Study of the possibility of obtaining metal nanoparticles under the action of a non-equilibrium plasma on aqueous solutions of salts

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Abstract. Dispersions of metal nanoparticles were obtained at the gas discharge treatment of aqueous solutions of CuCl₂, CuSO₄ and AgNO₃. Direct current discharge was excited between a metal cathode located in the air and metal salt solution being used as an anode at a current of 5–25 mA. The average sizes of obtained nanoparticles were estimated using dynamic light scattering method. The sizes have been shown to depend on the solution concentration, discharge current and processing time. The obtained nanoparticles were applied from dispersions to medical dressings and their bactericidal activity was tasted. Samples treated with silver-containing particles showed bactericidal activity against bacteria Escherichia coli, Staphylococcus albus, Bacillus subtilis and microscopic fungus Candida albicans. Copper-containing samples did not show biological activity.

1. Introduction

Nanoparticles (NPs) of metals and oxides are used in catalysis, electronics and in the creation of new composite materials with exciting opportunities. Due to their unique properties, nanoparticles are widely used in the medical field, including antimicrobial effects [1], drug delivery [2], optical marks of cancer cells, etc. Especially, Ag, Cu and Cu₂O nanoparticles have been used extensively as microbicides [3, 4]. The use of plasma in contact with liquids for the synthesis of metal and metal oxide nanoparticles is discussed in reviews [5, 6]. As a rule, pulsed high-voltage discharges, which are excited between two metal electrodes immersed in water or in aqueous solutions of salts-precursors, are used for nanoparticles synthesis. For example, an atmospheric pressure glow discharge generated between the solid cathode and liquid anode was applied to produce AgNPs and deposition of them onto a polymeric films [7]. A plasma electrochemical method was used to synthesize cuprous oxide nanoparticles [8].

The purpose of this work is to study the possibility of forming nanoparticle dispersions when a discharge is excited in air at atmospheric pressure between a metal cathode and a liquid electrolyte anode, which is an aqueous solution of a metal salt.
2. Experimental part

The image and simplified scheme of the discharge cell are shown in Figure 1. A DC discharge \((i = 5 - 25\, \text{mA})\) in air at atmospheric pressure was excited between a copper electrode with 2 mm diameter and a solution surface, which was used as an anode of the discharge cell. The electrode gap was equal to 1 mm. The volume of the solution was 100 ml. An electrode made of graphite was immersed into the solution to provide an electric circuit. Aqueous solutions of CuSO\(_4\), CuCl\(_2\), and AgNO\(_3\) \((c = 1 \times 10^{-4} - 1 \times 10^{-2}\, \text{mol}\,\text{l}^{-1})\) were used as a liquid electrolyte anode. During the gas discharge treatment, the solution-anode was bombarded with electrons and negative ions formed in the plasma. The exposure time was 5–30 minutes. The particle size distributions were obtained using the dynamic light scattering method (“Zetasizer Nano ZS”, Malvern Instrument, UK). Studies of the bactericidal activity of the obtained particles were performed after they were applied to medical dressings “WD Silkofix” with a viscose sorption pad. Microbiological tests were performed according to the procedure described in [9].

![Figure 1. Experimental setup: 1 – power supply, 2 – ammeter, 3 – electrodes, 4 – liquid anode, 5 – plasma](image)

3. Results and discussions

The formation of dispersions was observed in the surface layer of the solution in contact with the plasma as it is sown in Figure 2. The color intensity of dispersions changed with the discharge burning time. When using solutions of CuCl\(_2\), a yellow-brown color appeared. The color of the dispersions that were formed during the processing of the AgNO\(_3\) solution varied from gray to black, and during the processing of the CuSO\(_4\) solution, from light green to brown.

Experiments have shown that the hydrodynamic diameters of the obtained particles, found by the dynamic light scattering method, depend on the solution concentration and the discharge current. Thus, with an increase in the concentration of CuSO\(_4\) from \(5 \times 10^{-4}\) to \(1 \times 10^{-2}\, \text{mol}\,\text{l}^{-1}\), the average particle size changed from 1300 to 300 nm, and the \(\xi\)-potential – from 18.6 to \(-1.56\, \text{mV}\) (Table 1).

An increase in current from 5 to 25 mA was accompanied by an increase in the average particle size. In Figure 3 shows examples of particle size distributions obtained from the solutions of copper sulphate and copper chloride \((c = 5 \times 10^{-3}\, \text{mol}\,\text{l}^{-1})\) under the same conditions of plasma treatment \((i = 5\, \text{mA}, t = 5\, \text{min})\). It is obvious that the average particle size is influenced not only by the discharge current and the concentration of the solution, but also by the nature of the salt anion. Thus, dispersions with average particle sizes of 324 and 54 nm, respectively, were obtained from solutions of CuSO\(_4\) and CuCl\(_2\) under the same treatment conditions.
Figure 2. The formation of a dispersion of nanoparticles in a solution of CuSO$_4$ at different times of gas discharge treatment.

Table 1. The average size and $\xi$-potential of particles obtained by plasma treatment of CuSO$_4$ solutions with different concentrations ($i = 5$ mA, $t = 5$ min).

| $C$ (mol $l^{-1}$) | $5\times10^{-4}$ | $1\times10^{-3}$ | $3\times10^{-3}$ | $5\times10^{-3}$ | $1\times10^{-2}$ |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $d$ (nm)          | 1316±154        | 1204±129        | 764±34          | 352±30          | 345±56          |
| $\xi$ (mV)        | 18.6±1.3        | 3.40±0.05       | 0.56±0.07       | -0.79±0.17      | -1.56±0.05      |

It is known that nanoparticles of silver, copper and a number of other metals exhibit bactericidal activity. Samples of dispersions obtained by the plasma treatment of CuSO$_4$ and AgNO$_3$ solutions were applied to the surface of medical dressings of the “WD Silkofix” trademark with viscose sorption pad. In these experiments polymer samples were placed in the solution being treated 5 mm below liquid-gas interface. After plasma treatment the samples were washed in distilled water to remove water-soluble precursors and dried at room temperature in the open air. Then the samples were placed on the surface of a dense nutrient medium (meat-peptone agar and Saburo) pre-seeded with cultures of bacteria Escherichia coli, Staphylococcus albus, Bacillus subtilis and microscopic fungus Candida albicans. Microbial cultures were incubated at 37 °C for 24 hours, after which the sizes of the growth inhibition zones were measured. The results of some experiments are shown in Figure 4 and Table 2. Samples loaded with silver-containing particles showed bactericidal activity, while copper-containing samples did not have a biological activity.

Figure 3. The size distribution of particles obtained by gas-discharge treatment of CuSO$_4$ and CuCl$_2$ solutions.
Figure 4. The results of microbial tests with *E. coli*: 1 - untreated sample; 2–8 - samples treated with dispersion of copper-containing nanoparticles obtained under different conditions of plasma treatment, 9, 10 - samples treated with dispersion of silver-containing nanoparticles.

| Sample | *Escherichia coli* | *Staphylococcus albus* | *Bacillus subtilis* | *Candida albicans* |
|--------|-------------------|-----------------------|--------------------|-------------------|
| #1-8   | -                 | -                     | -                  | -                 |
| #9     | 22                | 21                    | 20                 | 17                |
| #10    | 20                | 24                    | 22                 | 17                |

Table 2. Size of the inhibition zone (mm) for microorganisms on nutrient media with samples treated with dispersions of nanoparticles obtained by the plasma action on CuSO₄ and AgNO₃ solutions.

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