Structure of copper-containing nanocomposites obtained by electrochemical synthesis

I Yu Isaeva¹, G Yu Ostaeva¹, I V Odinokova¹, E A Eliseeva¹ and V I Busko²

¹ Moscow Automobile and Road Construction State Technical University (MADI), Leningradskii pr. 64, Moscow 125319, Russia
² D. Mendeleev University of Chemical Technology of Russia, Miusskaya Square 9, Moscow 125047, Russia

E-mail: irina-razumova-xim@yandex.ru

Abstract. The properties of copper nanocomposites obtained by electrochemical reduction in an aqueous-alcohol electrolyte solution (CuSO₄) with the addition of poly(N-vinylpyrrolidone) were investigated. Electrolysis was carried out at direct current using copper electrodes: the anode is made as a hollow cylinder, and the cathode in the form of a bundle of insulated wires with open cross sections, placed inside the cylinder with a working solution. The stabilizing properties of the polymer and the influence of the cathode on the electrochemical deposition processes were shown. The composition, morphology and size characteristics of synthesized copper-containing nanocomposites were determined. The resulting nanoparticles have a crystal cut, and also a high copper content.

1. Introduction
There are a large number of methods that allow obtaining metal ultrafine powders by electrochemical methods [1-6]. The proposed methods have a number of disadvantages: high cost, labor intensity technology, low efficiency and heterogeneity of the final product composition, etc. [7,8]. In this matter, it is particularly important to find fairly simple, effective, economical and environmentally friendly ways to synthesize ultrafine materials. One of the most environmentally friendly and economically justified ways to obtain fine-dispersed metal-containing materials is electrochemical reduction of metal ions. Also, with electrochemical reduction, it is possible to control the process by varying the conditions. For example, the nature and concentration of the electrolyte and solvent, the value of the cathode potential, the current density, the time of the experiment, etc.

Most often, nanoscale copper and its compounds are used to create new generation materials. However, the properties of nanostructured systems strongly depend on their dimensional characteristics and the uniformity of the final product composition.

Earlier, we obtained and studied copper-containing nanoparticles. The synthesis of copper nanocomposites was carried out by reducing Cu²⁺ ions in aqueous media using poly(N-vinylpyrrolidone) (PVP) [9,10]. The reduction was performed by tert-butylamine borane at room temperature under air. The particles obtained in this way had a spherical shape and a narrow size distribution. The nanoparticles protected from aggregation by macromolecular screens polymeric protector of poly(N-vinylpyrrolidone). The phase composition of the synthesized copper nanoparticles was determined as a mixture of copper and its oxide (Cu⁰ ~75 mass%), (Cu₂O~25 mass%).
This work focuses on the study of the mechanism of electrochemical processes occurring in a system containing Cu$^{2+}$ ions in an aqueous alcohol solution of an electrolyte with the addition of PVP when using electrodes with an increased surface area, the structure of the particles obtained in this way.

2. **Experimental**

Copper sulfate was used to prepare a working solution, as a stabilizing component of PVP, ethyl alcohol (95%). The water was distilled twice. The concentrations of copper salt and PVP varied from 0.01 to 0.02 mol/L. Ethyl alcohol was added at a rate of 15 ml based on the concentration of the aqueous solution containing the copper salt.

The working solution is electrolyzed by direct current in an electrolysis cell with a copper cathode and an anode with the deposition of copper particles.

A copper anode in the form of a copper foil with an area of 1 dm$^2$ was immersed in a glass with a capacity of 1 L. The cathode, a section of insulated copper wire connected to the cathode of the power source, was placed in the center of the glass. Open sections of wire with a diameter of 0.5 mm, distributed over the volume, served as a working surface The current was brought to 1 A. The electrolysis time was 1 hour. The copper accumulated in the form of black globular growths at the ends of the wires, broke off under the influence of gravity and sank to the bottom of the glass.

The morphology of the samples was examined in a dual beam scanning electron microscope/ focused ion beam (SEM/FIB) Versa 3D (FEI, USA), equipped with a concentric backscatter detector (CBS). The samples were prepared by decanting the resulting sediment, followed by centrifugation and drying at room temperature.

3. **Results and discussion**

The copper nanoparticles obtained in this way have a crystalline faceting with a particle size distribution of up to 100 nm. The number of agglomerates is insignificant. Figure 1 depicts SEM and EDX images of the final product.

![Figure 1](image-url)

**Figure 1.** (a, b) SEM image and (c) EDX of copper-polymer nanoparticles obtained by electrochemical reduction of copper ions in an aqueous alcohol solution with PVP.
The composition of the samples is identified as Cu metal (~87 mass%). This is explained by the features of the electrochemical synthesis used in this work, which is that the anode was made in the form of a hollow cylinder, and the cathode was made in the form of a bundle of several copper insulated wires evenly distributed in the volume of the working solution inside the hollow cylinder (anode). This version of the cathode allows obtaining a total current density of up to 100 A/cm², which contributes to the production of nanoscale copper particles. Due to the proposed form of the cathode migration and diffusion of cations to such a cathode is carried out from all sides, that is, it is three-dimensional. It should be noted that the anode, made in the form of a hollow cylinder, reduces the migration time of the cation from the anode to the cathode.

In addition, a small area of the cathode facilitates the interaction of copper particles with the polymer, which in turn is not only a “regulator” of the size of nanoparticles in the process of electrochemical synthesis, but also a stabilizer from aggregation. In other words, the nanoparticle screened with a polymer chain. This is due to the fact that the polymer macromolecules interact with the growing nanoparticle during the reduction of metal ions and control the size of the metal particles, forming a polymer screen. [11].

The presence of ethyl alcohol in the system provides the most efficient and stable performance of the electrochemical recovery process. The main advantage is to slow down the competing hydrogen ion release reaction, which increases the current output for copper. Optimal conditions for diffusion transfer of copper ions to the cathode are made. This allows getting a fine-dispersed, uniform sediment.

Thus, the optimal composition of the electrolyte was obtained, which contributes to the production of highly dispersed copper precipitation.

A sample of copper nanoparticles obtained without adding ethyl alcohol, but with the same process characteristics is shown in figure 2.

![Figure 2](image)

**Figure 2.** (a, b) SEM and (c) EDX image of the product of copper nanoparticle synthesis obtained by electrochemical reduction of copper ions in an aqueous polymer solution.

The samples are mostly irregularly shaped particles with crystal facets. In addition to the Cu⁰ metal (~60% by mass), sulfur and oxygen are also present. This result is due to the absence of ethyl alcohol in
the working solution. Alcohol has a weakly alkaline environment, which slows down the competing reaction of hydrogen release. In this system, there is no alcohol, which eventually leads to a low Cu content in the final product.

4. Conclusions
The new technology including the reduction of copper ions by electrochemical reduction in an aqueous-alcohol electrolyte solution (CuSO$_4$) with the addition of poly(N-vinylpyrrolidone) at room temperature in air is applied for the synthesis of copper nanoparticles. It is shown that the addition of ethyl alcohol led to significant changes in the composition of the final product. The addition of ethyl alcohol leads to an increase in the concentration of Cu metal (~87 mass%). Thus, the optimal concentration of reagents of the working mixture and the selected conditions for electrochemical reduction of the most highly dispersed and homogeneous particles are formed. The Cu-containing particles up to 100 nm in size have a uniform shape with crystalline faceting. The features of the electrodes used, as well as the presence of ethyl alcohol in the electrochemical synthesis of copper-containing nanocomposites, allowed obtaining a product that can be used in various fields of industry, such as pharmacology, mechanical engineering, energy, etc.

Acknowledgment
This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project no. FSFM-2020-0010) within the framework of a basic part of the state assignment in the field of scientific research.

References
[1] Chulovskaya S A and Parfenyuk V I 2008 Electronic Processing of Materials 1 58
[2] Chulovskaya S A and Parfenyuk V I 2007 Chemistry and Chemical Technology 50 49
[3] Chulovskaya S A, Kuzmin S M and Parfenyuk V I 2009 Electronic Processing of Materials 5 24
[4] Noskov A V, Chulovskaya S A, Balmasov A V and Parfenyuk V I 2010 Chemistry and Chemical Technology 53 43
[5] Anand V, Harshavardhan and Srivastava V C 2015 J. of Nano RESEARCH 31 81
[6] Tesakova M V, Parfenyuk V I and Godlevsky V A 2008 Electronic Processing of Materials 6 56
[7] Kreicberg G N, Golikov I V, Zavoistii I V, Gracheva I E and Kreicberg O G 2011 Pat. of the Russian Federation No 2410471 appl. 01.09.2009, publ. 27.01.2011
[8] Kreicberg G N, Golikov I V, Zavoistii I V, Gracheva I E and Kreicberg O G 2011 Pat. of the Russian Federation No 2410472 appl. 01.09.2009, publ. 27.01.2011
[9] Ostaeva G Yu, Isaeva I Yu, Morenko I V, Eliseeva E A and Litmanovich A A 2019 Polymer Science, Series B 61 254
[10] Ostaeva G Yu, Isaeva I Yu, Grushina V V, Stuzhuk A N and Odinokova I V 2018 Polymer Science, Series B 60 455
[11] Litmanovich O E 2008 Polymer Science, Series C 50 63