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Sonoelectrochemical Synthesis of Silver Nanoparticles in Sodium Polyacrylate Solution

Orest Kuntyi ¹^(b), Mariana Shepida ^{1,*}^(b), Martyn Sozanskyi ²^(b), Yuriy Sukhatskiy ¹^(b), Artur Mazur ¹^(b), Andriy Kytsya ³^(b), Liliya Bazylyak ³^(b)

- ¹ Department of Chemistry and Technology of Inorganic Substances, Lviv Polytechnic National University, Lviv, 79013, Ukraine
- ² Department of Physical, Analytical and General Chemistry, Lviv Polytechnic National University, Lviv, 79013, Ukraine
 ³ Department of Physical Chemistry of Fossil Fuels of the Institute of Physical-Organic Chemistry and Coal Chemistry
- named after L.M. Lytvynenko of the National Academy of Sciences of Ukraine, Lviv 79060, Ukraine
- * Correspondence: maryana_shepida@ukr.net;

Scopus Author ID 57203884662

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Abstract: The paper shows the effectiveness of a "green" synthesis of silver nanoparticles (AgNPs) in sodium polyacrylate (NaPA) solutions by sonoelectrochemical method using silver sacrificial anodes. Using the cyclic voltammetry in the ultrasonic field in the range of E from 1.0 to -1.0 V, the temperature and NaPA concentration are the main parameters influencing the rate of synthesis and the size of AgNPs. As these parameters increase, the rate of nanoparticle synthesis increases. According to TEM studies, with increasing temperature and decreasing NaPA concentration, there is a tendency to increase the size of AgNPs. However, in all of the cases, the size of AgNPs does not exceed 30 nm. Using the UV–Vis spectroscopy, it was found that the position of the absorption peak at c.a. 500 nm, corresponding to the silver nanoparticles, is practically not shifted during numerous cycles. This fact may indicate the stability of sonoelectrochemical synthesis of AgNPs in time. Synthesized AgNPs revealed high antibacterial activity against gram-positive and gram-negative strains of typical pathogens of nosocomial infections, demonstrating the prospect of using sonoelectrochemical technique for obtaining silver colloids as a component of bactericidal drugs.

Keywords: sonoelectrochemical synthesis; silver nanoparticle; sodium polyacrylate; silver electrode, antimicrobial activity.

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1. Introduction

Silver nanoparticles (AgNPs) are the most investigated objects among known ones at present and have great potential in a broad range of applications [1] due to their catalytic activity, high antimicrobial efficiency, they are effective as drug-delivery carriers; at the same time, they possess by anti-thrombogenic, antiplatelet and antihypertensive properties [1–4]. Due to the problem of bacterial resistance [4], AgNPs are considered as alternative antibacterial nanobiotics.

The functional properties of AgNPs significantly depend on their geometry, *i. e.*, shape, and size [4–6].

In the tuple "method and parameters of synthesis \rightarrow geometry of nanoparticles \rightarrow properties \rightarrow function \rightarrow field of application" the first element is crucial. Therefore, the maximum control over nanoparticles' formation at the stages of their nucleation and growth is

one of the main criteria for choosing the synthesis method [6–9]. At present, the most common are chemical methods, which include reduction of Ag⁺ ions to Ag⁰ and stabilization of the formed nanoclusters (AgNCs) and AgNPs [3, 7, 10–12]. At the same time, in the last decade, we can observe a trend towards "green" synthesis, which involves the use of non-toxic precursors, and, above all, of natural origin [11, 12]. They mainly represent by themselves the reducing agents and surfactants simultaneously. However, regardless of the nature of precursors, the chemical reduction does not provide in the process of synthesis of a stable concentration of reducing agent, metal ions, and the ratio of their concentrations. Accordingly, the controllability of the synthesis of metal nanoparticles becomes more complicated in terms of their geometry. These parameters are decisive for the rate of nucleation and growth of nanoparticles [13–15]. Therefore, in the last decade, we can observe an increased interest in the electrochemical synthesis of AgNPs, which allows regulating the rates of these processes by the values of cathode potentials or cathode current densities [16–21]. The last parameters are controlled, and the formation of nanoparticles is controlled accordingly. Also, electrochemical synthesis is performed without a chemical reducing agent, and for electrolysis with sacrificial silver anodes [17, 19–21] without Argentum salt. This reduces the number of precursors in the solution, contributing to the control of AgNPs synthesis and meets the criteria of "green" technologies.

In the last decade, the studies of the effects of ultrasonic fields on the intensification of the electrochemical synthesis of metal nanoparticles (MNPs) increased [22–27]. In addition, sonoelectrochemical synthesis increases the design possibilities of MNPs and makes the method highly competitive with the more conventional ones. However, the references have a little description of the mutual influence of the parameters of sonoelectrochemical synthesis and the nature of the surfactant on the formation of metal nanoparticles' solutions. This hinders the creation of theoretical foundations of sonoelectrochemical synthesis of MNPs and, accordingly, hinders the development of controllable techniques of their production.

The proposed study aimed to study the "green" synthesis of AgNPs in sodium polyacrylate (NaPA) solutions by sonoelectrochemical method using silver sacrificial anodes. NaPA is a non-toxic anionic polymeric surfactant, which is used as an effective stabilizer of silver nanoparticles during chemical [28, 29] and electrochemical [20, 21] syntheses.

2. Materials and Methods

2.1. Electrochemical measurements.

Cyclic voltammetric studies were carried out using a standard three-electrode electrochemical cell (volume is 50 mL) and potentiostat PI-50-1. Silverplate (14,4 cm²) were used as working and auxiliary electrodes. The reference electrodes Ag/AgCl (EVL-1M4 was purchased from "Systema Optymum" Lviv, Ukraine) mounted in a Luggin capillary containing 1 mol L⁻¹ KNO₃ were used. The working electrode was polished using alumina slurry (0.5 μ m) before each scan. The scan rate of the potential was 50 mV s⁻¹ in the range of E from +1.0 to -1.0 V. The study of the anode behavior of silver was carried out in solutions of NaPA at pH = 8.0...9.5, t = 2...60 °C and the concentration of NaPA was 1...10 g L⁻¹.

For sonoelectrochemical synthesis of colloidal solutions of silver nanoparticles, an ultrasonic emitter of the magnetostrictive type "Ultrasonic Disintegrator" UD-20 (Poland) was used (Figure 1). The frequency of ultrasonic radiation is 22 kHz. The useful specific power of ultrasonic radiation is 40...62.5 W dm⁻³ Isothermal conditions of sonoelectrochemical

synthesis of colloidal solutions of silver nanoparticles were provided by UTU-4 ultrathermostat.

The UV-vis spectra of the colloidal solutions containing silver particles were recorded by UV/vis spectrophotometer ULab 108UV (ULab, China) using 1 cm cuvette at wavelength range 190–1100 nm. The comparison solution is distilled water.



Figure 1. Sonoelectrochemistry set-up used in the production of colloid solutions silver nanoparticle.

TEM images of the samples were recorded using a JEM-I230 (JEOL, Tokyo, Japan) with an acceleration voltage of 80 kV. The samples for TEM investigations were prepared by drying 0.05 μ L of silver sol on the carbon grid at room temperature. The diameters of obtained AgNPs were determined using TEM images by comparing individual particles' sizes with the scales presented on images.

2.2. Investigations of the antimicrobial activity of AgNPs.

Staphylococcus aureus ATCC 25923 (gram-positive bacteria), Escherichia coli ATCC 25922 (gram-negative bacteria), and Candida albicans ATCC 885-653 (fungi) were used as test strains for the investigations of antimicrobial activity of synthesized AgNPs. These strains are typical pathogens of nosocomial infections. Suspensions (suspensions density equals 0.5 units on the *McFarland* scale) with test strains of each microorganisms species were preliminarily prepared using a *Densi-La-Metr* instrument. A container containing 1 cm³ of suspension with a certain test strain, 9 cm³ of colloidal solution of synthesized AgNPs was added. After 1, 6, 18, and 48 hours of exposition, the reseeding of a system consisting of a suspension with a specific test strain and a colloidal solution of AgNPs stabilized with NaPA solution on Petri dishes with a solid selective medium were performed. As a nutrient media for *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans*, the yellow-salt agar, Endo agar, and Saburo agar were used, respectively.

3. Results and Discussion

During the electrochemical synthesis of AgNPs by nonstationary current supply [20] (cyclic voltammetry), in particular, in NaPA solutions and the presence of sacrificial anodes, undergo the reactions of the formation of $[(Ag^+)_mPA]^{(n-m)-}$ (1) complexes followed by their reduction and the formation of nanoclusters $[(Ag^0)_mPA]^{n-}$ (2). The number of atoms (m) in https://biointerfaceresearch.com/

nanoclusters and, accordingly, their sizes depend on the duration of the reduction process and the concentration of PA^- ions. Moreover, the growth process is multi-stage with the formation of intermediate positively charged "magic" cluster Ag_{x^+} [28].

In the anode period:
$$mAg + PA^{n-} \rightarrow [(Ag^+)_m PA]^{(n-m)}$$
 (1)
In the cathode period: $[(Ag^+)_m PA]^{(n-m)-} + me \rightarrow [(Ag^0)_m PA]^{n-}$ (2)

In the ultrasonic field, there is an intensification of processes in the anode and cathode periods. Thus, the anode currents increase by *c.a.* 30 % (Figure 2) and, accordingly, the rate of generation of the precursor $[(Ag^+)_m PA]^{(n-m)-}$ for the synthesis of AgNPs via reaction (1) is increased. The reason for this is the depolarizing effect of ultrasound due to the acceleration of diffusion in the electrode layer.



Figure 2. Cyclic voltammograms of the redox processes of silver in a water solution of NaPA (5 g L⁻¹) in the ultrasonic field and without it.

Ultrasound also significantly accelerates the reduction of ions $[(Ag^+)_mPA]^{(n-m)-}$ with the formation of AgNPs (Figure 3). This is because simultaneously with the electrochemical reduction in the cathode period (2), there is a reduction by radicals formed during sonolysis of water [30, 31] and the decomposition of organic compounds [32]. First of all, these are the radicals H· (3) and R· (4). The latter can be formed by sonolysis of surfactant. Therefore, the sonochemical reduction of Ag(+) by radicals can be represented by the reaction equation (5, 6).

H ₂ O))) \rightarrow H· + ·OH	I			(3)
			0 (77.)		

$$RH + \cdot OH(\cdot H) \quad))) \rightarrow R \cdot + H_2O(H_2) \tag{4}$$
$$[(Ag^+)_m PA]^{(n-m)-} + mH \cdot \rightarrow [(Ag^0)_m PA]^{n-} + mH^+ \tag{5}$$

$$[(Ag^{+})_{m}PA]^{(n-m)-} + mR \cdot \rightarrow [(Ag^{0})_{m}PA]^{n-} + mR' + mH^{+}$$
(6)

Using the UV–vis spectroscopy, it was found that in the presence of the ultrasonic field, the AgNPs formation rate in times exceeds the AgNPs formation rate without the action of the ultrasonic field. This fact is illustrated in Figure 3 by increasing the absorption peak at 500 nm, which corresponds to the absorption of AgNPs. This indicates the crucial role of reactions (5, 6) in reducing Ag(I). The reactions (5, 6) cause the formation of nanoclusters, in particular, the intermediate positively charged "magic" cluster Agx⁺ [28], which corresponds to the maximum absorption in the ultraviolet region about 350 nm (Figure 3, *a*). Over time, the intensity of this maximum is decreased, and in 2-3 days, it is disappeared. Simultaneously, the intensity of the



maximum at 500 nm increases, which is due to the process of reduction of the "magic" cluster Ag_x^+ and their subsequent enlargement with the formation of AgNPs nanoparticles.

Figure 3. UV-Vis spectra of silver nanoparticles synthesized in a water solution of NaPA (5 g L⁻¹) in the ultrasonic field (*a*) and without it (*b*), t = 20 °C.

The ultrasonic field also promotes the formation of nanoparticles smaller in size compared to AgNPs electrochemically synthesized without ultrasound (Figure 4). This is due to the acceleration of mass transfer in the bulk of the solution (overall mass transport, increasing reaction rates). Accordingly, the reduction reactions of Ag(+) proceed with higher rates, which contributes to the process of nucleation, *i.e.*, the formation of nanoclusters. The latter corresponds to a clear maximum of 350 nm (Figure 3, *a*). During electrochemical synthesis without ultrasound (Figure 3, *b*), only the "shoulder" at ~300 nm is observed, which can be attributed to the so-called "magic" cluster Agx⁺ [28].



Figure 4. TEM images of AgNPs synthesized in solution NaPA (5 g L^{-1}) by cyclic voltammetric (during 20 cycles) without ultrasonic field (a) and in the ultrasonic field (b), t = 20 °C.

During numerous voltammetry cycles in the ultrasonic field, the values of anodic currents corresponding to silver dissolution by reaction (1) are changed slightly (Figure 5, a). The absorption maxima positions at 350 nm and 500 nm, corresponding to the nanoclusters and nanoparticles of silver, respectively, are practically not shifted during numerous cycles (Figure 5, b). Therefore, sonoelectrochemical synthesis of AgNPs is stable over time.



Figure 5. Cyclic voltammograms of silver in water solution NaPA (5 gL⁻¹) (a) and UV-Vis spectra of silver nanoparticles synthesized in the ultrasonic field (b), t = 20 °C.

The main factors influencing the process of synthesis of AgNPs by non-stationary electrolysis and sacrificial electrodes are the surfactant's temperature and concentration [20, 21].

3.1. Influence of temperature.

With an increase of temperature by 10 0 C, the increase of the anode currents' values does not exceed 40 % (Figure 6, *a*), which indicates the diffusion nature of the process.

The effect of temperature on the rate of formation of AgNCs and AgNPs is much more noticeable only in the range of 20... 30 0 C (Figure 6, *b*). Thus, the maxima at 350 and 500 nm with increasing temperature from 20 to 30 0 C increases in ~1.5 and ~3 times, respectively. Some increase in AgNCs and AgNPs formation rate is also observed in the range of 30-50 0 C. A further increase of the temperature does not cause an increase in the maximum at 500 nm, and the maximum at 350 nm is transformed into the "shoulder". Such transformation of UV–vis spectra may indicate that the increase of a temperature accelerates the transformation of AgNCs into AgNPs.

One of the features of sonoelectrochemical synthesis of nanoparticles in solution is a sharp increase of temperature and pressure in the collapse of cavitation bubbles, leading to heating of the solution due to thermal conductivity. Intensification of diffusion processes as well as heat and mass transfer processes is one of the primary effects of ultrasonic (acoustic) cavitation.

At the temperature of 20 0 C, the dispersing effect of cumulative high-velocity microjets (secondary effect of ultrasonic cavitation), which occur in the final stage of flattening of cavitation bubbles, causes the uniform distribution of Ag⁰ nuclei in the volume of solution and promotes the formation of silver nanoclusters and their subsequent slow transformation into nanoparticles. Therefore, a synergistic effect of these factors (namely, dispersing action and the presence of a stabilizer) in creating of steric barriers and, accordingly, an energy barrier, to counteract of *Van der Waals* forces between nanoparticles, which hindered their agglomeration (~ 60 % of nanoparticles with sizes in the range of 4... 6 nm, Fig. 7 *a'*) was observed.

At higher temperatures (30 and 50 0 C) the intensity of desorption of surfactant molecules (sodium polyacrylate) from the surface of nanoclusters and silver nanoparticles increases significantly. The rheological characteristics of the solution (viscosity and density) are decreased, which increases the probability of nanocluster collisions in solution. In addition, the long-term dispersing effect of ultrasonic radiation on solutions of silver nanoparticles

contributes to the emergence of uncompensated charges on the surface of nanoparticles, i. e. an increase of surface energy.



Figure 6. Cyclic voltammograms (*a*) and UV-Vis spectra (*b*) of silver nanoparticles synthesized in water solution NaPA (5 gL⁻¹) at different temperatures t = 20-60 °C. Scan rate of 50 mVs⁻¹.



Figure 7. TEM images of AgNPs, synthesized in solution NaPA (5 g L⁻¹) at different temperatures t = 20 (*a*), 30 (*b*), 50 (*c*) °C and histograms of the normal distribution of AgNPs at appropriate temperature (*a'*, *b'*, *c'*).

The synergism of three factors (desorption of surfactant molecules from the surface of nanoclusters and silver nanoparticles; decrease in density and viscosity of the solution; the occurrence of uncompensated surface charges) caused the formation of the thermodynamically unstable system, and it was illustrated by the agglomeration of nanoclusters and silver nanoparticles, *i. e.* by increasing of the size of obtained AgNPs. That is why at higher temperatures (30, 50 °C), the removal of steric interference increases the rate of transformation of nanoclusters into nanoparticles. As a result, at a temperature of sonoelectrochemical synthesis of 30 °C the, size of about 60 % of nanoparticles were in the range of 6...8 nm (Fig. 7 *b*'), but at a temperature of 50 °C the, sizes of ~ 60 % of nanoparticles were larger and were in the range of 10...12 nm (Fig. 7 *c*').

With increasing temperature, there is a tendency to increase the size of nanoparticles (Figure 7). However, even at 50 0 C, the diameter of AgNPs does not exceed 20 nm. Therefore, the temperature range of 20-50 0 C is rational for the sonoelectrochemical synthesis of AgNPs.

3.2. The effect of NaPA concentration.

Increasing the concentration of surfactants, which are polymeric ligands, promotes the anodic reaction (1). This causes an increase of the anode currents (Figure 8) and, accordingly, the generation of complexions $[(Ag^+)_mPA]^{(n-m)}$. Since such complexes are the precursors of AgNPs, increasing the concentration of NaPA is an effective factor in the increase in the rate of sonochemical synthesis of nanoparticles.



Figure 8. Cyclic voltammograms of silver at different NaPA concentrations at 50 °C. Scan rate of 50 mVs⁻¹.

As the concentration of polyacrylate ions increases, there is a tendency to decrease the size of AgNPs (Figure 9). This is due to the increase of the efficiency of stabilization of nanoparticles and is characteristic for chemical [28, 29] and electrochemical [20, 21] methods of metal nanoparticles preparation.

3.3. Antibacterial activity of solutions of synthesized AgNPs.

High antibacterial efficiency of silver nanoparticles is achieved due to their developed surface, which provides maximum contact with the environment. Such nanoparticles are also quite small and can penetrate cell membranes to affect intracellular processes from within. The bactericidal effect of silver nanoparticles strongly depends on their size and increases with decreasing size of AgNPs. The main requirements for AgNPs as for component of antimicrobial drugs for biomedical purposes (in particular, in the manufacturing of bactericidal solutions, bandages, etc.) are their hydrophilicity and low toxicity. From this point of view, obtained AgNPs solutions are very promising due to 1) sonoelectrochemical synthesis involves the absence of toxic precursors; 2) NaPA as a stabilizer is a hydrophilic and low toxic agent [33]. That is why the antimicrobial activity of obtained colloidal solutions of AgNPs was investigated (see Tables 1 and 2).



Figure 9. TEM images of AgNPs obtained in NaPA solution (t= 50 °C) C = 1 g l^{-1} (a); C = 5 g l^{-1} (b) and histograms of the normal distribution of AgNPs at appropriate concentrations (a', b').

10 J g/L.							
Test strain	Exposure time, hours	The number of microorganisms, CFU/cm ³	Disinfecting action				
	1	150	—				
Staphylococcus aureus	1 150 2000000000000000000000000000000000000	not found	+				
ATCC 25923	18	not found	+				
	48	not found	+				
	1	not found	+				
Escherichia coli	6	not found	+				
ATCC 25922	18	not found	+				
	48	not found	+				
	1	not found	+				
Candida albicans	6	not found	+				
ATCC 885-653	18	not found	+				
	48	not found	+				

Table 1. Antimicrobial (disinfectant) properties of AgNPs synthesized at 20 0 C and NaPA concentration equal to 5 g/L

CFU - colony-forming units;

+ pronounced antimicrobial (disinfecting) effect (no growth of microorganisms);

– no antimicrobial (disinfectant) action (available growth of microorganisms).

Test strain	Exposure time, hours	The number of microorganisms, CFU/cm ³	Disinfecting action			
	1	180	—			
Staphylococcus aureus	6	3	_			
ATCC 25923	18	not found	+			
	48	not found	+			
	1	40	_			
Escherichia coli	6	9	_			
ATCC 25922	18	not found	+			
	48	not found	+			
	1	not found	+			
Candida albicans	6	not found	+			
ATCC 885-653	18	not found	+			
	48	not found	+			

Table 2. Antimicrobial (disinfectant) properties of AgNPs synthesized at 50 0 C and NaPA concentration equal to 5 g/L.

The antimicrobial properties of AgNPs can be explained by two different mechanisms: 1) fixation of AgNPs on cell membranes subsequent by their penetration into the cell with subsequent damage of the membrane and release of cell contents (so-called "*trojan-horse mechanism*") [34]; 2) release of Ag⁺ ions, which have antimicrobial properties.



Figure 10. Antimicrobial activity of colloidal solutions of AgNPs synthesized by sonoelectrochemical method at 20 ⁰C against *S. aureus* ATCC 25923 (*a*); *E. coli* ATCC 25922 (*b*) and *Candida albicans* ATCC 885-653 (*c*).

The antimicrobial (disinfection) effect of colloidal solutions of AgNPs synthesized by sonoelectrochemical method at 20 0 C is absolute for strains *Escherichia coli* ATCC 25922 and *Candida albicans* ATCC 885-653 (Fig. 10). The antimicrobial activity of AgNPs colloidal solutions synthesized by sonoelectrochemical method at a temperature of 50 0 C is less pronounced and is absolute only for the *Candida albicans* ATCC 885-653 (Fig. 11).



Figure 11. Antimicrobial activity of colloidal solutions of AgNPs synthesized by sonoelectrochemical method at 50 °C against *S. aureus* ATCC 25923 (*a*); *E. coli* ATCC 25922 (*b*) and *Candida albicans* ATCC 885-653 (*c*).

The lower level of inactivation of strains of microorganisms *Staphylococcus aureus* ATCC 25923 and *Escherichia coli* ATCC 25922 by colloidal solutions of AgNPs synthesized at 50 $^{\circ}$ C may be caused by the higher content of AgNPs with larger sizes (Fig. 7 *c'*), compared to the content of such particles in solutions synthesized at 20 $^{\circ}$ C (Fig. 7 *a'*). This means that the increase of the size of AgNPs makes it difficult to fix them on cell membranes by mechanism 1 (*vide supra*) and, accordingly, leads to a decrease of the antimicrobial activity of the synthesized solutions of AgNPs.

4. Conclusions

It was shown that spherical AgNPs ($\lambda_{max} = 500 \text{ nm}$) with sizes up to 30 nm are formed in NaPA solutions by sonoelectrochemical method using silver sacrificial anodes. The use of silver electrodes under cyclic voltammetry at E = 1.0...-1.0 V in the ultrasonic field allows the synthesis of nanoparticles in a solution of surfactant only. This minimization of the number of precursors contributes to the controllability of the process of formation of AgNPs in size and meets the requirements of "green" synthesis. In addition, the balance of the rates of anodic dissolution of silver and reduction of the formed Ag(I) ions meets the technological requirements. The rate of AgNPs synthesis increases with increasing of temperature solution and NaPA concentration. As the temperature increases, there is a tendency to increase the size of AgNPs. An increasing increase in the concentration of NaPA leads to a decrease in the size of AgNPs. These parameters are the main in the proposed sonoelectrochemical method of synthesis. The antimicrobial activity of synthesized AgNPs against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans*, which are pathogens of nosocomial infections, was studied. It was observed that the obtained silver colloids could inhibit the growth of microorganisms.

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Conflicts of Interest

The authors declare no conflict of interest.

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