

PHYSICS OF SEMICONDUCTORS AND DIELECTRICS

THE INFLUENCE OF ULTRAVIOLET RADIATION INTENSITY ON THE FORMATION OF SILVER NANOPARTICLES BY CAVITATION-DIFFUSION PHOTOCHEMICAL REDUCTION

G. F. Kopytov,¹ D. I. Shashkov,² A. A. Basov,^{2,4} V. V. Malyshko,^{3,4}
M. E. Sokolov,² A. P. Storozhuk,⁴ A. V. Moiseev,⁵ A. M. Barysheva,⁶
N. V. Zubova,¹ V. A. Isaev,² and A. A. Dorokhova^{2,3}

UDC 538.9; 620.3

The effect of different intensities of ultraviolet radiation (UV radiation) on the formation of silver nanoparticles (Ag NPs) synthesized by cavitation-diffusion photochemical reduction is studied. It is found out that with a decrease in the UV radiation intensity, the average size of silver nanoparticles increases, while the scatter of Ag NPs diameters increases. It is also noted that with a decrease in the UV radiation intensity by 50% or more, there is an increase in the proportion of organic material in the matrix of the dry residue of the studied solutions, and against the background of the most significant decrease in the level of the studied UV radiation (by 75% of the initial power), nanoparticles are identified on the surface of this organic structure. In addition, the effect of lower intensity UV radiation (<50% of the original power) on nanoparticle size is primarily characterized by a significant decrease in the amount of the most biologically active Ag NPs (15 nm in diameter or smaller).

Keywords: silver nanoparticles, ultraviolet radiation intensity, nanoparticle synthesis.

INTRODUCTION

The search for new ways of synthesizing highly functional silver nanoparticles (Ag NPs) and upgrading the existing technologies for their synthesis has been still in the focus of scientific attention, [1, 2]. The methods of so-called green synthesis, based on the production of nanoparticles using biological substrates of a plant or microbial origin, have become widespread [3, 4]. A change of the synthesis conditions of Ag NPs has a significant impact on the physicochemical properties of the resulting nanoclusters and can be used for their targeted modification in accordance with the scientific and technical research objectives [5]. Nanoparticles of small sizes (less than 15 nm) are widely used for medical purposes as an antimicrobial, antitumor, and antifungal agents [6, 7]. Relatively large nanoparticles (with a diameter of over 50 nm) are used quite extensively, both for modifying the materials to protect them from microwave radiation [8] and in the formation of films in periodic plasmonic sensors used, for example, for diagnosing Alzheimer's disease [9].

¹Razumovsky Moscow State University of Technology and Management, Moscow, Russia, e-mail: g137@mail.ru; na448@yandex.ru; ²Kuban State University, Krasnodar, Russia, e-mail: shinix88@mail.ru; sokolovme@mail.ru; son_sunytch79@mail.ru; vliisae.v@yandex.ru; ³Southern Scientific Center of the Russian Academy of Science, Rostov-on-Don, Russia, e-mail: intro-2@rambler.ru; 013194@mail.ru; ⁴Kuban State Medical University, Krasnodar, Russia, e-mail: ilya.bh@mail.ru; ⁵Kuban State Agrarian University, Krasnodar, Russia, e-mail: moiseew_a@rambler.ru; ⁶Kuban State Technological University, Krasnodar, Russia, e-mail: alisa_barysheva03@mail.ru. Original article submitted January 24, 2024.

The methods for preparing Ag NPs, based on the use of ultraviolet radiation (UV radiation), are among the most common approaches to the synthesis of various silver nanoclusters. The factors influencing the final properties of the resulting nanostructures include the irradiation time, the UV radiation intensity, and the concentration of the initial solution components, although the key influence belongs to the duration and intensity of UV radiation on the resulting nanomaterials [10]. The influence of a particular spectral range of light radiation on the properties of the resulting Ag NPs was also proven. A recent study has shown that changing the optical wavelength has a significant effect on the size of the resulting nanoparticles, their oxidative potential and antimicrobial activity against pathogenic microorganisms [11]. Based on the data described, it seems appropriate to study a number of modifications of similar methods for producing silver nanoparticles in order to create structures consisting of particles of relatively larger sizes, or to optimize the uniform deposition of these nanoparticles, for example, on special surfaces (substrates).

This paper presents the results of a study of the size range of silver nanoparticles synthesized by cavitation-diffusion photochemical reduction at different ultraviolet irradiation intensities.

EXPERIMENTAL MATERIAL AND PROCEDURE

During the experiment, the equipment and technical devices of the Collective Use Center for Diagnostics of the Structures and Properties of Nanomaterials of the Kuban State University (Krasnodar) were used. The resulting Ag NPs were assessed using electron microscopy of freshly prepared solutions. An aqueous solution of Ag NPs was subsequently prepared by the method of cavitation-diffusion photochemical reduction, which involves the reduction of ions together with polyvinylpyrrolidone [12]. The reduction reaction was performed under a combined exposure to ultrasonic waves (radiation frequency 1.7 MHz) and ultraviolet radiation for 60 minutes [13]. The UV radiation intensity during the experiment was decreased by 25%, 50% and 75% with respect to the original value through the use of a light filter (with maximum absorption at 257, 277 and 325 μm). The level of UV radiation was measured with a MEGEON-21170 luxmeter. The experimental data obtained were processed using the variation statistics methods. The reliability of the differences found between the indicators of Ag NPs on different fibers and in different size ranges was assessed using the nonparametric Mann-Whitney U test. The differences were thought to be significant at $p < 0.05$.

RESULTS AND DISCUSSION

As a result of the experiment, it was demonstrated that reducing the intensity of ultraviolet exposure has a significant effect on the formation of nanostructures. When the intensity of ultraviolet radiation was decreased by 25%, an electron microscopy examination of the dry residue of solutions in the reflected electron detection mode (COMPO) revealed the presence of an amorphous organic matrix, consisting of light elements (mainly carbon) and various nanoparticles (Fig. 1) consisting from heavier silver atoms, in the solution volume. It was found out that about 42% of the detected particles were larger than 30 nm (Fig. 1), which indicates the formation of fairly large nanoclusters under the conditions of even a slightly lower UV radiation level. The proportion of remaining nanoparticles in the range from 15 to 30 nm was 51% (while the content of Ag NPs with a diameter of 15–20 nm did not exceed 22% of the total number), and nanostructures of a smaller range (<15 nm) were present in the micrographs in 7% cases only (Fig. 1).

It should be noted that under the initial conditions (with 100% retention of ultraviolet radiation power [14]), the formation of silver nanostructures with a significant predominance of nanoparticles with a diameter of up to 15 nm was observed (Fig. 2). In the vast majority of cases, Ag NPs with a size of 10 to 15 nm were identified among them (97%, $p < 0.05$ compared to the number of Ag NPs revealed after the UV intensity was decreased by 25%). The presence of an insignificant number of nanoparticles with the sizes ranging from 15 nm to 30 nm was also noted (3% of all Ag NPs, $p < 0.05$, Fig. 2) with a complete absence of nanostructures measuring more than 30 nm, which indicates a significantly greater effect with these synthesis parameters using cavitation-diffusion photochemical reduction to form primarily biologically active silver nanoparticles compared to the case of an even slightly lower (by 25%, Fig. 1) UV radiation level.

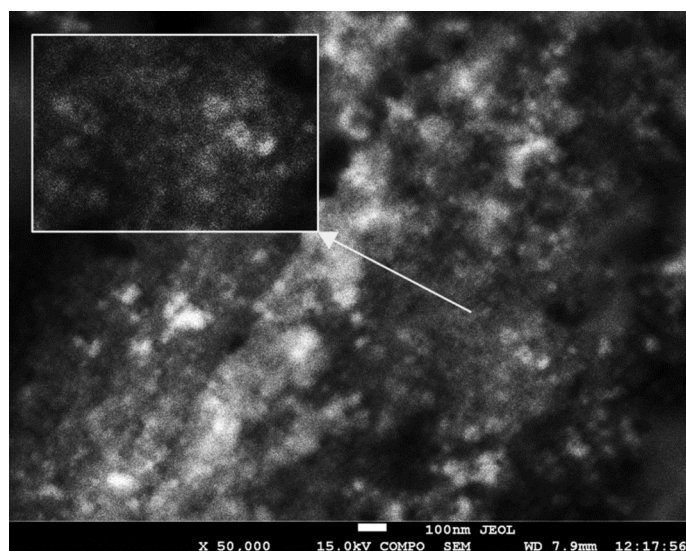


Fig. 1. Electron micrographs of a solution of nanoparticles (magnification $\times 50,000$) in EBSD mode (COMPO). UV radiation power 75%.

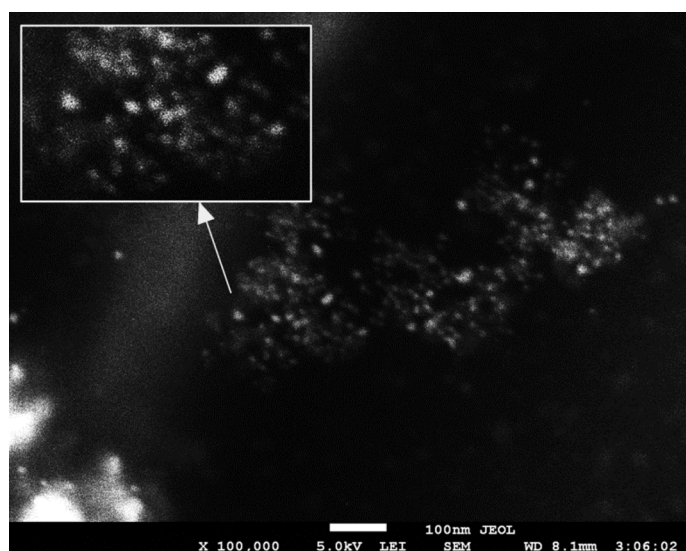


Fig. 2. Electron micrographs of a solution of nanoparticles (magnification $\times 50,000$) in EBSD mode (COMPO). UV radiation power 100%.

With a further decrease in the level of ultraviolet irradiation (Figs. 3 and 4), a continuation of the trend towards the formation of increasingly larger structures was noted, including not only silver, but also possibly a ligand residue. For example, when the intensity of UV radiation was decreased by 50%, the micrographs revealed the formation of aggregates, probably consisting of unreacted components of the solution. At the same time, on the surface of the matrix of the dry residue there are individual more contrasting formations corresponding to Ag NPs (Fig. 3), which have a significantly larger spread in the sizes compared to those of nanoparticles formed at 100% and 75% UV power ($p < 0.05$, Fig. 1, Fig. 2). About 65% of the detected particles were in the larger than 30 nm size range, which indicates the formation primarily of large nanoclusters. Another 21% of Ag NPs had the diameters between 15 and 30 nm, and only 14% of the detected particles were smaller than 15 nm in size (Fig. 3).

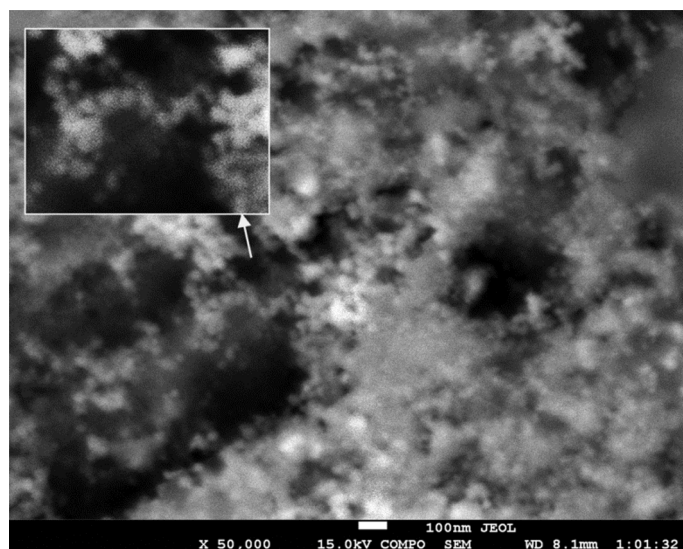


Fig. 3. Electron micrographs of a solution of nanoparticles (magnification $\times 50,000$) in EBSD mode (COMPO). UV radiation power 50%.

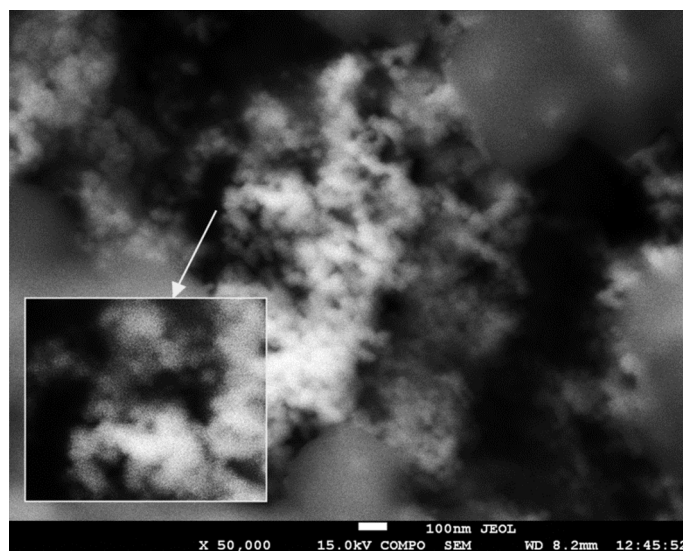


Fig. 4. Electron micrographs of a solution of nanoparticles (magnification $\times 50,000$) in EBSD mode (COMPO). UV radiation power 25%.

At the same time, in the image taken at the 25% UV emitter power (Fig. 4), a loose structure was revealed, occupying most part of the microphotograph. It should be noted that the contrasting formations in its structure have a significant spread in diameter: 77% of the detected particles were larger than 30 nm, 18% had a size from 15 to 30 nm, and Ag NPs smaller than 15 nm accounted for no more than 5% of the total number of identified nanoclusters. Note that a decrease in the intensity of UV radiation in all studied cases (by 25%, 50%, 75%) does not lead to the formation of silver nanostructures with a diameter of more than 100 nm, although a decrease in the total number of silver nanoparticles is clearly observed as the intensity of radiation affecting the components of the original solution during the synthesis of Ag NPs is decreased.

CONCLUSIONS

The phenomena observed in this study are probably due to the fact that the light filter used does not transmit the ultraviolet radiation range corresponding to the silver absorption spectrum, as a result of which the silver atoms do not have sufficient energy to form nanoparticles, and the solution components partially settle in the form of aggregates. Thus, with a decrease in the intensity of ultraviolet irradiation during cavitation-diffusion photochemical reduction, an increase in the size of silver nanoparticles was revealed, which can be potentially used in the technological processes for formation of larger nanostructures. This is evidenced by a large number of nanoparticles larger than 30 nm, especially when the radiation level is decreased by 50% and 75% ($p < 0.05$ compared to the number of Ag NPs at the initial synthesis parameters). It is also necessary to note a certain non-selectivity of this approach, since in some micrographs relatively small nanoparticles (smaller than 15 nm in diameter, Fig. 3) were also detected, even in the cases of a twice lower irradiation intensity compared to the initial level. At the most dramatically decreased UV radiation level (by 75% of the initial power), the formation of silver nanoclusters was accompanied by a sharp increase in the scatter of their diameters with a pronounced tendency towards the formation of Ag NPs larger than 30 nm ($p < 0.05$ compared to the number of Ag NPs at the initial synthesis parameters [15]). It should also be noted that in the course of synthesizing silver nanoparticles for medical and biological purposes, it is imperative to exclude any drop in the level of UV radiation throughout their production, since even a relatively small (25%) radiation intensity decrease during the synthesis of Ag NPs significantly reduces the number of small nanoparticles that are most functional in this regard (with a diameter of smaller than 15 nm, Fig. 1) compared to the initial level of ultraviolet exposure ($p < 0.05$, Fig. 2). Furthermore, it should be noted that in order to prepare homogeneous solutions with larger silver nanoclusters, it is advisable to reduce the intensity of ultraviolet radiation by at least 50% of its initial level [16]. Such an approach will make it possible to synthesize nanostructures suitable, for example, for designing materials with increased protection from microwave radiation [8], potentially applicable in the technologies for manufacturing various multifunctional nanomaterials, including diagnostic sensors [9].

COMPLIANCE WITH ETHICAL STANDARDS

Author contributions

Conceptualization: Basov A. A.; methodology: Malyshko V. V., Shashkov D. I.; formal analysis: Storozhuk A. P., Sokolov M. V.; writing, original draft preparation: Basov A. A., Malyshko V. V.; writing – review and editing: Moiseev A. V., Zubova N. V., Isaev V. A.; visualization: Dorohova A. A.; supervision: Kopytov G. F.

All authors have read and approved the final manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Funding

This work was carried out under the state assignment of the Ministry of Education and Science for the Kuban State University (FZEN-2023-0006).

REFERENCES

1. P. Pushankina, M. Baryshev and I. Petriev, *Nanomater.*, **12(23)**, 4178 (2022). <https://doi.org/10.3390/nano12234178>.
2. I. S. Petriev, M. G. Baryshev, K. A. Voronin, I. S. Lutsenko, P. D. Pushankina and G. F. Kopytov, *Russ. Phys. J.* **63**, 457 (2020). <https://doi.org/10.1007/s11182-020-02056-w>.
3. A. A. Gawai, A. R. Kharat, S. S. Chorge and S. A. Dhawale, *J. Mol. Recognit.* **36(10)**, e3051 (2023). <https://doi.org/10.1002/jmr.3051>.
4. R. Hazrati, N. Zare, R. Asghari-Zakaria and P. Sheikhzadeh, *Appl. Microbiol. Biotechnol.* **107(19)**, 5963 (2023). <https://doi.org/10.1007/s00253-023-12683-1>.
5. J. T. Kurian, B. Balasubramanian, A. Meyyazhagan, M. Pappuswamy, A. M. Alanazi, K. R. Rengasamy, V. A. Arumugam, J. K. Sebastian and J. T. Chen, *Front. in Bios. Land.* **28(8)**, 169 (2023). <https://doi.org/10.31083/j.fbl2808169>.
6. H. S. Sofi, T. Akram, A. H. Tamboli, A. Majeed, N. Shabir and F. A. Sheikh, *Int. J. Pharm.* **569**, e118590 (2019). <https://doi.org/10.1016/j.ijpharm.2019.118590>.
7. A. A. Basov, S. R. Fedosov, V. V. Malyshko, A. A. Elkina, O. M. Lyasota and S. S. Dzhimak, *J. Wound Care.* **30(4)**, 312 (2021). <https://doi.org/10.12968/jowc.2021.30.4.312>.
8. E. Palaimiene, J. Macutkevič, J. Banys and A. Selskis. *Materials (Basel)* **15(20)**, 7100 (2022). <https://doi.org/10.3390/ma15207100>.
9. O. E. Eremina, N. R. Yarenkov, G. I. Bikbaeva, O. O. Kapitanova, M. V. Samodelova, T. N. Shekhovtsova, I. E. Kolesnikov, A. V. Syuy, A. V. Arsenin, V. S. Volkov, G. I. Tselikov, S. M. Novikov, A. A. Manshina and I. A. Veselova, *Talanta* **266(Pt 1)**, 124970 (2024). <https://doi.org/10.1016/j.talanta.2023.124970>.
10. B. Pascu, A. Negrea, M. Ciopec, N. Duteanu, P. Negrea, L. A. Bumm, O. Grad mBuriac, N. S. Nemeş, C. Mihălcea and D. M. Duda-Seiman, *Int. J. Mol. Sci.* **24(1)**, 255 (2022). <https://doi.org/10.3390/ijms24010255>.
11. R. Iqbal, T. Khan, T. A. Sherazi, A. Jalal and G. S. Ali, *Photochem. Photobiol.* 2023. <https://doi.org/10.1111/php.13853>.
12. S. S. Dzhimak, V. V. Malyshko, A. I. Goryachko and M. E. Sokolov, *Nanotech. in Rus.* **14**, 48 (2019). <https://doi.org/10.1134/S199507801901004X>.
13. A. Basov, S. Dzhimak, M. Sokolov, V. Malyshko, A. Moiseev, E. Butina, A. Elkina and M. Baryshev, *Nanomaterials.* **12**, 1164 (2022). <https://doi.org/10.3390/nano12071164>.
14. S. S. Dzhimak, M. E. Sokolov, A. A. Basov, S. R. Fedosov, R. V. Vlasov, O. M. Lyasota, M. G. Baryshev and V. V. Malyshko, *Nanotech. in Rus.* **11**, 835 (2016). <https://doi.org/10.1134/S1995078016060082>.
15. S. S. Dzhimak, A. I. Goryachko, M. E. Sokolov, A. A. Basov, D. I. Shashkov, G. F. Kopytov, M. G. Baryshev, V. A. Isaev, V. V. Malyshko and A. V. Moiseev, *Russ. Phys. J.* **62(2)**, 314 (2019). <https://doi.org/10.1007/S11182-019-01714-Y>.
16. G. F. Kopytov, V. V. Malyshko, A. V. Moiseev, A. A. Basov and S.S. Dzhimak, *Russ. Phys. J.* **65(6)**, 1022 (2022). <https://doi.org/10.1007/s11182-022-02727-w>.