

# Influence of Silver Nanoparticles Conditions Synthesis on their Electrochemical Properties

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**Abstract.** The shape, size, optical properties and electrochemical activity of silver nanoparticles (AgNPs) obtained by chemical reduction methods depending on the preparation conditions were investigated. Silver sols consist of AgNPs of different shapes. They are as follows spherical – 30 nm, polyhedral – 35 nm, 50 nm nanorods. It was shown that the position of the absorption spectrum peak in AgNPs depend on the molar ratio of mixture  $\text{AgNO}_3:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ . The maximum of the absorption spectrum peak of AgNPs is shifted by 10 nm to longer wavelengths area in presence excess of a reducing agent or the increasing of boiling time. After storage for one week the spectrum intensity of AgNPs obtained in the mixture  $\text{AgNO}_3:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 = 1:1$  is increased in comparison with freshly prepared AgNPs, which is caused by the increase of AgNPs quantity of a given size. The AgNPs obtained in the mixture  $\text{AgNO}_3:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 = 1:3$  have the most electrochemical activity. The conditions that the AgNPs have the most electrochemical activity were found.

## INTRODUCTION

The scientific and practical interest to AgNPs originated from the time they first obtain. It was originally due to their bacterial and antiviral activity [1-3]. Nowadays AgNPs have used as a signal enhancer in the spectroscopy, material for creating optical devices, sensors [4]. Methods of AgNPs synthesis were described in [5-8]. The development of techniques for the controlled synthesis of nanoparticles of defined size, shape and surface morphology possessing unique electrical, optical as well as biological properties was described in works [9, 10]. Besides AgNPs are non-toxic, they have relatively chemically stability, conductivity, cost effective and eco-friendly in nature.

They have adsorption capacity, ability to scatter light and exhibit catalytic properties that are widely used to produce sensors for the determination of biologically active substances [11]. The electrochemical sensors have special properties of electrode surface area due to the large surface area to facilitate improving sensitivity, selectivity and reproducibility of the biological substances' determination. At the same time, electrochemical methods of biological substances determination on the surface electrode based on metal nanoparticles are essentially simpler and cheaper, than most of other methods such as optical and chromatographic techniques, used in biochemistry, molecular biology, and medical diagnostics [12-14]. Despite a wide range of materials used as mediator, the use of platinum group metals and silver are preferable. In this regard, the purpose of this work is to establish the dependence of the electrochemical activity and optical properties of AgNPs on their preparation conditions.

## EXPERIMENTAL PART

All the chemicals were of analytical grade from Merck. All solutions were prepared on the base of distilled water.

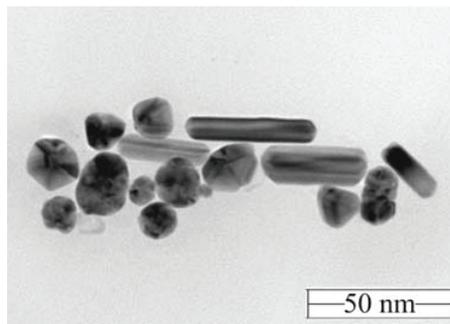
The AgNPs were synthesized by reducing aqueous silver nitrate ( $\text{AgNO}_3$ ) by sodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ ) in the following molar ratios 1:1, 1:3, 1:5 in the absence of stabilizer. Citrate ions play part both reductant and stabilizer that result in the AgNPs formation is particularly sensitive to synthesis conditions.

The obtained mixtures are boiled for 10-15 minutes. The color of the sol depends on the boiling time. Color of first silver sol is changed from colorless to yellow after boiling for 10 minutes. Color of second silver sol is changed from colorless to yellow and to brown after boiling for 15 minutes. Further these sols are cooled to room temperature and stored in a closed vessel.

Fluorescence experiments were performed on a Carry 80 spectrophotometer in glass trays 1 cm thick at room temperature. Transmission Electron Microscope (TEM) images were captured using JSM-5500 (Japan). Voltammetric experiments were performed with electrochemical analyzer TA-2 (Russia) with a conventional three electrode system. The Ag/AgCl (3M KCl) and GE were used as reference, auxiliary and working electrodes respectively. Prior to every experiment the GC electrode was polished by filter paper and the cleaning the surface GE was electrochemically, then was rinsed thoroughly with water. 0.1M NaOH,  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$ , phosphate buffer (pH 6.86) solutions were used as supporting electrolytes. The AgNPs were deposited on the GE surface at accumulation potentials ( $E_{\text{acc}}$ ) from -1.0 to 0.0 V and the accumulation time ( $t_{\text{acc}}$ ) is equal from 50 to 300 s, at potential change rate of 100 mV/s.

## RESULTS AND DISCUSSION

The silver sols are mixtures of silver ion and metal forms. The size and shape of AgNPs was viewed under TEM (Fig. 1).

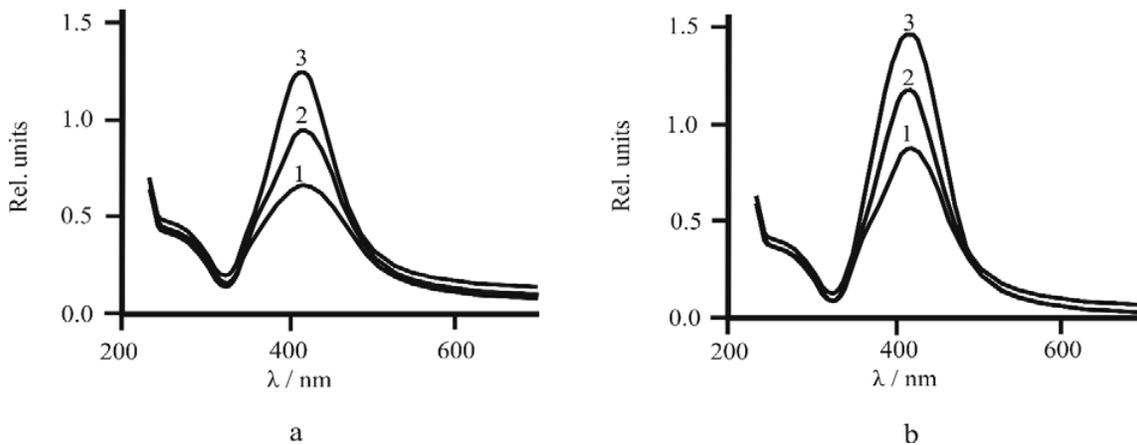


**FIGURE 1.** TEM images of AgNPs

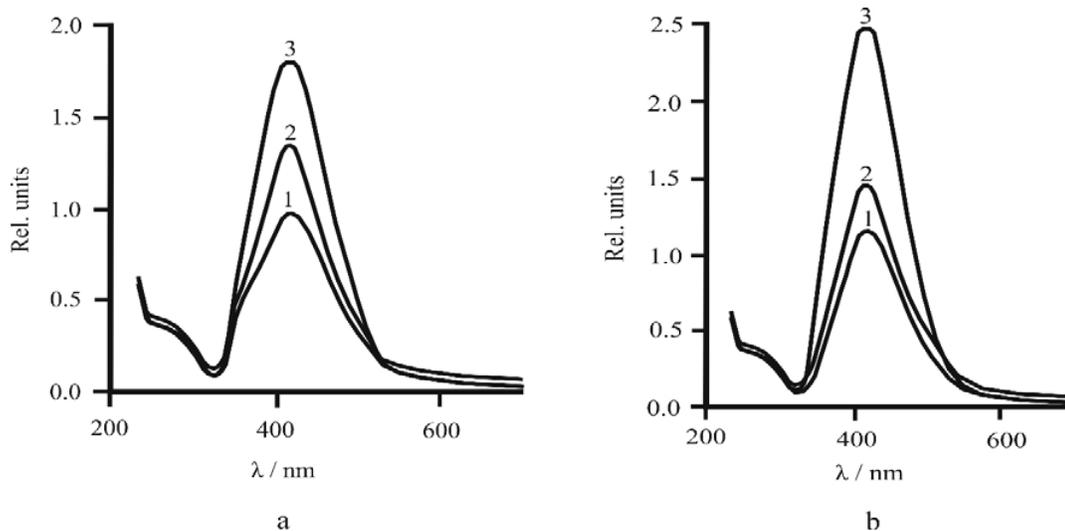
TEM images shows AgNPs that have particles of different shape. They are as follows well-separated spherically shaped, nanorods, polyhedral particles. The average size of polyhedral particles is 35 nm, one of spherical particles is 30 nm and one of nanorods is 47 nm.

The formation of AgNPs was studied by the spectrophotometric method. The UV-vis absorption spectra of prepared samples are shown in Fig. 2, 3. The yellow AgNPs obtained under a molar reactant ratio of 1:1 displayed absorption peak, the characteristic surface plasmon resonance (SPR) band for silver, centered from 402 nm. As can be seen from Fig. 2 (curves 1-3). The increased volume of reducing agent AgNPs intensity of SPR decreases. The maximum absorption bands of AgNPs is red-shifted to 409 nm due to the increased size of Ag-NPs [15, 16].

The first addition of  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$  (curve 2, Fig. 2a) led to the broadening of the AgNPs SPR peak relative to the sample 1 (curve 1, Fig. 2a). Greater volumes of  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$  (curve 3) increased the absorbance due to increases in silver concentration [15].



**FIGURE 2.** The UV-visible spectra of yellow Ag-NPs prepared under different molar ratio  $\text{AgNO}_3:\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 = 1:1$  (1), 1:3 (2), 1:5 (3) (a) and storage (b).

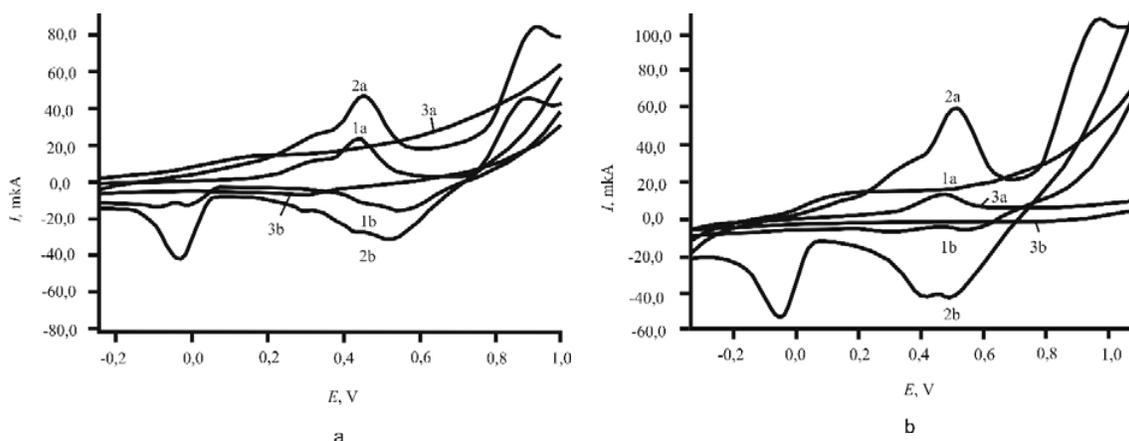


**FIGURE 3.** The UV-visible spectra of brown Ag-NPs prepared under different molar ratio  $\text{AgNO}_3:\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 = 1:1$  (1), 1:3 (2), 1:5 (3) (a) and storage (b).

The obtained brown AgNPs displayed absorption peak, the characteristic SPR band for silver, centered from 414 indicating the formation of AgNPs with size of 30-50 nm (Fig. 2b). These results demonstrated good agreement with the results obtained in the TEM images of Ag-NPs (Fig. 1).

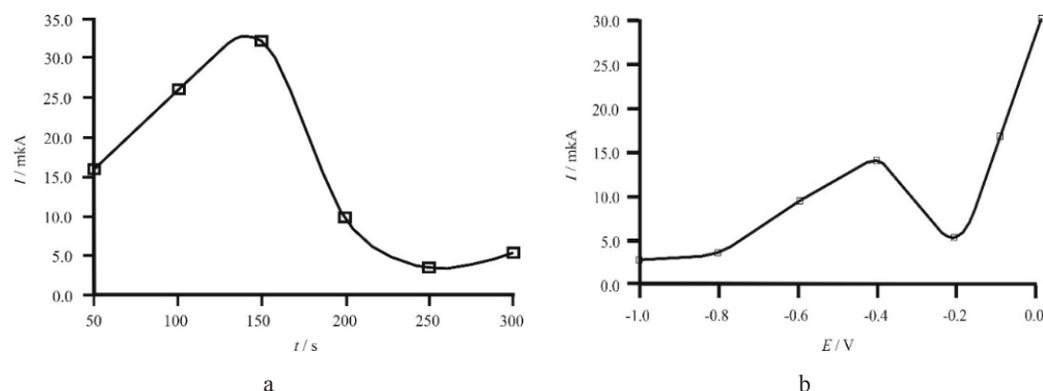
Thus the maximum absorption band of AgNPs is red-shifted to 417 nm by increasing the boiling time and increasing the amount of reducing agent indicating a greater amount of AgNPs obtained at excess reductant.

The optical density of yellow and brown AgNPs obtained under a molar reactant ratio of 1:1 after storage for a week (curve 1, Fig. 2a, 3a) is larger than one of freshly prepared AgNPs (curve 1, Fig. 2b, 3b) which is caused by increasing amounts of AgNPs of the same size. The optical density of yellow (curve 2, 3, Fig. 2b) and brown AgNPs (curve 2, 3, Fig. 3b) under a molar reactant ratio of 1:3, 1:5 slightly change. The maximum position does not change indicating the stability of AgNPs at this ratio. This fact is due to the formation of more amount AgNPs of determined size.



**FIGURE 4.** Electrochemical activity of yellow AgNPs (a), brown AgNPs (b) from  $(\text{AgNO}_3:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7)$ : 1:1 – 1, 1:3 – 2, 1:5 – 3 in 0.1 M NaOH.

Electrochemical activity of yellow AgNPs reduced with increasing amounts of the reducing agent (curves 2-3, Fig. 4a). In the presence excess of citrate ion potentials of the anode (curve 2a) and cathode (curve 2b) maxima shift to field of negative potentials values. Therefore, the AgNPs oxidation process is facilitated, the activation energy decreases.



**FIGURE 5.** Electrochemical activity yellow AgNPs from accumulation time (a), from accumulation potential in 0.1 M NaOH.

Brown AgNPs prepared under a molar reactant ratio of 1:3 are the most electrochemically active (curve 2, Fig. 4b). Their activity is 1.3 times more than the yellow AgNPs in the same molar ratio of reagents (curve 2, Fig. 4b). AgNPs obtained under a molar reactant ratio of 1:1 are not active which is due to complete reduction of silver ions in the elementary state (curve 1, Fig.4b). The electrochemical activity of brown AgNPs obtained in excess of sodium citrate is three times less than one of AgNPs obtained under equimolar ratio of reagents (curve 3, Fig. 4b).

Thus, the most electrochemically active brown AgNPs obtained in a molar ratio of 1:3.

To select the conditions in which AgNPs have the most electrochemical activity factors determining the height of the anode current dissolving silver were investigated: the nature of the supporting electrolyte, the accumulation potential ( $E_{\text{acc}}$ ) and the accumulation time ( $t_{\text{acc}}$ ). It is shown that the height of the anode current dissolving Ag is greatest in the supporting electrolyte NaOH. While in neutral supporting electrolytes such as  $\text{K}_2\text{SO}_4$ ,  $\text{NaNO}_3$  phosphate buffer (pH 6.86) electrochemical signals is 6 times less than in NaOH.

It is shown that at first the height of anodic current dissolving Ag from sol is increased with increasing accumulation time from 60 to 150 s (curve (a), Fig.5). Then the height of anodic current dissolving Ag is decreased with increasing accumulation time. Therefore the accumulation time of silver was chosen 150 s on the GE surface. As can see that the height of the anode current silver dissolution has the two greatest values at potentials  $E = -0.4$  V

and 0.0 V (Fig. 5 b). The increase in the height of the anode current dissolving silver at  $E = 0.0$  V is due to the large contribution of adsorption. To avoid the adsorption on AgNPs oxidation the accumulation potential of silver has been selected -0.4 V. Thus, the conditions in which AgNPs are most electrochemically active have been chosen. They are as follows accumulation potential of silver  $E_{acc} = -0.4$  V,  $t_{acc} = 150$  s, supporting electrolyte 0.1 M NaOH.

## CONCLUSION

Silver sols were obtained by citrate reduction method of  $\text{AgNO}_3$  solution in molar ratios of  $\text{AgNO}_3:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 = 1:1, 1:3, 1:5$  in a neutral medium. These silver sols consist of AgNPs of different shapes. They are as follows spherical – 30 nm, polyhedral – 35 nm, 50 nm nanorods.

It was shown that the position of the absorption spectrum peak in AgNPs depends on the molar ratio of  $\text{AgNO}_3:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ . The maximum of the absorption spectrum peak in silver sols is shifted by 10 nm to longer wavelengths area in presence excess of a reducing agent. After storage for one week the spectrum intensity of AgNPs obtained at equimolar ratio of reagents is increased in comparison with freshly prepared AgNPs, which is caused by the increase of AgNPs quantity of a given size. When stored for a week the spectra intensity of AgNPs obtained in the presence excess of a reducing agent changes slightly, that indicates at the stability of these AgNPs.

It was shown that the AgNPs obtained in molar ratios 1:3 have the most electrochemical activity. The conditions in which AgNPs have the greatest electrochemical activity were found. They are as follows: consist of silver sols  $\text{AgNO}_3:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 = 1:3$ ,  $E_{acc} = -0.4$  V.  $t_{acc} = 150$  s, supporting electrolytes 0.1 M NaOH.

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