

# THE EFFECT OF SHAPE AND SIZE OF SILVER NANOPARTICLES ON ELECTROCHEMICAL ACTIVITY OF SENSOR TO HYDROGEN PEROXIDE

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## ABSTRACT

The work considers the influence of the morphological characteristics of the AgNPs (form, sizes of silver nanoparticles (AgNPs), the average size of the area) from the composition of the reducing agent and their influence on the optical characteristics and electrochemical activity of the sensor based on the AgNPs to H<sub>2</sub>O<sub>2</sub>. The intensity of the optical spectra of absorption AgNPs and the electrochemical activity of the sensors based on them correlate with the size and shape of the particles. It is shown that the greatest electrochemical activity of H<sub>2</sub>O<sub>2</sub> is possessed by AgNPs-based sensors obtained by using sodium citrate. The reason for increasing the electrochemical activity of the sensor based on the AgNPs obtained in the presence of the soft restorer of sodium citrate is an increase in the area of their active surface 1.3–2.7–3.3 μm<sup>2</sup> due to the non-spherical form of particles (triangular, prismatic, pyramidal form), compared with spherical particles obtained using borohydridictrate and borohydride-based reducing agents.

**Keywords:** Silver Nanoparticles, Voltammetry, UV Spectroscopy, Optical Characteristics, Electrochemical Activity.  
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## INTRODUCTION

Recently, metal nanoparticles have attracted special attention from researchers due to their unique physical and chemical properties associated with their significant surface-to-volume ratio and other dimensional effects.<sup>1,2</sup> The establishment of the relationship between morphological characteristics (size, shape, and active area of the surface of metals) and their electrochemical properties are of interest to study from both fundamental and applied points of view. At the same time, studies in this area are at the stage of accumulation of experimental data and do not allow to unambiguously determine the causes of the influence of dimensional and structural factors on the electrochemical activity of the sensors based on them, in comparison with optical methods, where the spectrum shift and strengthening the analytical signal depends on the form of particles.<sup>3-5</sup> The non-spherical particles are of particular interest due to the anisotropy of optical properties along various faces (nano-rods, flat particles, triangles, etc.) and the vertexes<sup>6-9</sup>, and, consequently, increased chemical activity.<sup>10-12</sup> Spherical particles show lower amplification caused by a minimum surface with a given volume, with a more compact location, and frequent aggregation by reducing the distance between the particles up to their overlapping. AgNPs are promising for several analytical applications, including long-term monitoring of the dynamics of processes occurring in the cells of living organisms.<sup>13,14</sup>

As a model, we took a reaction of oxidation of hydrogen peroxide to the AgNPs. The silver nanoparticles were chosen due to low cost and availability compared to other noble metals, and secondly, by the high affinity of silver to oxygen, and, consequently, to hydrogen peroxide. In this regard, the purpose of this work was to establish the relationship of optical characteristics, shape, and size of AgNPs from the composition of the reducing agent and their influence on the electrochemical activity of the sensor based on the AgNPs to H<sub>2</sub>O<sub>2</sub>.

## EXPERIMENTAL

### Materials

All chemical reagents used the analytical purity, produced by Merc (Darmstadt, Germany).  $\text{H}_2\text{O}_2$  solutions were prepared immediately before experimental definitions on bidistilled water. The mass concentration of  $\text{H}_2\text{O}_2$  was determined by the permanganate metric analysis method according to the standard method.

### AgNPs Synthesis

AgNPs of various sizes and forms were synthesized using three production methods.<sup>15</sup> In all cases, silver nitrate ( $\text{AgNO}_3$ ) was used as a precursor.

#### The Citrate Technique (C)

Into a 10 ml flask containing  $1 \cdot 10^{-4}$  M  $\text{AgNO}_3$  30 ml of  $10^{-4}$  M  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  and 60 ml of bidistilled water were added, and the resulting mixture was heated and boiled until the yellow sole remained.

#### Borhydritcitrate Technique (BGC)

Into a 10 ml flask containing  $1 \cdot 10^{-4}$  M  $\text{AgNO}_3$  30 ml of  $10^{-4}$  M  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  and 60 ml of bidistilled water were added, after which 0.015 M  $\text{NaBH}_4$  was added drops until yellow sole remained.

#### Borohydride Technique (BG)

Into 10 ml containing  $1 \cdot 10^{-4}$  M  $\text{AgNO}_3$  85 ml of bidistilled water was added, and the solution was stirred. Then 0.03 ml of 0.015 M  $\text{NaBH}_4$  was added to the resulting solution until the yellow sole remained.

### AgNPs Characterization

The shape and size of AgNPs were determined by the transmission electron microscopy PEM (JEM-2100F) (Japan, Jeol LTD). Samples were prepared by applying a drop of the reaction system to copper nets with a carbon substrate, followed by drying in the air. The UV spectra of the silver sol were recorded using the Cary 60 spectrophotometer (USA, Agilent Cary Technology).

### Obtaining an Electrochemical Sensor Based on the AgNPs

The surface of the graphite electrode (GE) was renewed mechanically using filter paper, then carried out electrochemical polarization of the GE was as follows: GE was placed in an electrochemical cell filled with 0.1 M  $\text{HNO}_3$  and kept in the potentials of  $E = (0.0-1.0)$  V for  $t = 60$  s. Next, GE was rinsed and placed in an electrochemical cell containing 10 ml of the silver sol. AgNPs were allowed to precipitate on the surface of GE with the potential  $E = -0.8$  V for  $t = 300$  s. Then the GE was immediately removed from the silver sol, rinsed with bidistilled water, and transferred to another electrochemical cell filled with 0.1 M NaOH, for the registration of voltammetric  $\text{H}_2\text{O}_2$  curves.

### Equipment

Cyclic voltammetric  $\text{H}_2\text{O}_2$  curves were recorded using the TA-2 analyzer (Russia, Tomsk, TomAnalit LLC) using a three-electrode electrochemical cell consisting of an indicator electrode, a reference electrode, and an auxiliary electrode. GEs modified with AgNPs were used as indicator electrodes, the AgNPs were obtained in the absence of high molecular weight stabilizers using various reducing agents. They are as follows: GE modified with AgNPs obtained by citrate method (Ag-GE-C), GE modified with AgNPs obtained by borhydritcitrate method (Ag-GE-BGC), GE, modified AgNPs obtained by borohydride technique (Ag-GE-BG). Chloride-silver electrodes were used as a reference electrode and an auxiliary electrode.

### The Analytical Procedure

The work used a three-electrode electrochemical cell filled with 10 ml 0.1 M NaOH. The cyclic voltammetric curve of the supporting solution was recorded in a cyclic voltammetry mode on GE - AgNPs in the scan of potentials from -1.0 V to +1.5 V at a potential scanning speed of 100 mV/s. Then, 50  $\mu\text{l}$   $10^{-11}$  M  $\text{H}_2\text{O}_2$  was added to the electrochemical cell, the solution was mixed and the  $\text{H}_2\text{O}_2$  voltammetric curve was recorded under the same conditions.

## RESULTS AND DISCUSSION

Figure-1 shows UV-visible AgNPs spectra obtained using one reducing agent and its mixture. The spectra of all AgNPs samples have absorption strips with  $\lambda_{\max}$  in the range of 340-502 nm. Samples obtained using one reducing agent (dependencies 2 and 3, Fig.-1) have wider stripes compared to the sample obtained when using a mixture of two reducing agents (dependence 1, Fig.-1). AgNPs micrographs are presented in Fig.-2. The distribution of AgNPs in size depending on the used recoverer is presented in Fig.-3.

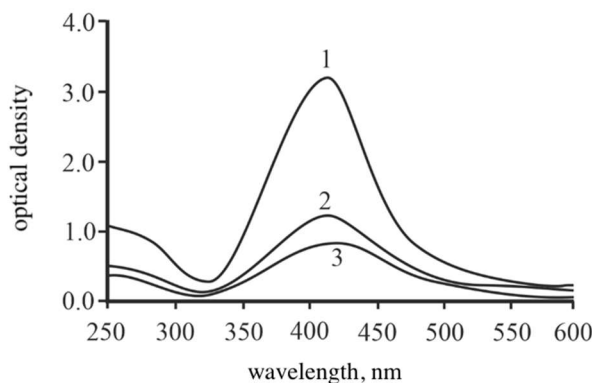


Fig.-1: Optical Spectra of AgNPs: 1 - BGC, 2 - C, 3 - BG

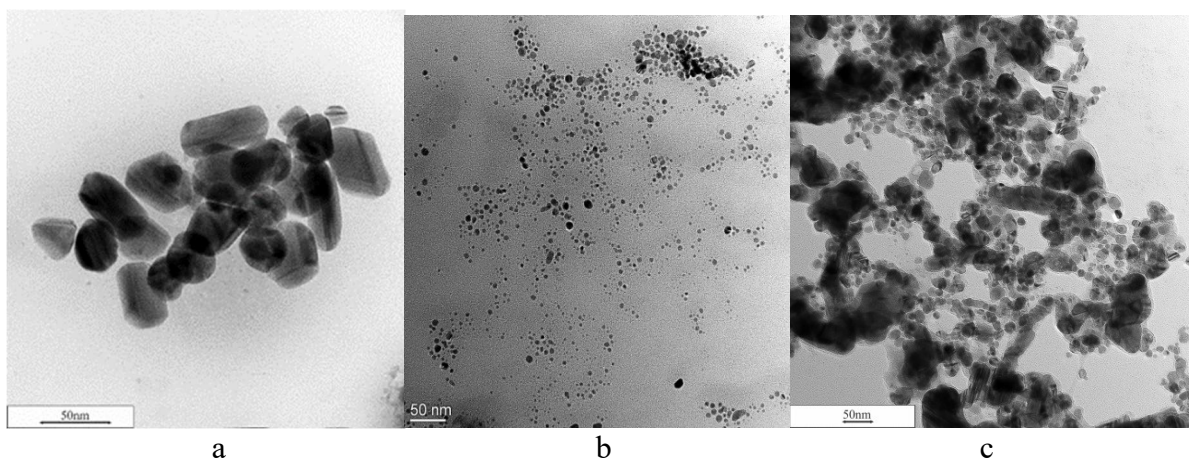


Fig.-2: AgNPs Microphotography Obtained using Sodium Citrate (a), Borohydride And Sodium Citrate (b), Sodium Borohydride (c)

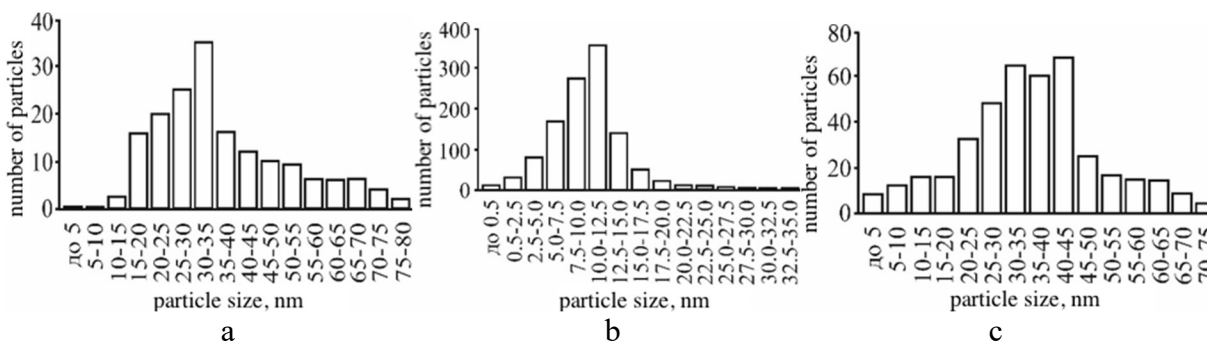


Fig.-3: The AgNPs Distribution Curves Obtained Using Sodium Citrate (a), Borohydride and Sodium Citrate (b), Sodium Borohydride (c) in Size

Previous works<sup>10</sup> show that the type of spectrum,  $\lambda_{\max}$  position, and the distribution of particle diameters are determined by the shape and size of the particles. The highest intensity of the absorption band and the lower wavelength is observed at  $\lambda_{\max} = 411$  nm (curve 1, Fig.-1) for AgNPs-BGC, which is due to the absorption by smaller particles 0.5-17.5 nm (Fig.-3b). The displacement of the plasmon resonance line to

the long-wave region (about 415 nm) (curve 2, Fig.-1) is due to the appearance of an AgNPs-C of larger 10–45 nm size (Fig.-3a). The use of sodium borohydride as a reducing agent leads to a displacement of the absorption band up to 417 nm (curve 3, Fig.-1). This fact is explained by the formation of particles of a spherical form and further agglomeration (Fig.-2b) with a significant increase in particles in the amount of up to 65 nm (Fig.-3b), which is consistent with.<sup>16</sup> PEM images and their distribution in size show that AgNPs-C is the prevailing particle with a size of 10–45 nm, the AgNPs -BGC has 0.5–17.5 nm, and in AgNPs -BG-10–65 nm (Fig.-3a, 3b and 3c), respectively. As can be seen from PEM, AgNPs -BGC have a spherical shape (Fig.-3b), AgNPs -C have particles of various shapes with faces (Fig.-2a), AgNPs -BG has a spherical shape, agglomerated (Fig.-2b). Next, voltammetric studies of the AgNPs received using various reducing agents were conducted. The study of the AgNPs voltammetric curve depending on the composition of the reducing agent, without adding and with the addition of  $\text{H}_2\text{O}_2$  are presented in Fig.-4a and Fig.-4b, in a solution of supported electrolyte 0.1 M NaOH.

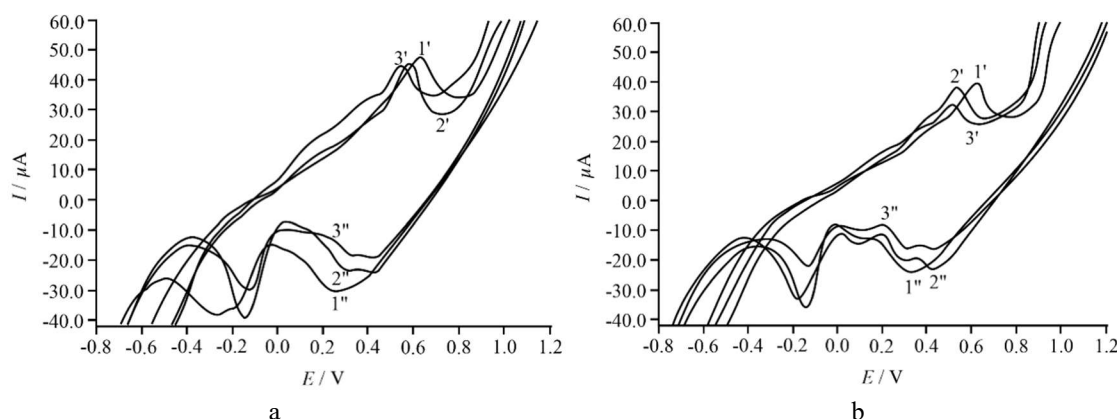


Fig.-4: Voltammetric Curves of AgNPs (a) and AgNPs +  $\text{H}_2\text{O}_2$  (b) in 0.1 M NaOH,  $w = 100 \text{ mB/c}$ : 1', 1'' – AgNP-BGC; 2', 2'' – AgNP-C; 3', 3'' – AgNP-BG

As can be seen from Fig.-4a are AgNPs-C the most electrochemically active (curves 2', 2''). Smaller electrochemical activity in comparison with AgNPs -C has AgNPs-BGC (curves 1', 1''). AgNPs-B has the smallest electrochemical activity (curves 3', 3''). To study the model oxidation reaction between hydrogen peroxide and AgNPs,  $\text{H}_2\text{O}_2$  was added to the electrochemical cell. Figure-4b shows that on the cathode branches of all cyclic curves, there is an additional maximum that meets the  $\text{H}_2\text{O}_2$  reduction process.<sup>17</sup> The potential of this additional maximum in all voltammetric dependencies lies in the potential range from 0.0 to 0.2 V. The maximum activity to  $\text{H}_2\text{O}_2$  was registered with AgNPs-C (curves 2', 2''). Sensors based on AgNPs -BGC (curves 1', 1'') and AgNPs -BG (curves 3', 3'') have less activity.

Table-1: The Average Size of the AgNPs Area Obtained using Various Reducing Agents

| Particles                                     | AgNP-BG                                             | AgNP-BGC                     | AgNP-C                                                                                                              |
|-----------------------------------------------|-----------------------------------------------------|------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Average area, $\mu\text{m}^2$ /particle shape | 0.04–0.09/ spherical<br>(3.7–18.8/<br>agglomerated) | 0.01–0.04–0.09/<br>spherical | 3.3/ parallelepiped<br>1.3/ pyramidal<br>2.7/ prismatic<br>4.4/ cylindrical<br>3.1/ frustum<br>3.0/ hexagonal prism |

Table-1 presents the average size of the AgNPs area obtained using various recovers.

## CONCLUSION

The shape, size, and quantity of AgNPs are determined by the composition of the reducing agent. Thus, the AgNP obtained by simultaneously using borohydride and sodium citrate as reducing agents have spherical shapes with the smallest size of 0.5 to 17.5 nm and an average area of 0.01-0.04-0.09  $\mu\text{m}^2$ . AgNPs obtained using sodium citrate are a mixture AgNPs of various shapes: cylinder-shaped, prismatic, triangular, and pyramidal with particles size from 10 to 55 nm and a large average area of 1.3-2.7-3.3  $\mu\text{m}^2$ . AgNPs obtained

using sodium borohydride as a reducing agent are spherical and agglomerated to particles of 65 nm. The surface area of individual spheres is  $0.04\text{--}0.09\ \mu\text{m}^2$ , with agglomeration, the surface area increases from  $3.7$  to  $18.8\ \mu\text{m}^2$ . Based on spectrophotometric studies, the amount of AgNPs obtained using two reducing agents simultaneously: citrate and sodium borohydride, 3 times more than the amount of AgNPs obtained using just sodium borohydride as a reducing agent. The absorption maximum of such particles is shifted into the field of short waves of waves. It is observed at  $\lambda = 411\ \text{nm}$ , which indicates the smallest amount of particles obtained using two reducing agents. Thus, spectrophotometric studies are consistent with data obtained by translucent electron microscopy. The electrochemical activity of the AgNP-based sensors to  $\text{H}_2\text{O}_2$  also depends on the composition of the reducing agent. The AgNP-based sensor obtained using sodium citrate had the highest electrochemical activity to  $\text{H}_2\text{O}_2$ . The reason for the increase is associated with the form of nanoparticle faces, for example, pyramidal, prismatic; cylindrical nanoparticles have a large surface area of  $1.3\text{--}3.3\ \mu\text{m}^2$ .

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### CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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