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CYCLIC FREEZING EFFECT ON SILVER NANOPARTICLE ADSORPTION ON POLISHED COLLAGEN FIBER

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The paper studies the sorption activity of silver nanoparticles (AgNPs) on polished collagen fibers after 10 freezing–thawing cycles at alternating temperature of 0.0 to –37.0°C. The sorption activity is studied for the chitosan-containing Argogel and polyvinylpyrrolidone-stabilized silver nanoparticles obtained by cavitation-diffusion photochemical reduction. After incubation of polished catgut fibers in the chitosan-containing Argogel followed by the freezing–thawing treatment, silver-containing nanostructures are found on the catgut fibers. This is probably explained by the interaction between nanoparticles and protein matrix of the suture material.

Keywords: catgut, cyclic freezing, collagen fiber, silver nanoparticles polished

INTRODUCTION

Collagen fibers as a dissolvable suture of natural origin, is widely used today in medicine, including featural surgery, dentistry, gynecology [1−4]. Catgut is produced from submucous tissue of bovine animals and represents the collagen fiber, which can also be used in fabrication of wound coverings, dressings, dermal grafts [5]. This can be provided by not only pharmacological modification of a common catgut material for creating an effective fixation of pharmaceuticals followed by the retarded release of noncovalent pharmaceuticals in the traumatic area, but also by different-quality collagen fibers due to their different surface treatment [6, 7].

As is known, the production process of modified catgut may include the additional polishing stage, which decreases the scraping effect *via* its surface roughness reduction, thereby making the suture passage through tissues less traumatic. Such a treatment improves the nanoparticle sorption activity when deposited onto a polished surface, that is demonstrated by Gallo *et al*. [8] with titanium compounds. In this case, the antibacterial activity of polished implants increases in relation to Staphylococcus epidermidis and Escherichia coli. Moreover, in depositing of about 1% of silver nanoparticles (AgNPs) onto the polished surface of a silicon substrate, the properties of the latter can significantly change [9] indicating to the high effectiveness of these nanoparticles in modifying various materials [10, 11]. One of the additional factors significantly affecting the AgNP adsorption on the surface of various materials, is a low temperature [12, 13].

The purpose of this work is to study the silver nanoparticle adsorption on the surface of suture materials comprising collagen fibers during freezing–thawing cycles.

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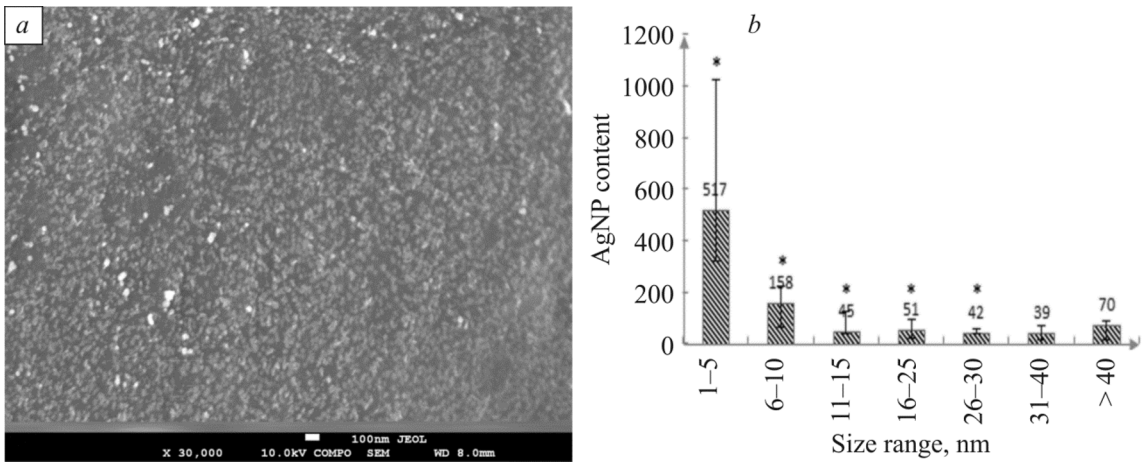

Fig. 1. SEM image of polished Catgut surface treated with gel composition after 10 freezing–thawing cycles. Magnification: 30,000× (*a*); respective AgNP size distribution (*b*). The sign * indicates $p < 0.05$ compared to the same size range in using the Argogel.

EXPERIMENTAL

The cavitation-diffusion photochemical reduction method was used to obtain silver nanoparticles, in which ultrasonic (1.7 MHz) and ultraviolet (280 nm) radiations were combined and applied for 60 min at a continuous mixing with a ligand based on polyvinylpyrrolidone (PVP) [14]. The highest effect from the AgNP treatment of the suture material, the gel composition was prepared by the AgNP solution reduction to 5 μg/mL followed by a 60°C thermostat control and gelatin addition to obtain the gel composition with a 0.9% concentration [15, 16]. Also, the Argogel containing chitosan and PVP-stabilized silver nanoparticles was used to compare the AgNP sorption activity with that recommended by the manufacturer.

The AgNP sorption activity was investigated on the collagen fiber-based polished Catgut (Volot, Russia) of 2.0 metric size. The collagen fiber of 1 cm length was immersed in the gel composition with silver nanoparticles. After 24 hours, the collagen fiber was extracted and subjected to 10 cycles of freezing and thawing in the temperature range of 0.0 to −37.0°C, both for 24 hours. The temperature processing was conducted in a Haier DW-86L288 Ultra Low Temperature Storage Freezer (Haier Medical and Laboratory products Co., Ltd., China).

A field emission scanning electron microscope JSM-7500F (JEOL, Japan) was used to investigate AgNP sorption/desorption/aggregation activities at 10 kV accelerating voltage, 30,000× magnification, in the back-scattered-electron collection mode. The scanning electron microscopy (SEM) observations were conducted at the Core Facility Center of Diagnostics of Nanomaterial Structure and Properties of Kuban State Medical University, Krasnodar, Russia [17]. The obtained data were processed using variation statistics methods. The confidence estimation of the AgNP activity was performed by using the Mann-Whitney *U* test for paired comparison and Kruskal–Wallis H test for comparing two or more independent samples of equal or different sample sizes. The experimental data were expressed as median and percentiles (25th–75th); the level of statistical significance was <0.05.

RESULTS AND DISCUSSION

The SEM image in Fig. 1 shows the Catgut surface treated by the gel composition containing AgNPs synthesized by cavitation-diffusion photochemical reduction. The AgNP size ranges mostly from 1 to 5 nm ($p = 0.0005$). The content of 6 to 10 nm silver nanoparticles decreases by 69.6%, while medians of other size ranges are

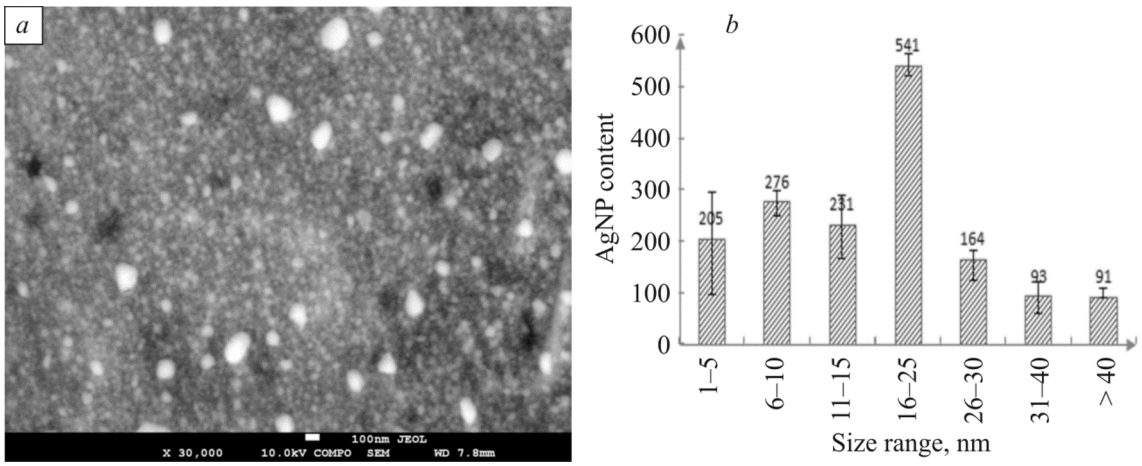

Fig. 2. SEM image of polished Catgut surface treated with the Argogel after 10 freezing–thawing cycles. Magnification: 30,000× (*a*); respective AgNP size distribution (*b*).

characterized by more pronounced differences quantitatively lower than 1 to 5 nm range, i.e., they are minimum 86.5% lower for the size range higher than 40 nm and maximum 92.6% lower for the size range of 31 to 40 nm.

SEM observations of polished Catgut treated with the Argogel, show a 1.74 times increase in silver nanoparticles (see Fig. 2, $p < 0.05$), although their size distribution significantly differs within the indicated ranges. AgNPs with the average size of 16 to 25 nm ($p < 0.00047$) demonstrate the highest content, while the content of AgNPs of the finer size is considerably lower, namely by 62.1% in the size range of 1 to 5 nm; by 48.9% in the size range of 6 to 10 nm, and by 57.4% in the size range of 11 to 15 nm (Fig. 2). The AgNP content lowers by 69.6–83.2% ($p < 0.00047$) with increasing size range up to 25 nm and larger.

It should be noted that quantitative differences between AgNPs adsorbed on the polished Catgut surface treated with the proposed gel composition and the Argogel, are consistent with the size range of 1 to 30 nm. Thus, after the treatment with the proposed gel composition, 1 to 15 nm nanoparticle concentration is 152.3% ($p < 0.0249$) higher than after the incubation of the polished Catgut in the Argogel (see Figs 1 and 2). On the other hand, 6 to 10 nm, 11 to 15 nm, 16 to 25 nm and 26 to 30 nm nanoparticle concentration is higher already after the polished Catgut treatment with the Argogel, namely by 75.2% ($p = 0.0151$), by 414.5% ($p < 0.004$), by 959.8% ($p = 0.0039$), and by 291.2% ($p < 0.01$), respectively. The analysis of 30 to 40 nm ($p = 0.0649$) and >40 nm ($p > 0.17$) size ranges, shows no difference in the content of adsorbed AgNPs, depending on the treatment with the gel composition.

Moreover, the SEM image in Fig. 3 demonstrates the formation of the nanoparticle agglomeration on the polished Catgut surface, which reminds the linear AgNP aggregation discovered in our early research [18] during the nanoparticle adsorption on the Dexon suture surface.

The AgNP agglomeration was observed on the polished Catgut surface treated with the proposed gel composition containing AgNPs synthesized by the cavitation-diffusion photochemical reduction method. That was probably associated with the formation of 1) linear nanocomposites enabled by the accelerated oxidation-reduction reaction involving silver ions in the Ag^+–AgNPs system and induced by the freezing–thawing treatment [19] and 2) structures similar to the silver nanofilm forming due to the similar chemical reaction, but having different composition and properties (higher adsorption, surface roughness, current-voltage characteristics) acquired by the material surface after its modification [13].

CONCLUSIONS

The experimental data showed that the additional mechanical treatment of the collagen fiber facilitated the adsorption of more active 1 to 5 nm nanoparticles on the Catgut surface (see Fig. 1). The identified content of

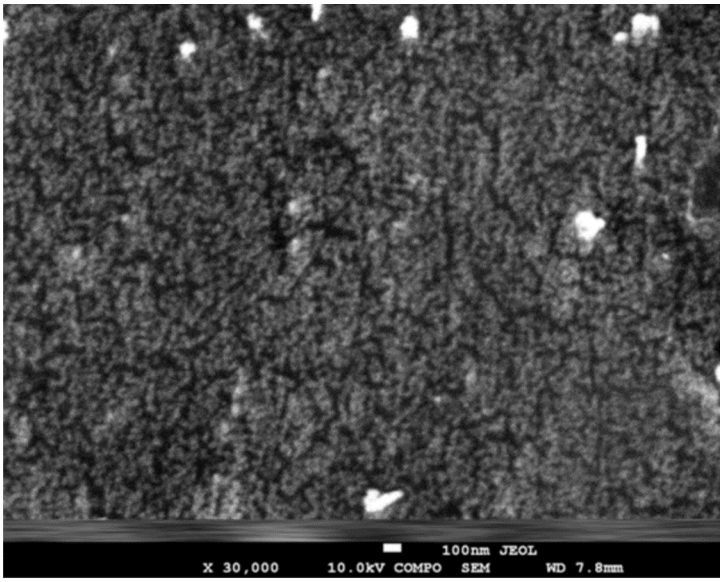

Fig. 3. SEM image of polished Catgut surface treated with the gel composition after 10 freezing–thawing cycles. Magnification: 30,000×.

comparatively fine nanoparticles adsorbed on the Catgut surface could be attributed to their formation after the redox reaction between silver ions and catechin fragments of polymer which was a gelatin derivative [20]. It was shown that 20 nm AgNPs manifested a significant antimicrobial effect in relation to both gram-negative and gram-positive bacteria. AgNPs were actively caught by the hydrocarbon gel matrix with their successive retarded release from this matrix (8.7% during 14 days), that reduced their cytotoxicity and demonstrated the higher AgNP biocompatibility in combination with *in situ* antibacterial activity [20]. Moreover, the redox reaction was probably accelerated by the additional freezing–thawing treatment up to −37.0°C of the Catgut surface with adsorbed AgNPs, that probably caused the formation of linear nanostructures presented in Fig. 3.

The AgNP adsorption and agglomeration on the polished Catgut surface, can be used to give it antiseptic properties, including bacterial and virus infection agents [21]. The development of wound coverings based on polished collagen fibers treated with the gel composition containing AgNPs synthesized by cavitation-diffusion photochemical reduction, is rather promising because the domination of 5 nm nanoparticles (56.2% of the total amount of adsorbed AgNPs), can induce the fracture of even mature biofilms formed on the surface of infected wounds, especially during the retarded release of nanoparticles from gelatin-based composition [22], and also the creation of additional conditions for the *in situ* decrease in the AgNP cytotoxicity [20].

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