

APPROACHES FOR SUBSTRATE FUNCTIONALISATION WITH SILVER NANOPARTICLES

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СПОСОБЫ ФУНКЦИОНАЛИЗАЦИИ ТИТАНОВЫХ ИМПЛАНТАТОВ НАНОЧАСТИЦАМИ СЕРЕБРА

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***Аннотация.** Работа посвящена поиску оптимального метода функционализации металлических титановых подложек наночастицами серебра для формирования антибактериального интерфейса на поверхности экспериментальных образцов.*

Introduction. Pure titanium is commonly used as implants in both dental and orthopedic clinics because of its biocompatibility and mechanical properties [1]. It is commonly known that an implant may be rejected by the human body. Moreover, a wide range of local tissue reactions, in particular inflammation, giant cell formation and fibrosis can be induced. A promising solution to this problem is fabrication of an antibacterial bioactive coating on the implant surface, which allows one to avoid rejection and speed up the treatment and recovery process [2]. A good way to overcome this challenge is functionalization of implant surface with silver nanoparticles (AgNPs) as antibacterial agent. The remarkable mechanism of the antimicrobial activity of AgNPs is connected with the formation of free radicals and consequent free-radical-induced oxidative damage of the cell membranes of bacteria [3, 4]. The purpose of these bioactive surfaces is to disrupt the metabolic machinery of the microbes or to prevent bacterial adhesion to the implant and, consequently, the development of biofilm [5]. Among the existing methods, the chemical methods have been mostly used for production of AgNPs. Chemical methods provide an easy way to synthesize AgNPs in solution [6, 7]. The most recently available methods for the fabrication of antibacterial films include electron beam lithography and nanoimprint lithography, both can completely control the micromorphology of the nanostructures for the design with unique localized surface plasmon resonance spectrum [8]. However, these methods require sophisticated fabrication equipment and are limited by either expensive cost or small sample size in practical applications. Instead, some simpler bottom-up approaches based on self-assembly, e.g., Langmuir-Blodgett, dip coating, and electrochemical deposition, have shown great convenience in large-scale fabrication [9]. Such techniques allow producing noble metal nanoparticle thin films with large areas.

Experimental part. The paper considers a series of rapid and simple methods of silver coatings fabrication, such as dip coating, sessile droplet and room temperature electrophoretic deposition (EPD).

According to [10] the AgNPs were synthesized in aqueous solutions: PVP-stabilized NPs with a diameter of the metallic core of 70 ± 20 nm, and negative charge of -15 mV.

The deposition of PVP stabilized AgNPs on titanium substrates was carried out using three approaches:

- *Drop drying or sessile droplet* - the process which is based on the formation of a droplet 120 μL of the working solution with concentration $60 \mu\text{g mL}^{-1}$ in water and following drying at 55.5°C .
- *Dip-coating* - the sample was dipped into 5 mL of the working solution with the same concentration and kept for 24 hours with the subsequent drying at 55.5°C .
- *Electrophoretic deposition* - the deposition was achieved by the motion of charged PVP-coated AgNPs particles dispersed in working solution towards an electrode under the applied electric field.

Prior to electrophoretic deposition, two types of working solutions were prepared. The first solution was prepared with distilled water and the second one was based on absolute ethanol with the concentration of $60 \mu\text{g mL}^{-1}$. Electrophoretic motion of the charged particles during EPD results in the accumulation of particles and the formation of a homogeneous and rigid deposit at the relevant (deposition) electrode-titanium sample. Figure 1 shows the results of titanium substrate functionalized with AgNPs.

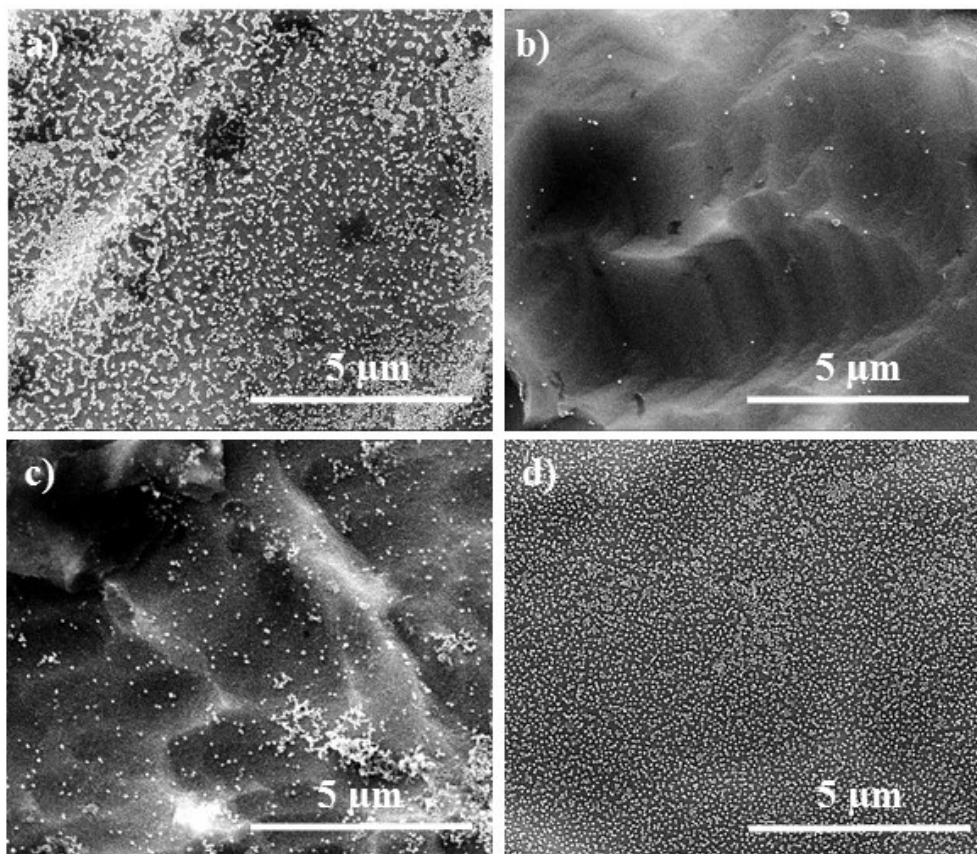


Fig. 1. Titanium substrates functionalized with PVP-stabilized AgNPs a) sessile droplet 120 μL , b) dip-coating, c) EPD in water (3 V, 60 min), d) EPD in ethanol (50 V, 30 min). The concentration of the working solution was $60 \mu\text{g mL}^{-1}$ in each experiment.

Results. Figure 1 shows that the most effective approaches for surface functionalization are sessile droplet and EPD. The SEM analysis confirmed the ability to attain a uniform distribution of AgNPs in case of

EPD approach. Sessile droplet method has the disadvantage associated with the surface tension and consequently the samples are not fully coated with AgNPs. The sessile droplet method has the disadvantage associated with the deposition process on special design implants.

Conclusion. Functionalization of titanium substrates with AgNPs was carried out using sessile droplet, dip-coating and EPD approaches. According to the SEM results the most effective methods for surface functionalization was EPD. The PVP-stabilized AgNPs with a diameter of the metallic core of 70 ± 20 nm, negative charge of -15 mV were synthesized in aqueous solution indicating monodisperse system and absence of large agglomerates.

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REFERENCES

1. Hanawa T. (2010) Biofunctionalization of titanium for dental implant. Japanese Dental Science Review, vol. 46, no. 2, pp. 93–101.
2. Farooq I., Irman Z., Farooq U., Leghari A., & Ali U. (2012) Bioactive Glass: A Materials for the Future. World Journal of dentistry. no. 3, pp. 199–201.
3. Gupta K., Singh R. P., & Pandey A. (2013) Photocatalytic antibacterial performance of TiO₂ and Ag-doped TiO₂ against *S. aureus*, *P. aeruginosa* and *E. coli*. Beilstein Journal of Nanotechnology, no 4, pp. 345–351.
4. Hwang E. T., Lee J. H., Chae Y. J., Kim Y. S., Kim B. C., Sang B. I., & Gu M. B. (2008) Analysis of the toxic mode of action of silver nanoparticles using stress-specific bioluminescent bacteria. Small, no. 4, pp. 746–750.
5. Ketonis C., Parvizi J., & Jones L. C. (2012) Evolving Strategies To Prevent Implant-associated Infections. JAAOS, no. 20, pp. 478–80.
6. Chen S., & Zhang H., (2012) Aggregation kinetics of nanosilver in different water conditions. Adv. Nat. Sci.: Nanosci. Nanotechnol, no. 3, p. 035006.
7. Dang T. M. D., Le T. T. T., Fribourg-Blanc E., & Dang M. C. (2012) Influence of surfactant on the preparation of silver nanoparticles by polyol method. Adv. Nat. Sci.: Nanosci. Nanotechnol, no. 3 p. 035004.
8. Berkovitch N., Ginzburg P., & Orenstein M. (2010) Concave plasmonic particles: broad-band geometrical tunability in the near-infrared. Nano Lett, no. 10, pp. 1405–1408.
9. Zhang X. Y., Hu A., Zhang T., Lei W., Xue X. J., Zhou Y., & Duley W. W. (2011) Self-assembly of large-scale and ultrathin silver nanoplate films with tunable plasmon resonance properties. ACS Nano, no. 5, pp. 9082–9092.
10. Sharonova A., Loza K., Surmeneva M., Surmenev R., Prymak O., & Epple M. (2016) Synthesis of positively and negatively charged silver nanoparticles and their deposition on the surface of titanium. IOP Conference Series: Materials Science and Engineering, no. 116, p. 012009.