The synthesis of Fe-Ag and Fe-Cu bimetallic nanoparticles by electrical explosion of wires

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Abstract. In the present study, we obtained antibacterial Fe-Cu and Fe-Ag bimetallic nanoparticles by electrical explosion of two twisted wires. This method allows obtaining nanoparticles of a given composition and morphology. As-synthesized nanoparticles were characterized by electron microscopy, X-ray diffraction, micro electrophoresis techniques and magnet technique. In result we observed the formation of nanoparticles with Janus-like structure with distinct separation of components inside the particle. These nanoparticles have a strong antibacterial activity against two bacteria strains. The high antimicrobial activity of the nanoparticles is due to the prolonged ion release in media. Taking into account the possibility of easy magnetic separation of the novel bimetallic demonstrate the potential for their use as promising new generation antibacterial agents for advanced antimicrobial water treatment technologies.

1. Introduction

Recently, the synergetic effect in antibacterial activity has made of bimetallic nanoparticles popular nanomaterial for biomedicine [1]. Such nanoparticles are promising due to a unique combination of physical and chemical properties, such as high antimicrobial activity, controlled ion release in physiological media, storage stability, etc. Antibacterial agents based on bimetallic nanoparticles can be used as an alternative to antibiotics and antiseptics [2]. The synthesis of bimetallic nanoparticles of immiscible or limited miscible metals, such as Fe, Cu, Ag, is the one of the most difficult problem [3]. According to [4], metal pairs Fe-Cu and Fe-Ag can dissolve only in a narrow concentration range. Usually chemical and mechanochemical syntheses are usually used to obtain Fe-Cu and Fe-Ag nanoparticles. [5]. Chemical methods are based on chemical reduction of metals from the salt precursor. But these methods are sensitive to the synthesis conditions and have only laboratory scale. Also, the nanoparticles prepared are to be stabilized by surfactant or by the deposition on the template.

Mechanochemical methods are attractive only to produce nanoparticles of the solid solutions [6]. However, the production of the bimetallic core-shell nanoparticles as well and multilayer structures by the methods is difficult.

Physical methods, such as gas phase, laser ablation, electrical explosive of wire, etc. enable to prepare bimetallic particles of diverse structures – core-shell, Janus-like, as well as particles with full or partial mutual dissolution of components. Physical methods are more environmentally friendly and productive.

In the present work, the method of electric explosion of two wires was used to synthesize bimetallic Fe-Ag and Cu-Ag nanoparticles from metals that are prone to components separation in the solid phase.
Their antimicrobial properties against two bacteria strains were studied and the characteristics obtained were compared with those of Cu and Ag metal nanoparticles.

2. Materials and methods

Fe-Cu and Fe-Ag nanoparticles were obtained by electrical explosion of two twisted wires in argon atmosphere. The main explosion conditions are given in the table.

| Sample  | Wire | diameter of metal wire $d$, mm | length of metal wire $l$, mm | atomic ratio $N$, at.% | energy $\Delta H$, kJ/g | energy storage capacitance $C$, $\mu$F | energy storage voltage $U_0$, kV |
|---------|------|---------------------------------|-------------------------------|-----------------------|------------------------|-------------------------------|-----------------------------|
| Fe-Ag   | Fe   | 0.30                            | 95                            | 50                    | 50                     | 34                            | 30                          |
|         | Ag   | 0.36                            |                               |                       |                        |                               |                             |
| Fe-Cu   | Fe   | 0.30                            | 80                            | 50                    | 116                    | 2.4                           | 30                          |
|         | Cu   | 0.20                            |                               | 50                    |                        |                               |                             |

The samples were characterized by transmission electron microscopy (JEM-2100, Japan) with the integrated energy-dispersive analysis system X-Max (Oxford Instruments, GB), X-ray diffraction (XRD) method (Shimadzu XRD 7000, Shimadzu Corporation, Japan), microelectrophoresis (ZetaSizer Nano ZS, Malvern, GB). To plot size distribution histogram, the sizes of at least 3000 particles were measured.

The antibmicrobial activity of the nanoparticles was determined against E. coli and ATCC 25922 and MRSA ATCC 43300. To prepare the inoculum, a 24-hour bacterial culture was used, which was suspended to a turbidity of 0.5 McFarland standard, which corresponded to $1 \times 10^8$ CFU/mL for the studied bacterial strains.

To evaluate antimicrobial activity of nanoparticles were used agar-well diffusion method. Müller-Hinton broth (MHB) which is recommended as a medium for testing the sensitivity of aerobic microorganisms, was used as the testing medium. To test the antimicrobial activity of nanoparticles we used E. coli ATCC 25922 and MRSA ATCC 43300 bacterial strains. The bacterial culture was inoculated in Muller-Hinton broth (NICF, Russia) and incubated 24 h at 37 °C. The bacteria concentration was $10^5$ CFU/ml.

3. Result and discussion

Fe-Cu and Fe-Ag nanoparticles were produced by electrical explosion of two twisted wires in argon atmosphere at $3 \times 10^5$ Pa pressure. Scheme of process are shown on Figure 1.

![Figure 1. The scheme of electrical explosion of wire](image-url)
Electrical explosion of wires is widely used to obtaining of bimetallic nanoparticles [7]. The productivity of the electrical explosion process is approximately 50 g/h, with the consumption of the electrical energy was 75 kW·h/kg. Synthesized bimetallic nanoparticles have a spherical shape and show normal-logarithmic particle size distribution (Figure 2, 3).

![Figure 2. TEM image (a, b, e, f), EDAX-TEM analysis (c, g) and particle size distributions (d, h) of Fe-Cu (a-d) and Fe-Ag (e-h) nanoparticles](image)

According to EDAX-TEM analysis data, iron and copper (or silver) are non-uniformly distributed over the volume of particles. The formation of a «Janus»-like particle is observed [8]. In the XRD patterns of Fe-Cu, the main reflexes correspond to the phases of Fe and Cu. According to the XRD-analysis, the electric explosion of Fe and Ag twisted wires in argon atmosphere results in formation of iron and cooper phase, deviations of the lattice parameters of metals from standard parameters are not observed. The average particle size $a_n$ of Fe-Ag nanoparticles is 82.5 nm, $a_n$ of Fe-Cu nanoparticles is 74.4 nm.

The agar-well diffusion method is a widely used for evaluation the *in vitro* antibacterial activity. This method is based on the ion or particle release in nutrient medium. For research, we used a modification of the method with the formation in the volume of agar medium of cylindrical wells in which a suspension of the bimetallic nanoparticles was placed. The results of evaluation of antibacterial activity against MRSA and *E.coli* are presented in Figure 3.
Figure 3. Photographs of semi-solid agar plates inoculated with MRSA (a-d) and E. coli (e-h) using nanoparticles by the agar-well diffusion method: a – control MRSA; e – control E. coli; b, f – Fe-Cu nanoparticles; c, g – Fe-Ag nanoparticles; d, h – colloidal silver as a positive control.

Results showed the measured diameters of inhibition growth zones around wells containing Fe-Cu nanoparticles and Fe-Ag nanoparticles are the same as those around wells containing colloidal silver nanoparticles. This result may be related to the synergistic effect of the structure of bimetallic nanoparticles.

4. Conclusion
The results show that synthesized nanoparticles Fe-Ag and Fe-Cu are active antimicrobial agents, the efficiency of which are close to and even exceed the efficiency of colloidal silver (20 nm). This result may be related to the synergistic effect of the Janus-like structure of bimetallic nanoparticles. Prepared nanoparticles are promising antimicrobials as an alternative to antibiotics for biomedical applications.

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