPs analyzer SMPS 3936 (TSI Inc.) and in a transmission electron microscope (TEM) JEM-2100 (JEOL). The gas path connected in series two zones - with a controlled temperature and with laser radiation brought inside, in which agglomerates of NPs were subjected to two types of impact: thermal, in a heated section of the gas path, and laser, in a quartz cell. The quartz cell consisted of two combined tubes, into one of which an aerosol stream was injected, and into the
other continuous laser radiation with wavelengths of 527 and 980 nm with the ability to control power in the range of up to 1.5 W for a green laser and up to 6 W for an infrared one (Figure 1). Thermal modification of agglomerates of NPs was carried out in a heated section of the gas path 40 cm long at a temperature of 750 °C.

Determination of the power of laser radiation was carried out by a power detector VEGA (Ophir).

**Figure 1.** Schematic of an experimental setup for studying the sintering processes of nanoparticle agglomerates obtained in a spark discharge generator of NPs.

Theoretical assessments were carried out in accordance with the model given in the article [10]. The calculations of the heating and melting times of NPs were carried out using the heat transfer equation in spherical coordinates:

\[ \rho_m C_m V \frac{\partial T_m}{\partial t} = P - (q_{rad} + q_{cond}) \],

where \( \rho_m \) – is the density of a metal nanoparticle, \( C_m \) – specific heat, \( T_m \) – temperature, \( V \) – volume of a nanoparticle, \( P \) – power loss of laser radiation on one agglomerate of NPs, \( q_{rad} \) and \( q_{cond} \) – heat received or given off by a nanoparticle due to radiation and heat transfer respectively. All theoretical calculations were performed for a spherical silver nanoparticle with a size of \( d = 180 \text{ nm} \). This is much greater than the mean free path in argon gas, which in this case is the carrier gas. This indicates that the change in the nanoparticle temperature depends mainly on heat transfer and is almost independent of radiation; therefore \( q_{rad} \) is neglected in this case. Formula for calculating \( q_{cond} \) or the case when the temperature of the particles is higher than the temperature of the medium:

\[ q_{cond} = SG(T_m - T_0) \],

where \( S \) – surface area of the nanoparticle, \( G \) – thermal conductivity of the nanoparticle-medium interface, \( T_0 \) – temperature of the gas medium. The power of laser radiation that is lost on one agglomerate of NPs can be estimated by knowing the length and diameter of the quartz cell - 160 mm and 3 mm, respectively, the diameter of the laser beam - 2 mm and obtaining data on the concentration of nanoparticle agglomerates in the carrier gas from an aerosol analyzer. Also, in this estimate, the melting point of silver will be taken as a temperature of 750 °C, and the transformation time of NPs agglomerate to an enlarged spherical nanoparticle is taken to be equal to the sum of the times of heating and complete melting of a nanoparticle with a size of 180 nm.
3. Results and discussion
It was experimentally established that at an output power of laser radiation of about 1.2 W for two wavelengths, an infrared laser has a significantly less effect on NPs than green laser radiation. A small change in the size of agglomerates of silver NPs at threshold powers is achieved due to the fact that agglomerates of NPs are modified by absorbing radiation. However, the absorption peak for silver NPs is in the blue region of the spectrum, which is much closer to 527 nm than to 980 nm.

![Figure 2](image.jpg)
Figure 2. Dependence of the power of laser radiation at the exit from a quartz cell on the power at the entrance with a carrier flux \( Q = 100 \text{ ml/min} \) at room temperature for a laser with an operating wavelength of 527 nm (left) and 980 nm (right).

Analysis of the power of laser radiation at the input and output of a quartz cell (Figure 2) showed that NPs absorb laser radiation with a wavelength of 527 nm more efficiently than 980 nm by about 2.5 times. It is worth saying that the coefficient \( K \) here reflects all the energy losses of laser radiation on particles, that is, extinction: scattering of radiation on particles and absorption of radiation by them. But in this work, the scattering of energy by particles in theoretical calculations is assumed to be small in comparison with absorption.

![Figure 3](image.jpg)
Figure 3. TEM images of silver NPs: primary (a), passed through a quartz cell with laser radiation of 527 nm at a power of 1.2 W (b) and optimized in a heated section of the channel at a temperature of 750 °C (c).

Analysis of the data obtained using an analyzer of aerosol NPs and the TEM showed that at a gas flow of 200 ml/min, agglomerates of NPs significantly change their shape, turning into spheres with an average diameter of 140 nm, determined from TEM images (Figure 3 (c)).

TEM images of NPs (Figure 3) confirm that thermal sintering of agglomerates of NPs at a temperature of 750 °C is more effective than sintering with laser radiation, in which the agglomerates of NPs do not undergo significant changes. However, it can be noted that agglomerates exposed to
laser radiation are a structure of individual NPs with more resolvable boundaries, in comparison with agglomerates of primary NPs.

| Heat temperature (s) | Final temperature of NP (°C) | Current power density (W/cm²) | Estimated power density of complete NPs sintering (kW/cm²) |
|---------------------|-----------------------------|-------------------------------|----------------------------------------------------------|
| Thermal optimizer   |                             |                               |                                                          |
| 6.0                 | 750                         |                               |                                                          |
| 527 nm CW laser     | 0.7                         | 31                            | 50                                                       | 7.9 |
| 980 nm CW laser     | 0.7                         | 36                            | 200                                                      | 15.0|

The results of theoretical calculations (Table 1) show that in the case of heating NPs using laser radiation under current conditions, a silver nanoparticle with a size of 180 nm will, on average, heat up by only 4-9 degrees during its flight through a quartz cell. This happens because the cooling factor of NPs upon collision with molecules of an unheated gas medium has a significant effect. Comparing the heating and melting time of a nanoparticle in a thermal element with that for a nanoparticle exposed to laser radiation, it is possible to estimate the power density of laser radiation at which it is possible to achieve the results of sintering agglomerates of NPs similar to those shown in the image (Figure 3 (c)). At the same time, having made similar estimates for a nanoparticle with a size of 10 nm, one can come to the conclusion that the current power density of laser radiation is sufficient for its heating and melting, which is consistent with the experimental results in the image, where one can see sintered small NPs on the surface of large particles in the composition agglomerate (Figure 3 (b)). The estimates made indicate that to improve the efficiency of modifying NPs in a gas cell, the radiation power density or radiation absorption efficiency should be two orders of magnitude higher for green and infrared lasers. This can be achieved, for example, by building a more complex optical system with a narrower laser beam. This development seems to be possible, since agglomerates of NPs moving along the tube in the gas flow are mostly distributed closer to the center of the tube.

4. Conclusion
As a result of a comparison of two types of exposure (thermal and laser), it was found that for sintering agglomerates of NPs to comparable sizes and shapes, it is necessary to increase the radiation power density by two orders of magnitude for wavelengths of 527 nm and 980 nm. In this case, either the absorption efficiency of radiation turns out to be higher for a wavelength of 527 nm, compared with a wavelength of 980 nm, which corresponds to the peculiarities of the absorption spectrum of silver NPs. This allows us to conclude that when changing the radiation wavelength to a closer to the peak of plasmon absorption of the NPs under study, one can also achieve comparable results with those obtained by modifying particles in the heated section of the gas path.

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References
[1] Kuznetsov A I, Miroshnichenko A E, Brongersma M L, Kiyshar Y S and Luk’yanchuk B 2016
Optically resonant dielectric nanostructures Science 354
[2] Devabharathi N, M. Umarji A and Dasgupta S 2020 Fully Inkjet-Printed Mesoporous SnO2-Based Ultrasensitive Gas Sensors for Trace Amount NO2 Detection ACS Appl. Mater.
Interfaces 12 57207-57217

[3] Palani G, Kannan K, Radhika D, Vijayakumar P and Pakiyaraj K 2020 Bioengineered metal and metal oxide nanoparticles for photocatalytic and biological applications (review) Physics and Chemistry of Solid State 21 571-583

[4] Ealia S A M and Saravanakumar M P 2017 A review on the classification, characterisation, synthesis of nanoparticles and their application IOP Conf. Ser.: Mater. Sci. Eng. 263 032019

[5] McDarby S P, Wang S J, King M E and Personick M L 2020 An Integrated Electrochemistry Approach to the Design and Synthesis of Polyhedral Noble Metal Nanoparticles Journal of the American Chemical Society 142 21322-21335

[6] Yu W-J, Geng P, Wen M and Chen Z-G 2020 Gelatin-mediated coprecipitation synthesis of copper sulfide nanoparticles for photothermal ablation of cancer cells Cailiao Gongcheng/Journal of Materials Engineering 48 68-74

[7] Mylnikov D, Efimov A and Ivanov V 2019 Measuring and optimization of energy transfer to the interelectrode gaps during the synthesis of nanoparticles in a spark discharge Aerosol Science and Technology 53 1393-1403

[8] Efimov A A, Arsenov P V, Borisov V I, Buchnev A I, Lizunova A A, Kornyushin D V, Tikhonov S S, Musaev A G, Urazov M N, Shcherbakov M I, Spirin D V and Ivanov V V 2021 Synthesis of Nanoparticles by Spark Discharge as a Facile and Versatile Technique of Preparing Highly Conductive Pt Nano-Ink for Printed Electronics Nanomaterials 11 234

[9] Lizunova A, Mazharenko A, Masnaviev B, Khramov E, Efimov A, Ramanenka A, Shuklov I and Ivanov V 2020 Effects of Temperature on the Morphology and Optical Properties of Spark Discharge Germanium Nanoparticles Materials 13 4431

[10] Xi Q, Li Y, Zhou J, Li B and Liu J 2019 Role of Radiation in Heat Transfer from Nanoparticles to Gas Media in Photothermal Measurements Int. J. Mod. Phys. 30 1950024