

ELECTRICAL EXPLOSION OF WIRES FOR MANUFACTURING BIMETALLIC ANTIBACTERIAL Ti–Ag AND Fe–Ag NANOPARTICLES

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*Using a simultaneous electrical explosion of two twisted wires, bimetallic Ti–Ag and Fe–Ag nanoparticles are synthesized, where the component ratios are 76–24 and 75–25, respectively. The resulting nanoparticles are characterized by the methods of X-ray diffraction analysis, transmission electron microscopy, thermal desorption of nitrogen, and microelectrophoresis. It is found out that the synthesized nanoparticles are mainly structured as Janus-nanoparticles, and in nanopowders they form weakly-bonded aggregates and hard agglomerates, where the particles are connected by silver ‘necks’. The negative charge of the particles and their ability towards degassing under ultrasonic action make it possible for the Ti–Ag and Fe–Ag to be used as effective antimicrobial modifiers of water-soluble polymers forming stable gel-like compositions. These compositions possess significant antimicrobial activity against methicillin-resistant *Staphylococcus aureus* (MRSA) bacteria, which exceeds that of similar compositions containing silver nanoparticles only.*

Keywords: electrical explosion of wires, nanoparticles, titanium, iron, silver, bimetallic nanoparticles.

INTRODUCTION

Bimetallic nanoparticles (BNs) are at present extensively investigated due to their application in promising antimicrobial materials [1]. Among the candidate nanoparticles, silver nanoparticles exhibit proven activity against a wide range of microorganisms, including gram-positive and gram-negative bacteria, viruses and fungi [2]. The use of silver-containing BNs instead of silver nanoparticles in aseptic ointments and gels allows reducing the content of silver in them and, hence, the cost and ineffective loss of the precious metal. Furthermore, the presence of biologically active metals in BNs diminishes the expressed cyto- and genotoxicity of silver [3]. In particular, Ag/Ni nanoparticles are more effective in suppressing the growth of *E. coli*, *S. pyogenes* and *C. albicans* [4] compared to the silver nanoparticles. Polyvinylpyrrolidone-stabilized colloid solutions for impregnation of Ag–Cu BN-based fibers, synthesized by the authors of [5], demonstrated an increased antibacterial activity against *C. albicans*, *E. coli* and *S. aureus*. Titanium and iron offer an optimal option for the second component of a bimetallic particle. A synergetic antibacterial effect was demonstrated by the titanium-based binary systems containing Ag, Cu, and Au [6]. Silver-containing titanium implants were resistant to bio-growth [7]. The Fe–Ag nanoparticles used in [8] inactivated a wide range of bacteria and fungi. The Fe–Ag BNs synthesized by green engineering exhibited a significant antibacterial and antioxidative activity [9]. It is possible to synthesize bimetallic Ti–Ag and Fe–Ag nanoparticles by the method of a simultaneous electrical explosion of titanium/iron and silver wires (EEW) in an inert atmosphere. By varying the EEW conditions one can fairly precisely regulate the rate of expansion of the explosion products, the degree of overheating of the dispersed

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TABLE 1. Electrophysical Parameters of Bimetallic Nanoparticle Synthesis

Specimen	Wire	Wire length, mm	d , mm	C , μF	w , wt.%	U_0 , kV	Gas pressure $\cdot 10^{-5}$, Pa
Ti76–Ag24	Ti	60	0.35	1.6	76	29	3.0 (Ar)
	Ag		0.15		24		
Fe75–Ag25	Fe	60	0.30	2.4	75	29	3.0 (Ar)
	Ag		0.20		25		

metals, the ratio of the metallic components, and to manufacture nanoparticles of the required structure and phase compositions [10].

The purpose of this work is to select the parameters of electroexplosive dispersion of titanium and silver and titanium and iron metallic wires aimed at producing bimetallic Ti–Ag and Fe–Ag nanoparticles and use them as modifiers in manufacturing antibacterial preparations.

EXPERIMENTAL PROCEDURE

Synthesis of bimetallic Ti–Ag and Fe–Ag nanoparticles

The Ti–Ag and Fe–Ag BNs were produced by an electrical explosion of a twisted pair of wires in an argon atmosphere. The wires were purchased from the producer-factories; the label amount of metal in them was no less than 99.9 wt.%. Before use, the surface contaminants were removed using an organic solvent. The Ti (Fe) and Ag metals belong to different electrophysical groups: Ti and Fe – high-boiling-point and high-heat-content metals at the melting point, while Ag has a low boiling point and heat content under melting. Therefore an explosion of the twisted wires occurs in a non-synchronous fashion. For this reason, in order to manufacture bimetallic particles with a prescribed component ratio in a particle some optimal electrophysical parameters were selected, such as the energy storage capacity (C), the energy storage charge voltage (U_0), the buffer gas pressure, and the wire diameter and length. The electrophysical parameters were to ensure a regime of wire dispersion close the critical mode, to which the maximum energy, deposited into the wire by the point of explosion, corresponds. The parameters of electroexplosive dispersion are presented in Table 1.

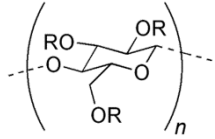
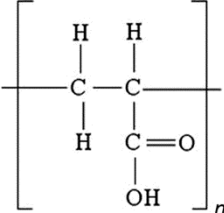
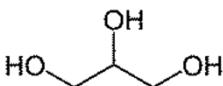
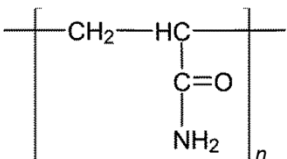
Synthesis of Ti–Ag–PM and Fe–Ag–PM composites

Nanopowders, before their introduction into a polymer matrix (PM), were deagglomerated in the reverse osmotic water at the temperature 25°C at atmospheric pressure using a Hilscher UP-100M ultrasonic immersion disperser at the frequency 30 kHz up to the formation of a stable suspension, varying the time (t) of treatment.

Polymer matrices have been chosen due to a possibility of designing soft medicinal preparations on their basis in the form of gels modified by nanoparticles. The method of preparing Ti–Ag–PM and Fe–Ag–PM composites involved the formation of a single-phase hydrophilic system with a good sorptive capacity on the wound surfaces, with the bimetallic nanoparticles uniformly distributed in it. The hydrophilic base was a 1 wt.% aqueous solution of polymers characterized by low toxicity and hypoallergenicity, which favored a slow release of the antimicrobial component, did not inhibit the skin gas exchange, and did not disturb the activity of endocrine glands. After selecting the deagglomeration parameters, the suspensions of nanoparticles were introduced into the water solutions of the respective polymers under the condition of continuous stirring. The principal characteristics of the matrices used in the synthesis of antimicrobial gels and ointments are given in Table 2.

The experimental compositions were prepared by mechanical stirring of a suspension of nanopowders and a water solution of a polymer or a ointment base (in the case of vaseline.). The resulting compositions in the form of gels and ointments demonstrated good skin application and even distribution. The gelled texture favored a uniform distribution of bimetallic nanoparticles in the bulk of the base and prevented their aggregation.

TABLE 2. Principal Characteristics of Bases for Synthesis of Antimicrobial Gels and Ointments

Matrix	Building block	Application in biomedicine
Polyvinyl alcohol	$\text{H}_2\text{C}=\underset{\text{OH}}{\text{CH}} \rightleftharpoons \text{CH}_3-\underset{\text{H}}{\text{C}}=\overset{\text{O}}{\text{H}}$	Used in medicine as components of medicinal preparations, embolization agents, and blood plasma substitutes
Carboxymethyl cellulose	 <p>R = H or CH₂CO₂H</p>	Present in encapsulating and tablet-forming agents. Adheres proper consistency and preserves shape for a long time
Carbopol		Used as a base for gels, regulates viscosity in creams and gels, and stabilizes emulsions
Glycerol		Widely used in medicine as components of medicinal drugs
Polyacrylimide		Applied in plastic surgery as a gel-forming agent, in contact lens production, and in molecular biology
Vaseline	Consists of a mineral oil and hard wax mixture	Popular in curing traumas, burns, and fissures

Characterization of nanoparticles

The morphology and dimensions of nanoparticles and their agglomerates were determined by the methods of transmission electron microscopy (JEOL-2000FX, JEOL Ltd., Japan) and sedimentation (CPS 24000, USA). In order to determine the average particle size from the TEM data, particle size distribution patterns were constructed using no less than 300 particles for each histogram. The phase composition was determined by the method of X-ray diffraction using CoK_α-emission (Dron-7 diffractometer, Russia). The phases were identified using a PDF-2 Release 2014 database. The zeta-potential was determined by the method of microelectrophoresis (ZetaSizer, Great Britain).

Antimicrobial activity of Ti–Ag–PM and Fe–Ag–PM composites

In this study, an ATSS 43300 bacterial strain of methicillin-resistant *Staphylococcus aureus* (MRSA) (BioVitrum, Russia) was used. The antimicrobial activity was determined by a standard procedure of serial microdilutions [11]. This method is common in determining the minimal concentration of nanoparticles inhibiting the

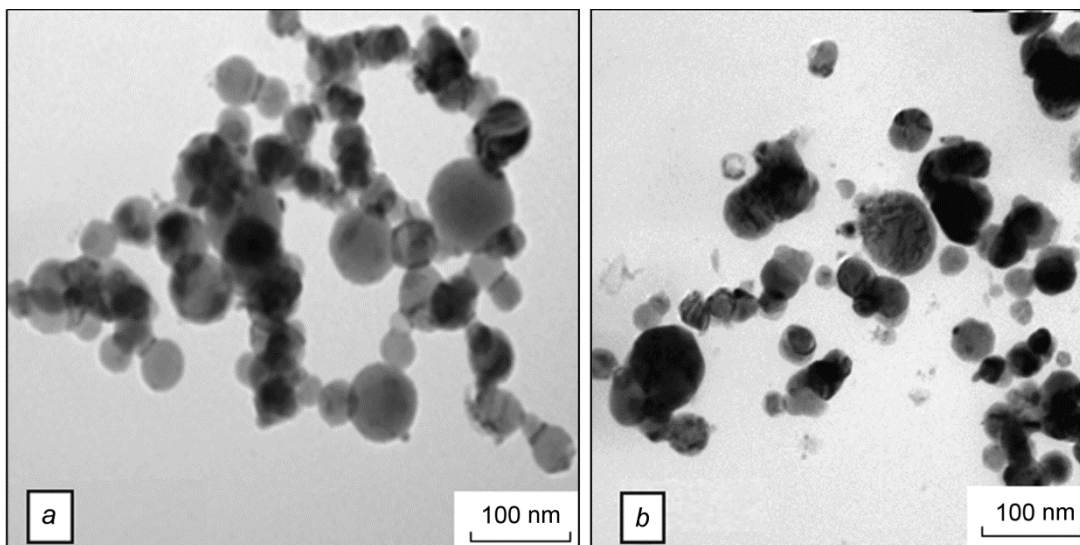


Fig. 1. TEM-image of Ti–Ag (a) and Fe–Ag (b) bimetallic nanoparticles.

microbial proliferation. For this purpose, 20 μl of the synthesized gels in a concentration of 10 mg/ml were introduced into a 96-well plate, and 150 μl of Mueller-Hinton broth (NICF, SPb, Russia) and 30 μl of the bacteria; suspension were added into each well in a concentration of 10^6 cfu/ml. At least five parallel test specimens (wells) were prepared. The microbial growth was evaluated after 2, 4, 6, 8, 10 and 12 h of culture incubation at 37°C using a Multiskan FC thermo-scientific microplate spectrophotometer (Thermo Fisher Scientific, USA). No less than five parallel measurements were performed for every concentration of nanoparticles. The wells containing only 10 mg/ml of water solution of the respective polymer were used as reference; the polymer contained silver nanoparticles synthesized exclusively by EEW. In order to rule out the influence of light absorption by nanoparticles, the optical density value was derived from the difference between the specimen absorption values before and after incubation.

RESULTS AND DISCUSSION

Figures 1 and 2 present characteristic TEM images and element distributions in the mode of mapping of bimetallic Ti–Ag and Fe–Ag nanoparticles. The ratio of metals in the nanoparticles is comparable with that in the dispersed wires. According to the energy dispersive analysis of the Ti–Ag specimen, the components are unevenly distributed over the volume of the particles, forming areas enriched in one of the components. It should be noted that silver islands are formed on the particle surface without forming a continuous coat (Fig. 1a).

An examination of the Fe–Ag particles (Fig. 1b) reveals that silver and iron are not evenly distributed over the particles. There are areas enriched in one of the components with distinct phase boundaries. The formation of such nanoparticles was observed in the cases of an Ag/Cu system under laser deposition in ultrahigh vacuum [12] or Cu/Pb nanoparticles, as shown in an earlier study [13]. According to the data on statistical processing of the TEM-images, the size distribution of bimetallic nanoparticles is lognormal for all specimens. The average sizes of the Ti–Ag and Fe–Ag particles are about 70 and 70–90 nm, respectively. The diffraction patterns contain a number of reflections corresponding to the phases of Ti and Ag or Fe and Ag metals. There are phases corresponding to solid solutions or intermetallics. The peak intensity ratio in the diffraction patterns is quite consistent with the metal ratio in the specimens. All of the experimental Ti–Ag and Fe–Ag specimens possess negative zeta potentials (-19.5 ± 0.6) mV and (-18.3 ± 0.7) mV, respectively.

In order to synthesize stable suspensions of nanoparticles and to introduce them into a polymer matrix, the water suspensions of nanoparticles were deagglomerated using ultrasonic (US) irradiation. The time of irradiation was up to 5 minutes at the power 50 W. Under these conditions, the nanopowder suspension did not set for 180 s, which was

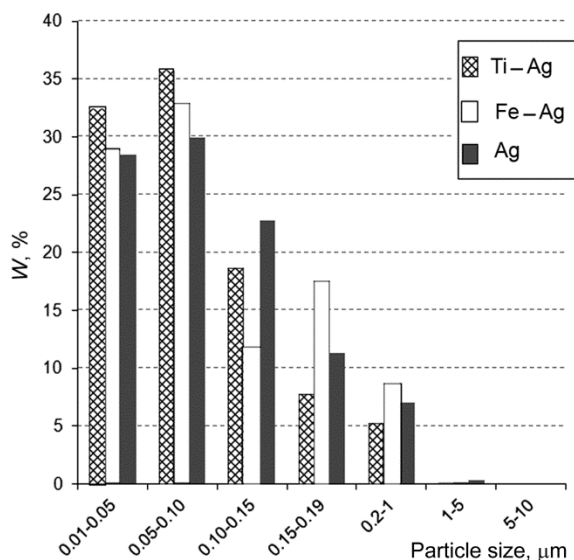


Fig. 2. Size distribution of nanoparticle agglomerates after ultrasonic treatment.

enough for nanoparticles to be introduced into the polymer matrix. An investigation of the treated agglomerates of Ti–Ag, Fe–Ag and Ag nanoparticles by the sedimentation method accompanied by their fixing by dynamic light scattering using a CPS DC 24000 disc centrifuge has demonstrated that all of the nanoparticles possess a bimodal size distribution (Fig. 2).

The first-mode maximum lies in the size range 0.01–0.05 μm and seems to be determined by the size of nanoparticles. The position of the second maximum at 0.1–0.2 μm is likely to control the size of the agglomerates not dispersed during preparation of the test specimen.

Agglomeration of nanoparticle presents a challenge during their introduction into polymer matrices. Monometallic nanoparticles with approximately similar dimensions form both aggregates (low temperature) and agglomerates (high temperature), depending on the temperature of their contact. In the aggregates, metal nanoparticles are weakly bonded by the Van der Waals adhesion forces, while in the agglomerates they are strongly bonded by the ‘necks’, forming hard agglomerates [14]. The particle aggregates are readily destroyed by an external action, e.g., by ultrasonic dispersion. A more complicated task is to destroy hard agglomerates formed of mechanically bonded nanoparticles. A capacity of nanoparticles to form agglomerates is determined by their surface energy (size factor) and the melting energy of a metal. Due to a small size, nanoparticles possess a high specific surface area and hence high surface energy, which determines their possible low-temperature melting in the contact point. The metal melting point in the contact point is controlled by the melting temperature of the bulk metal. Generally, the agglomeration of nanoparticles is the stronger, the lower the metal melting temperature. In addition to the factors mentioned above the ability to form hard agglomerates is affected by the oxide layers on the surface of nanoparticles. Let us look at the formation of agglomerates using the Ti–Ag system as an example. During passivation of electroexplosive titanium nanopowder a dense oxide layer is formed on the surfaces of nanoparticles, which impedes the formation of hard agglomerates (Fig. 3a), while chemically inert silver nanoparticles do form hard agglomerates (Fig. 3b). During a simultaneous explosion of titanium and silver wires nanoparticles form both agglomerates and aggregates. Agglomeration of nanoparticles, followed by the neck formation, occurs via the silver component of nanoparticles: Ti–Ag–Ti. No agglomerates of nanoparticles bonded via titanium (Ag–Ti–Ag) were observed (Fig. 3c).

The formation of hard agglomerates of nanoparticles bonded via their silver is accounted by the fact that the melting temperature of silver (962°C) is lower than that of titanium (1670°C).

An investigation of the physical-chemical characteristics of modified BNs of polymer materials has demonstrated that the resulting gels are homogeneous in their compositions and their pH index is in the range from 6.0

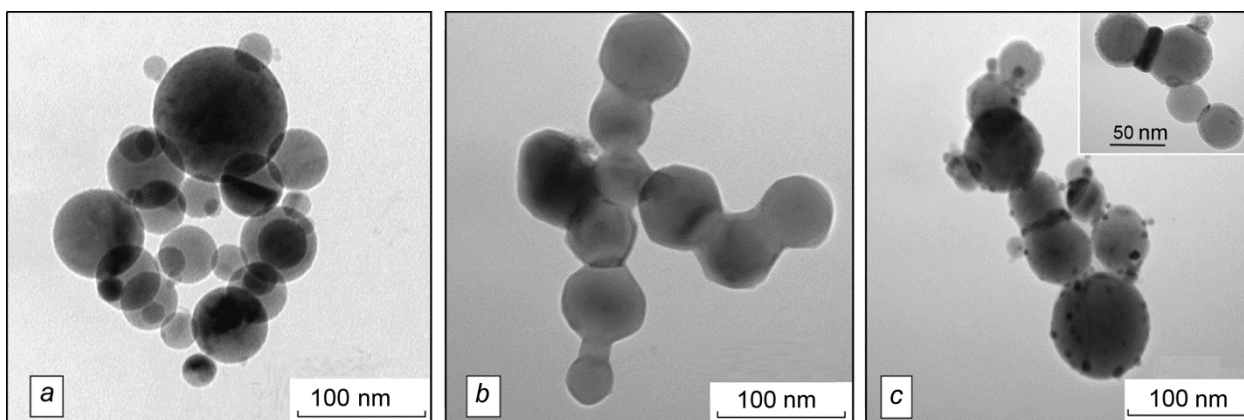


Fig. 3. TEM-images of agglomerates of titanium (a), silver (b) and Ti-Ag nanoparticles (c).

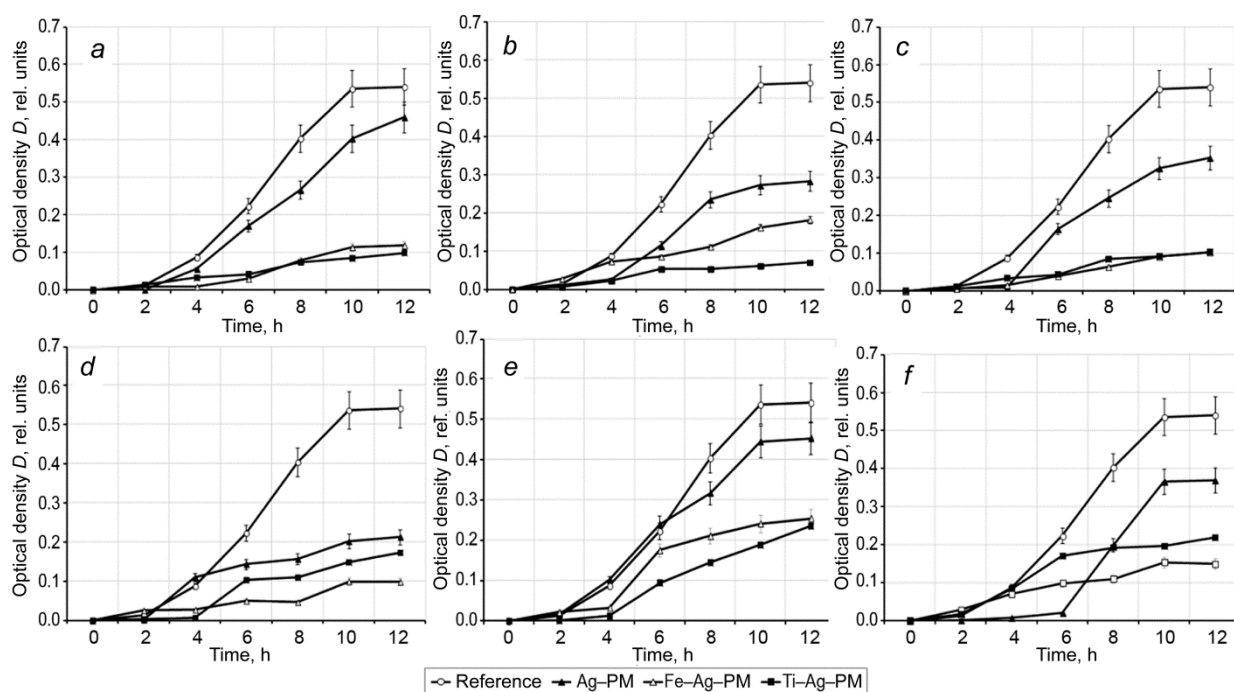


Fig. 4. Antimicrobial activity of ointments and gels modified with Ti-Ag nanoparticles in a concentration of 0.1 mg/ml, based on: a – polyvinyl alcohol, b – carboxymethyl cellulose, c – carbopol, d – glycerol, e – polyacrylimide, and f – vaseline.

to 6.5, which is close to the physiological value of pH of the human body skin. It was revealed that neither the organoleptic indices nor pH of the Ti-Ag-PM, Fe-Ag-PM, or Ag-PM composites changed after three months of storage. An investigation of the absorption spectra of the gels has demonstrated that they remain stable, there is no shifting of the absorption band or decrease in their intensity within three months of exposure to room temperature.

In order to determine the antibacterial activity of the gels under study, the suspension method was used. The investigations were performed on the methicillin-resistant *S. aureus* bacterial culture (clinical strain). The results of antimicrobial activity of the Ti-Ag-PM composite is presented in Fig. 4.

All of the test specimens of BP–PM composites in the form of ointments and gels exhibited a high antimicrobial activity MRSA, exceeding that of Ag–PM. The highest activity among the experimental compositions belonged to the Fe–Ag–PM gels with carboxymethyl cellulose and Ti–Ag–PM and Fe–Ag–PM gels with carbopol.

SUMMARY

Using the method of simultaneous explosion of two wires in an argon atmosphere, nanopowders have been synthesized from bimetallic Ti–Ag and Fe–Ag nanoparticles, representing weakly bonded aggregates of Janus-particles and hard agglomerates, where the particles are bonded by silver necks. A negative particle charge and their ability to degassing under ultrasound make it possible to use the resulting nanopowders as antimicrobial modifiers of a number of water-soluble polymers and vaseline, followed by the formation of stable gelled and ointment compositions. The antimicrobial activity of the modified compositions exceeds that of silver nanoparticles as concerns MRSA.

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