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PRODUCTION AND CHARACTERIZATION OF Al_2O_3+Ag COMPOSITE NANOPOWDERS

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Abstract. *The principal possibility of the composite particles production by the radiation-chemical method with acceptable productivity was shown. The composite particles were produced in the nanoscale range (50 and 80 nm) from aluminum oxide partially coated with silver. The coating percentage was from 2–3% for smaller particles to 16–40% for larger composite. The stability of the suspension before irradiation using different stabilizers was studied, and the reason for the change in the color of the suspensions after ultrasound treatment was determined. The biological activity of the nanopowder which showed a high level of antibacterial activity was investigated.*

Keywords: *Nanopowders, nanoparticles, nanosecond electron beam, antibacterial properties*

1. INTRODUCTION

In recent years, silver nanoparticles (NPs) have been actively studied due to a wide range of their properties: antimicrobial [1], antitumor [2], antiviral [3], antifungal [4], as well as photocatalytic [5] and others.

One of the applications of silver NPs in medicine is their combination with various substances that allows obtaining a complex effect of the composite and the economy of silver by reducing its amount. It is known that the combination of nanosilver with anticancer drugs has increased the level of cancer cell apoptosis, which can be used to treat cancer [2]. It was established that the interaction of nanosilver with other particles (Fe3O4, CaP) led to an increase in composite antimicrobial activity avoiding adhesion to the implant. In addition, this combination achieves high biocompatibility, increases mineralization ability, which can be used to create dental implants, as well as in bone regeneration [6, 7]. It was found that the combination of nanosilver with antibiotics increased antimicrobial capacity, which can be used to prevent particularly resistant infections [3].

Producing nanopowders by physical method using an electron beam at different puple repetition rates (at different absorbed dose), showed that the particle size decreases with increasing of electron fluence. Moreover, the use of nanosecond repetitive accelerators allows to control the time of impact on the components of the substance. For irradiation experiments, a compound was prepared of 50 g of xylitol, 100 ml of distilled water and 0.6 g of AgNO3. The prepared sample was irradiated on a nanosecond electron accelerator URT-0.5, then the mixture was drained, and the resulting nanopowders were washed in distilled water.

The aim of this work is to produce and study the properties of aluminum oxide NPs coated with silver, as well as to assess the prospects of using this system in the medical-pharmaceutical field. The relevance of this work is due to the need for the creation of new materials for the development of new methods of treatment of various diseases and pathologies, as well as for the development of biotechnology.

2. MATERIALS AND METHODS

For the first experiment on the silver coating, aluminum oxide NP was selected. The radiation-chemical technology of silver nanopowder production by nanosecond electron beam irradiation was adopted as a basis [8]. The essence of the technology is that when using solutions based on polyatomic alcohols, smaller silver particles are obtained (Table 1), so suspension based on sorbitol (hexatomic alcohol) was used in the experiment: 69 g of sorbitol was dissolved in 100 ml of distilled water, then 0.6 g of silver nitrate and 0.7 g of aluminum oxide were added to the resulting solution. The resulting suspension was irradiated in Petri dishes of 25 ml at a nanosecond electron accelerator URT-0.5 (accelerating voltage ~500 kV, beam current ~200 A, pulse duration at half-height ~60 ns) [8], and the absorbed dose was 37.4 kGy.

The structural properties and composition of the powders were analyzed by the electron microscope LEO 982 with the prefix Oxford instruments X-Max.

The evaluation of the suspension stability was carried out using the spectrophotometer Ekros PE-

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5400UV. Polyethylene glycol (PEG) and sodium citrate in a ratio of 1:1 with silver contained in silver nitrate were used as stabilizers. Previously, each suspension was sonicated for 40 minutes. The assessment of sedimentation stability was carried out immediately after sonication, in 60 minutes and in 24 hours.

Table 1. Results of experiments under different irradiation regimes [8]

Operation frequency of the accelerator, pps	Absorbed dose D, kGy	Specific surface area S, m²/g	
		Isopropyl alcohol	Xylitol
3.3	2.5	2.6/3.1*	39.14/5.5*
20	15	0.99/1.2*	13.7/1.9*
50	37.4	0.83/1*	7.05/1*

* the ratio of specific surfaces of powders to the surface at 50 pps.

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To determine the chemical composition, the suspensions were centrifuged using a high-speed centrifuge CN-10001 for 15 minutes at a speed of 2000 rpm and 2 ml aliquots of each solution were taken. 1 ml of a saturated solution of iron-ammonium alum was added to all solutions as an indicator and titrated with a prepared solution of potassium rodanide (KSCN, the molar concentration of 4.3 mmol) until a constant reddish color appeared.

To study the antibacterial properties of composite NP, wine yeast was used as cell cultures. The cell suspension was distributed in 5 cups, one of which was a control group. 1 mg and 2 mg of the initial aluminium oxide, silver and obtained by the method of [8] composites ($Ag+Al_2O_3$ and $Ag50c+Al_2O_3$) were added to each of the remaining cups. Thus, the concentration of NPs in each cup was 100 μg/cm² for the first series of experiments and 200 μg/cm² for the second series. Evaluation of antibacterial ability was carried out by counting the live (unpainted) and dead (colored) wine yeast using the Hemocytometer and light microscopy in 24, 48 and 72 hours after the addition of NP.

3. Results and discussion

After irradiation, the suspension was divided into 2 parts. The deposition time of silver NPs on aluminium oxide took 15 hours in the first part, in another – 4 days. After aging, the solution was drained, and the obtained powders ($Ag50c+Al_2O_3$ – powder at the first deposition mode and $Ag+Al_2O_3$ – at the second) were washed with distilled water (three times) and dried.

The results of microscopic and EDX analyses (energy-dispersive X-ray spectroscopy) are shown in Figure 1, Figure 2 and Table 2.

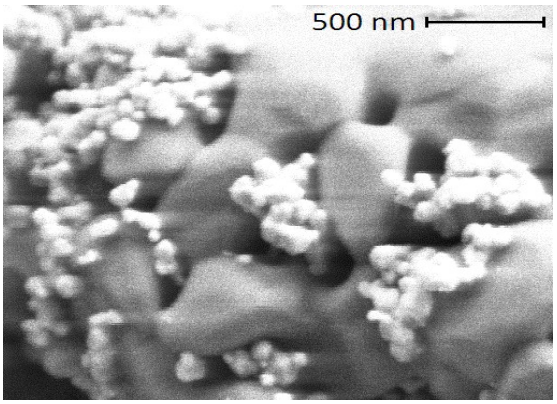

Figure 1. SEM photos of nanopowder $Ag+Al_2O_3$

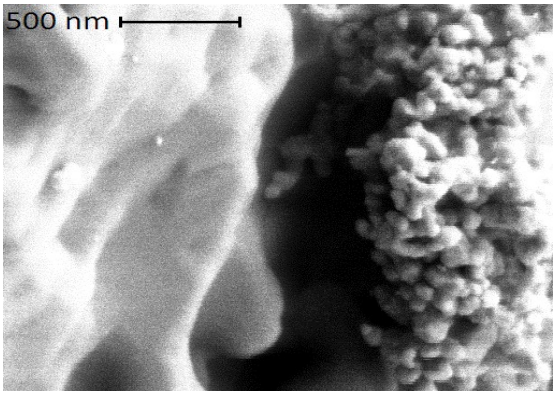

Figure 2. SEM photo of nanopowder $Ag50c+Al_2O_3$

Table 2. The results of EDX-analysis

Sample	Element	Line type	Weight, %	Atom,%
$Ag+Al_2O_3$	O	K series	31.92 (0.17)*	53.64
	Al	K series	39.00 (0.17)*	39.04
	Ag	L series	29.23 (0.25)*	7.32
	Sum		100.00	100.00
$Ag50c+Al_2O_3$	O	K series	42.50 (0.13)*	55.81
	Al	K series	46.85 (0.14)*	41.25
	Ag	L series	10.64 (0.17)*	2.95
	Sum		100.00	100.00

* - measurement error

Figure 1 shows that the average particle size of $Ag+Al_2O_3$ powder was 80 nm, $Ag50c+Al_2O_3$ – 50 nm. It is also seen that in some areas silver covers almost the entire surface of the NPs of aluminum oxide, in other areas the coating was partial. From the results of microscopic and EDX analyses, the degree of coverage of aluminum oxide with silver was calculated. The degree of coverage was calculated using the weight (from Table 2), the thickness of the layer, the average particle size of silver and aluminum oxide. The ratio of mass fractions Al_2O_3/Ag was calculated. With the ratio of densities and mass fractions of Al_2O_3/Ag, the fraction of silver coating for the obtained NP was calculated. The calculation results are presented in Table 3. It is well seen from the table data that the share of silver coating of $Ag+Al_2O_3$ powder was from 16 to 40%, for $Ag50c+Al_2O_3$ – 2-3%, which relates to the different amount of silver deposited on aluminum oxide.

Table 3. The results of the calculation of the degree of coverage

Value	$Ag+Al_2O_3$	$Ag50c+Al_2O_3$
The ratio of mass fraction of Al_2O_3/Ag from the EDX analysis	8.4	2.4
The diameter of the Al_2O_3 particles, nm	600-900	600-900
The Ag layer thickness, nm	100-200	350-550
The proportion of the silver coating, %	16-40	2-3

The stability of the suspension is characterized by sedimentation resistance, which is directly proportional to the optical density. Therefore, it is necessary to choose a stabilizer, thanks to which the suspension would have a high sedimentation resistance (optical density) in a given time interval. Measurements of optical density were carried out on the spectrophotometer Ekros PE-5400UV, then all values were rationed by the maximum value of optical density. The analysis of the dependence of the optical density on time (Figure 3) showed that during the day the sedimentation rates of the powder were 76%, 86% and 99% for the control sample, suspension with PEG and sodium citrate, respectively. Thus, initial suspension before irradiation has lower sedimentation stability as in the control sample, and with stabilizers. Therefore, it is necessary to continue the search of stabilizer for this suspension in order to obtain a more uniform coating.

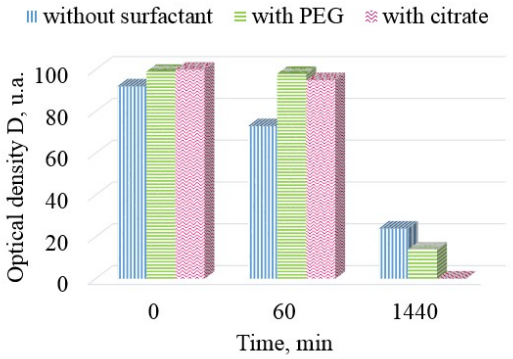

Figure 3. Sedimentation stability of suspensions

While being sonicated, each suspension changed its color: control sample and suspension with the addition of PEG became gray-brown, and the suspension with sodium citrate – mustard color. To determine the silver ion Ag^+ an adenomatous method has been used [9], which uses the following analytical reaction: $KSCN+AgNO_3=\downarrow AgSCN+KNO_3$. After titration, each solution acquired a reddish tint.

From the results, it was established that with the addition of a surfactant, such as sodium citrate, more than half of the silver fell into the precipitate in the form of metallic silver. However, after sonication, the ratio of metallic silver in the control suspension and the suspension with the addition of PEG amounts was 6% and 10%, respectively (Table 4). Thus, due to the influence of ultrasound, suspensions change colour, and the acquisition of different colors is due to the different sizes of the metallics formed during the reaction.

Table 4. Chemical composition

Suspension	Titrant volume, ml	Concentration of Ag ions, mmole/l	Share of non-metallic Ag, %
Control probe without ultrasound	14.0	29.9	100.0
Control probe with ultrasound	13.2	28.2	94.3
Sodium citrate with ultrasound	5.8	12.4	41.1
PEG with ultrasound	12.8	27.4	91.5

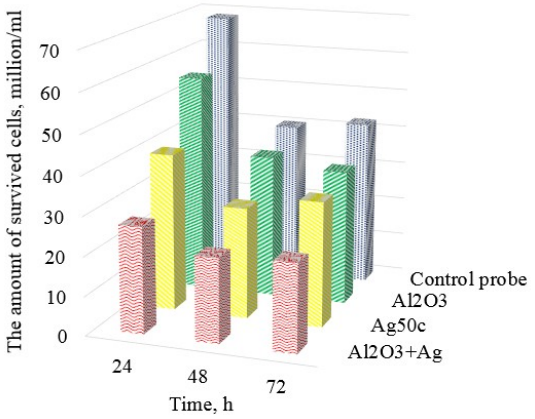

Figure 4. Antibacterial properties of composites $Ag+Al_2O_3$, Ag50c, Al_2O_3

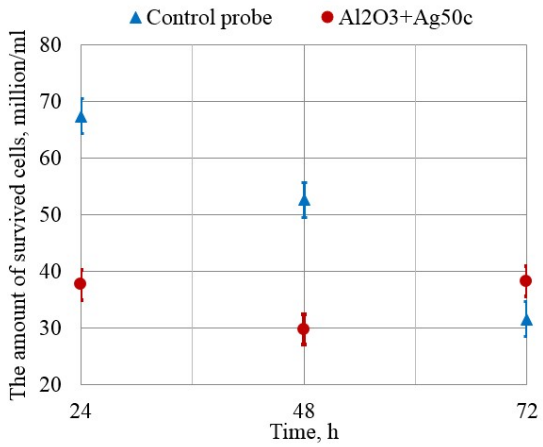

Figure 5. Antibacterial properties of the composite $Ag50c+Al_2O_3$

The evaluation of the biological activity of the obtained composites showed a high antibacterial ability, which exceeds the properties of aluminum oxide and silver nitrate with a separate effect on yeast, and the large composite ($Ag+Al_2O_3$) has greater biological activity in comparison with the small one ($Ag50c+Al_2O_3$). Different effects on yeast of large and small composites have been found: large NP maintains the same antibacterial effect throughout the whole time, and the efficiency of the small composite

decreases over time, which can be explained by the high content of silver in the large composite, in contrast to the small one (Figure 4 and Figure 5).

At a concentration of 200 μg/cm², NPs of larger composite have demonstrated high antibacterial efficiency to the yeast as NPs with 100 μg/cm², and antibacterial properties also exceeded the properties of aluminum oxide and silver.

Comparing the biological effectiveness of NP at different concentrations (Figure 6), it was found that the antibacterial effect at the concentrations of 100 μg/cm² and 200 μg/cm² depends in a complex way on the concentration of the used composite. At a concentration of 100 μg/cm², the biological efficiency decreased with increasing the exposure time, and at a concentration of 200 μg/cm², on the contrary – there was an increase in the antibacterial effect with increasing the duration of exposure to each NP. The error of the used method is 3%.

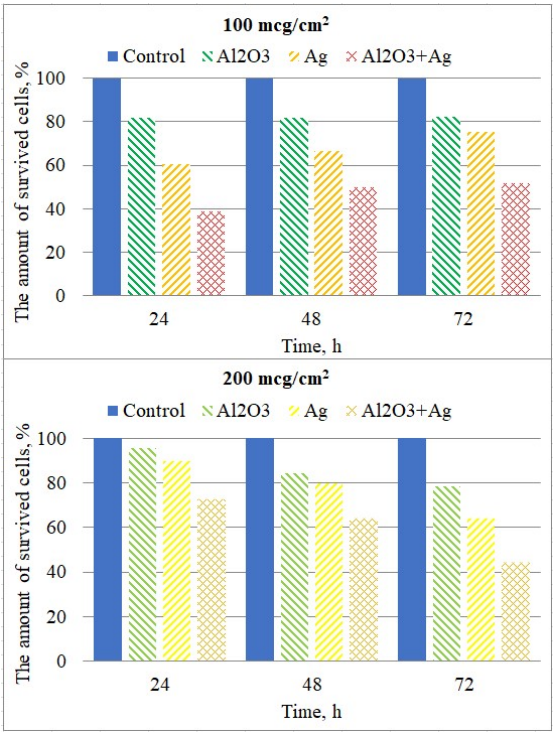

Figure 5. Comparison of antibacterial activity of composite NP at different concentrations

5. Conclusion

A sufficiently high efficiency of the method for the production of composite NPs was established, as well as the ability to control the deposition process and the type of silver coating on aluminum oxide NP by changing the deposition time.

In the study of the stabilization properties of NP before irradiation, the use of surfactants such as sodium citrate and PEG was determined to be irrelevant, which implies the further search for a suitable stabilizing agent.

Also, the high antibacterial ability of the NP on yeast was investigated. Further studies of biological activity and cytotoxicity assessment will determine the scope of composite NP. In addition, it is planned to assess the photocatalytic capacity of NP.

Obtaining composites based on other oxides by this method will allow selecting suitable materials for several applications, such as dental transplantology, drug delivery [10] and water disinfection.

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