

PHYSICS OF SEMICONDUCTORS AND DIELECTRICS

ESTIMATION OF THE SORPTION ACTIVITY OF SILVER NANOPARTICLES ON BIODEGRADABLE FIBERS OF NATURAL AND ARTIFICIAL ORIGIN

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The specific features of the sorption activity of silver nanoparticles (AgNPs) on biodegradable polymers of natural (collagen) and artificial (polyamide 6.6) origin have been established. The ability has been demonstrated for resorbable fibers of natural origin to more actively adsorb AgNPs with sizes from 1 to 10 nm during the first hour and stronger hold them on the surface during the first day of exposure to argogel. During the first hour of incubation of these polymers in a gel composition containing AgNPs obtained by the method of cavitation-diffusion photochemical reduction, their higher sorption activity was revealed in the size range from 1 to 10 nm in relation to the polyfilament synthetic material. After 24 h of exposure, a significant increase in the fraction of small AgNPs already on collagen fibers was observed, which was also accompanied by a significantly lower (19 times) content of AgNPs with a diameter above 40 nm on the catgut.

Keywords: sorption activity, polyamide, silver nanoparticles, electron microscopy.

INTRODUCTION

The development of new methods for the preparation of silver nanoparticles (AgNPs) remains one of the promising areas of development in various fields of science. Nanoparticles are used, for example, for the manufacture of nanofibers based on polyvinyl alcohol, which have an advantage in optics over traditional films due to their higher sensitivity and better radiation characteristics, and therefore, can be used for the production of LEDs, sensor devices, and lasers [1]. In turn, hybrid nanomaterials based on AgNPs and graphene (AgNWs-AgNPs-GN) have optimal electrical properties to reduce the resistivity of electrically conductive adhesive substrates, which is important, among other things, to improve the efficiency of portable devices and medical equipment [2]. In addition, according to recent studies, nanocomposite films based on nanoparticles of silver, graphene, and polyvinyl alcohol have an increased dielectric permittivity, which suggests a significant efficiency of embedding such nanocomposites into charge-accumulating devices [3]. Silver nanoparticles are also used for doping the membrane materials in order to accelerate hydrogen permeability in the processes of obtaining high-purity hydrogen [4]. For example, it was shown in [5] that in combination with palladium, nanosilver made it possible to synthesize pentagonal star-shaped nanoparticles with unique catalytic properties.

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Silver nanoparticles are also widely used in medicine [6, 7] due to their antiviral and immunomodulating activity, including in the respiratory tissue pathology [8, 9]. The described effect is achieved both due to the fixation of AgNPs to the viral glycoproteins, thereby blocking the penetration of viral particles directly into the cell, and by activating neutrophils in the lung tissue. The antimicrobial activity and cytotoxicity of silver nanoparticles vary greatly depending on the physicochemical properties of the polymer used as their carrier [10, 11]. For example, data were obtained on the effectiveness of the complex use of silver nanoparticles in the processing of polyamide 6.6 fibers, which made it possible to increase the antibacterial activity of the obtained samples against some strains of *S. aureus* and *E. coli*. [12].

At the same time, in one of the studies it was shown that electromagnetic radiation of the deci- and nanometer ranges enhances the attachment of silver nanoparticles on the surface of ultra-thin polypropylene fibers, preventing AgNPs agglomeration and ensuring their stabilization on the surface due to the formation of supramolecular structures, which ultimately significantly increase the microbicidal activity of the film [13]. Moreover, when processing biodegradable suture material with silver nanoparticles, it not only retains the antibacterial activity of the latter, but also accelerates wound healing. This additionally demonstrates the relevance of studying the sorption activity of AgNPs on the surface of a number of polymer structures [12, 14], taking into account certain difficulties in controlling the course of the wound process when using certain types of dressings [15, 16].

The aim of this study is to study the interaction of AgNPs, containing polyvinylpyrrolidone as a ligand, with biodegradable polymers, including synthetic ones, based on polyamide 6.6, and those of natural origin, consisting mainly of collagen fibers.

EXPERIMENTAL PROCESS

In the course of the work, silver nanoparticles of the official reference drug Argogel were used, and *ex tempore* AgNPs were obtained for gel composition A based on gelatin [17]. The concentration of the drug Argogel in the experiment corresponded to the manufacturer's recommendations. The gel composition A was prepared on the basis of an aqueous solution of AgNPs obtained by the method of cavitation-diffusion photochemical reduction. This method involves the reduction of silver ions together with a ligand (polyvinylpyrrolidone). In this case, the condition for obtaining AgNPs with the necessary physicochemical properties was the use of the complex action of ultrasonic waves (radiation frequency of 1.7 MHz) and ultraviolet radiation (wavelengths 280–400 nm) with continuous stirring of the Ag-containing solution for 1 h. Thus, the aqueous solution was diluted with distilled water to an AgNPs concentration of 5 µg/ml, after which a gelatin solution was added with simultaneous heating to 60°C (final content 0.9% [7]).

To assess the results obtained, we used technical devices and equipment of the scientific and educational center "Center for collective use of diagnostics of the structures and properties of nanomaterials" of the Kuban State University (Krasnodar). The activity of the process of the nanoparticle sorption on the surface of biodegradable fibers (polyfilament synthetic material (caproag) consisting of polyamide 6.6 and absorbable suture material of natural collagen tissue (catgut)) was determined using electron microscopy in the COMPO mode. Electron microscopy studies of the fibers under study were carried out after 1 h and 1 day of incubation of a 1 cm segment for each material in a corresponding gel at a temperature of 25°C. When preparing all samples for examination by electron microscopy, they were lyophilized.

EXPERIMENTAL RESULTS

Using electron microscopy, it was found that after 1 h of exposure of both studied polymer materials in argogel, the micrographs show a certain ratio of different size ranges of AgNPs for each type of biodegradable fibers (Fig. 1). According to the data obtained, nanoparticles of the 1–10 nm and 25–40 nm size ranges predominated in the micrographs of the collagen fibers (Fig. 1a), while on the artificial fibers consisting of polyamide, the predominance of nanoparticles with sizes of 25–40 nm and AgNPs larger than 40 nm was revealed (Fig. 1b). Taking into account that the micrographs in general represented all the size ranges of nanoparticles, it can be concluded that the sorption of AgNPs

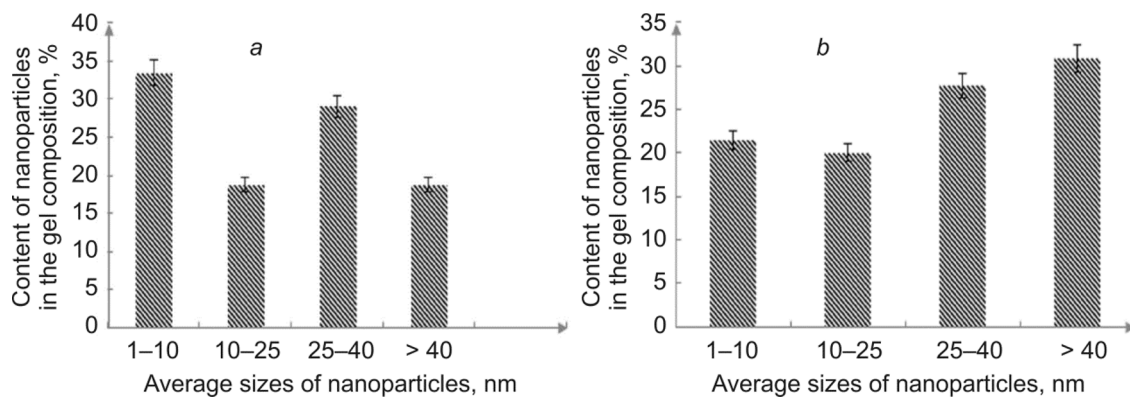


Fig. 1. Size distribution of silver nanoparticles obtained by analyzing the electron micrograph after exposure of catgut fibers (a) and caproag (b) in argogel for 1 h.

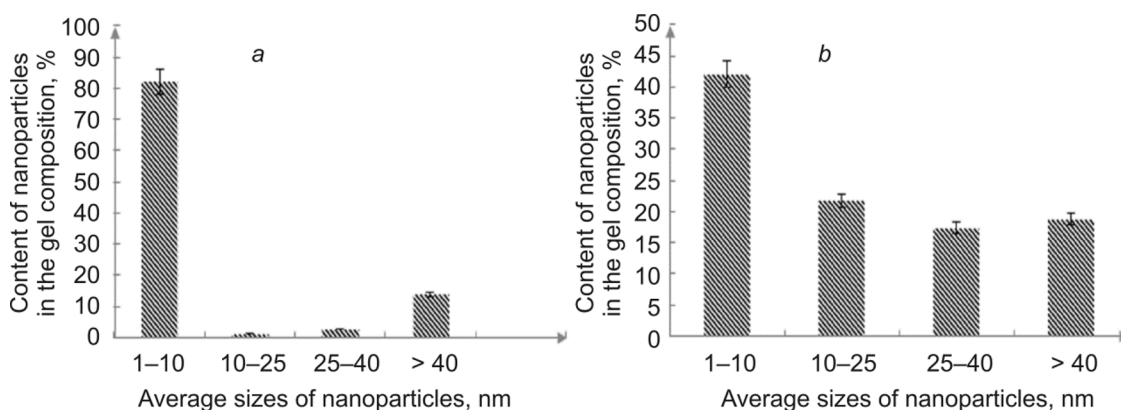


Fig. 2. Size distribution of silver nanoparticles obtained by analyzing the electron micrograph after exposure of the fibers of catgut (a) and caproag (b) in argogel for 1 day.

from the drug argogel is relatively uniform during the first hour. To a greater extent, this is characteristic of the synthetic fiber caproag.

A day later, a significant change was noted in the ratio of different sizes of AgNPs in the micrographs. For example, AgNPs of the size range 1–10 nm still prevailed on the surface of catgut, while the amount of AgNPs in other investigated size ranges significantly decreased (Fig. 2), which indicates a pronounced desorption of nanoparticles larger than 10 nm. In this case, the least pronounced desorption was observed for nanoparticles larger than 40 nm. Their amount decreased from 18.8 to only 13.7% ($p < 0.05$). On the surface of biodegradable artificial fibers, after 24 h of exposure, the predominance of the size range of 1–10 nm was also noted (Fig. 2b). However, the decrease in the absolute amount of AgNPs in other size ranges was not so pronounced.

When evaluating the results of electron microscopy obtained in the study of artificial fibers (caproag) exposed in gel composition A containing AgNPs for 1 h, the predominance of nanoparticles of size ranges 1–10 nm and 25–40 nm was determined (Fig. 3). The observed distribution has similar tendencies to the results obtained after exposure of natural catgut fibers in argogel, but it should be noted that the amount of AgNPs larger than 40 nm in size is significantly lower (Fig. 3b).

Under exposure of catgut in the studied gel composition A for 1 h, only large agglomerates of silver nanoparticles with sizes of more than 40 nm were observed (Fig. 4), which is clearly seen even with a magnification of 10000 times (Fig. 4).

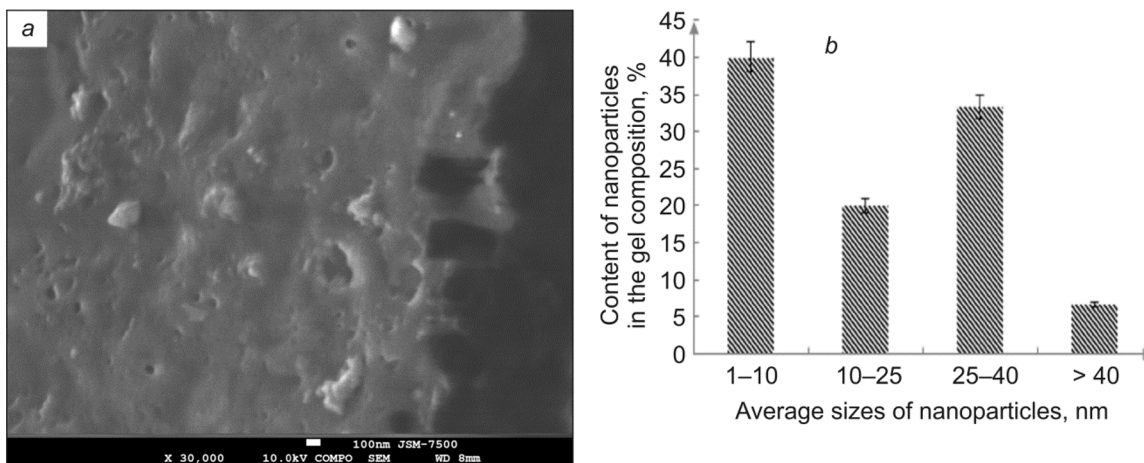


Fig. 3. Electron micrograph: caproag fibers exposed to gel composition A for 1 h (a) and size distribution of silver nanoparticles obtained from the image analysis (b), COMPO mode, magnification 30000 times.

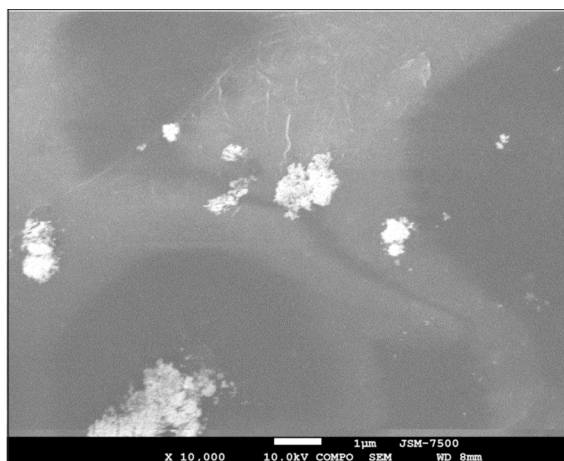


Fig. 4. Electron micrograph: catgut fibers exposed to gel composition A for 1 hour, COMPO mode, magnification 10000 times.

After 1 day of incubation in gel composition A, we determined the following distribution of nanoparticles on the biodegradable polymers of artificial and natural origin (Fig. 5). AgNPs of a size range of 1–10 nm predominated in micrographs of catgut fibers, and nanoparticles with sizes of 10–40 nm appeared (Fig.5a). The amount of nanoparticles from the previously prevailing range (above 40 nm) increased by more than 4 times ($p < 0.05$). Such dynamics of the amount of silver nanoparticles may indicate a significant activity of the AgNPs sorption process from the gel composition A during 24 h of incubation.

The micrographs of caproag fibers also showed an increase in the amount of AgNPs larger than 40 nm, while the amount of nanoparticles of other size ranges decreased (Fig.5b). This may indicate a pronounced process of desorption and possible agglomeration of previously sorbed AgNPs during the first exposure day of the artificial biodegradable polymer (Fig. 6).

Thus, the results obtained indicate a different affinity of silver nanoparticles containing polyvinylpyrrolidone as a ligand to biodegradable polymers of synthetic (based on polyamide 6.6) and natural (consisting of collagen) origin. This is manifested in the unequal rate of sorption of AgNPs of certain size ranges in the first hour of incubation, as well

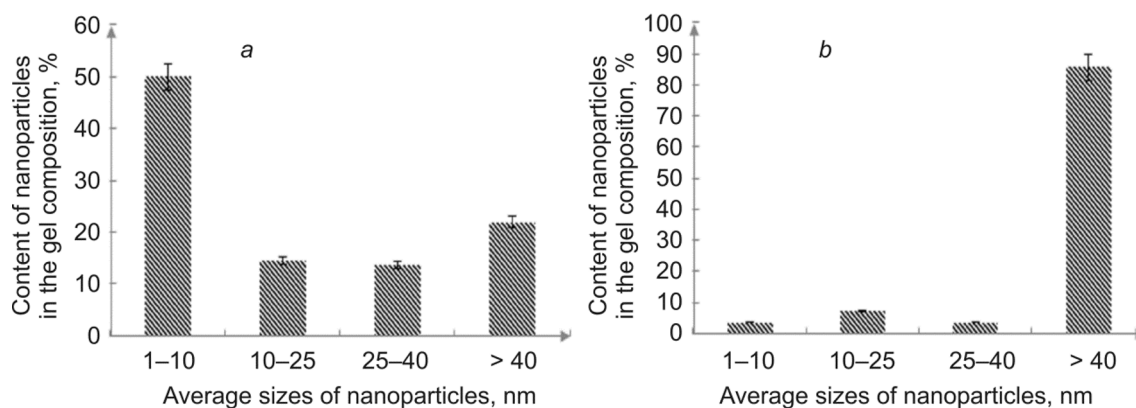


Fig. 5. Size distribution of silver nanoparticles obtained by analyzing the electron micrograph under exposure of catgut (a) and caproag (b) to gel composition A for a day.

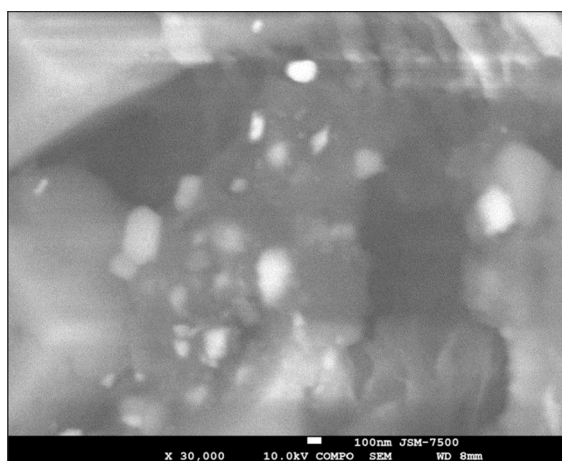


Fig. 6. Electron micrograph: caproag fibers when exposed to gel composition A for a day, COMPO mode, magnification 10,000 times.

as their differently pronounced desorption and agglomeration during the first day of exposure of these materials in both gel compositions.

CONCLUSIONS

This study has demonstrated the ability of biodegradable fibers of natural origin to more actively adsorb (by a factor of 3.3, $p < 0.05$) for 1 h the silver nanoparticles of a small (from 1 to 10 nm) size range and stronger hold these AgNPs (by 4.5%, $p < 0.05$) during the first day when exposed to argogel in comparison with artificial biodegradable polymers.

In turn, during the incubation of the same materials in a gel composition containing Ag nanoparticles obtained by the method of cavitation-diffusion photochemical reduction, in the first hour, a higher sorption activity of the latter's (in the size range from 1 to 10 nm) to a polyfilament synthetic material was revealed in comparison with catgut. After 24 h of exposure, there was a significant increase in the fraction of AgNPs (up to 50%, $p < 0.05$) on the collagen fibers, which exceeded the analogous characteristics of caproag by 46.4% ($p < 0.05$). At the same time, after 24 h, the relative

amount of nanoparticles larger than 40 nm in size increased mainly on the surface of the artificial biodegradable fiber, exceeding the similar characteristics of the content of large AgNPs on catgut by more than 19 times ($p < 0.05$).

Thus, the data obtained indicate a greater interaction of silver nanoparticles of various origins with the functionalized surface of the collagen fiber, which can be due to the increased affinity of AgNPs to carboxyl, hydroxyl, carbonyl, and primary amino groups, as well as nitrogen-containing heterocyclic side radicals of amino acids included in the polypeptide collagen chains. Such interactions between them significantly slow down the desorption process and, apparently, the agglomeration of small AgNPs, which makes it possible to obtain nanoparticles of the most acceptable size range (up to 10 nm) to achieve the expected microbicidal effect [18, 19]. At the same time, the use of synthetic polymers based on polyamide 6.6 to create functionalized antimicrobial materials is advisable only with a short (up to 1 h) exposure of them in a gel composition (containing AgNPs obtained by the method of cavitation-diffusion photochemical reduction), since under these conditions, the use of biodegradable fibers of natural origin seems to be less effective due to the presence of agglomerates exclusively larger than 40 nm on their surface.

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