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*O.A. Pivovarov^a, M.I. Skiba^a, A.K. Makarova^a, V.I. Vorobyova^b, O.O. Pasenko^a***PREPARATION OF SILVER NANOPARTICLES BY CONTACT NONEQUILIBRIUM LOW-TEMPERATURE PLASMA IN THE PRESENCE OF SODIUM ALGINATE**^aUkrainian State University of Chemical Technology, Dnipro^bNational Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv

The paper deals with the preparation of silver nanoparticles by means of contact nonequilibrium low-temperature plasma in the presence of naturally-occurring stabilizer (sodium alginate). The formation of silver colloidal solutions in the presence of stabilizer is confirmed by the presence of peak with $\lambda_{\max}=400-440$ nm in absorption spectra. The effects of concentration of sodium alginate and duration of processing by plasma discharge on the production of silver nanoparticles were studied. The content of sodium alginate in the reaction medium (5.0 g/l) is sufficient for nanoparticles stabilization. The content of nanoparticles grows with an increase in duration of plasma action on the solution; processing during 5 minutes provides formation of silver nanoparticles. The formation of silver metal particles is confirmed by X-ray diffraction analysis. The average size of the formed silver particles is up to 100 nm. The aggregative stability of silver nanoparticles is evaluated. Zeta-potential of plasma-chemically obtained colloidal solutions at various concentrations of stabilizer varies from -32.8 to -39.3 mV. The introduction of sodium alginate into silver nitrate solution before the treatment with contact nonequilibrium plasma allows obtaining colloidal solutions of silver which are stable during four weeks.

Keywords: nanoparticles, silver, contact nonequilibrium low-temperature plasma, stabilization, sodium alginate.

Introduction

Combination of the optical and antimicrobial properties of silver nanoparticles gives an opportunity of practical application thereof in various spheres of human activity. One of the main issues impeding their widespread use in different industries is the lack of ecological and innovative procedures for obtaining stable nanoparticles with specified properties. Therefore, development of new methods for the fabrication of stable solutions of silver nanoparticles is now a crucial task.

Colloidal stability of silver nanoparticles to a certain extent depends on the method of their production as well as on the nature of stabilizing agent. One of the innovative and environmentally safe methods for preparation of nano-sized compounds is the use of plasma discharges of various configurations as follows [1]: plasma discharge generated between the electrodes immersed in the liquid [2], plasma at gas-liquid phase interface at reduced pressure [3], plasma at the atmospheric pressure in the interaction with the liquid [4]. Among plasma-chemical discharges, contact nonequilibrium

low-temperature plasma (CNP) is a promising option from the point of view of practical application. Plasma discharge is generated between the electrode in the gaseous phase and surface of the liquid where the other electrode is located. Therefore, chemical transformations at the phase interface are conditioned by the combined effect of electrochemical oxidation-reduction, initiated photolysis reactions, UV radiation and flow of charged particles from the gaseous phase to the surface of the liquid medium [5]. By varying the composition of liquid phases it is possible, in some degree, to manage the paths of chemical transformations and composition of obtained products [6,7]. In previous work the authors showed the efficiency of CNP use for fabrication of silver nanoparticles from the aqueous solutions of metal salts by one-shot process without additional reducing agents [8]. The studies prove that plasma-chemically obtained silver nanoparticles in aqueous solutions are characterized by relative stability. However, for the subsequent practical application it is feasible to choose the stabilizer and establish characteristics of plasma-chemically fabricated nanoparticles with their

further use in various spheres of activity.

Natural and synthetic stabilizers are currently used as the substances of stabilizers of the silver colloidal solutions. The nature of the stabilizer functional group defines the properties of obtained silver nanoparticles. At present time, many natural polymers, such as chitosan, soluble starch, polypeptide, heparin and hyaluronan, are involved in "green" production of nanoparticles as a reducing/stabilizing agent [9]. A number of research papers indicate the effectiveness of the choice of sodium alginate to obtain stable silver nanoparticles and materials on their base which are characterized by antibacterial properties [10,11]. Alginate is a natural polyelectrolytic polysaccharide occurring in all types of brown algae and certain types of bacteria; it is a linear polymer consisting of units of α -L-guluronate (G) and α -D-mannuronate (M) in different proportions and sequence variants, being biocompatible and biodegradable in tissues. Besides, it is considered that sodium alginate is freely soluble in water due to the presence of negatively charged carbonyl groups. The benefits of using sodium alginate for the stabilization of silver nanoparticles are also its good ecological characteristics and compatibility for the pharmaceutical, biomedical and other technologies. So, the choice of sodium alginate for stabilization of silver nanoparticles is conditioned by such unique properties which distinguish this substance from the other known stabilizers. Studying the process of obtaining silver nanoparticles in the presence of stabilizer reagent, sodium alginate, under the action of plasma discharge, is of scientific and practical interest.

The aim of this work is to study the plasma-chemical preparation of colloidal solutions of silver nanoparticles with the use of the stabilizer, i.e. sodium alginate.

Materials and methods

Colloidal solutions of silver were prepared by dissolving silver nitrate (AgNO_3) of analytical reagent grade in distilled water. Sodium alginate was used as a stabilizer/reducing agent of silver. Sodium alginate was dissolved in distilled water in a glass of 100 ml with the use of magnetic stir bar. Colloidal solution of silver was added to the obtained solution with specified ratios of reagents. The resulting reaction mixture was treated in the reactor with the discharge of contact nonequilibrium low-temperature plasma. The research was carried out in the batch gas-liquid reactor of 100 ml volume with the use of X18H10T stainless steel electrodes. Cathode (diameter of 4 mm) was located in the liquid part; anode (diameter of 2.4 mm) was placed at the distance of 10 mm

from the surface of solution. The volume of solution in the reactor was equal to 70 ml. Cooling of reaction mixture was provided by continuous circulation of cold water. The pressure in the reactor was maintained at 80 ± 4 kPa. For obtaining plasma discharge the voltage of 500–1000 V was applied to the electrodes. The current was maintained at the level of 120 ± 6 mA. The duration of plasma processing of solutions was ranged from 1 to 5 minutes.

To characterize the nanoparticles of silver formed, the reaction mixture after the plasma treatment was analyzed via spectrophotometry. The spectra of colloidal solutions were obtained by means of spectrophotometer UV-5800 PC using quartz cuvettes in the wavelength range of 190–700 nm. Zeta potential and particle size distribution of colloidal solutions were measured by means of Zetasizer Nano-25 analyzer (Malvern Instruments Ltd., Malvern, England). Microphotographs of nanoparticles were obtained by scanning microscope JEOL JSM-6510LV (JEOL, Tokyo, Japan). The disperse phase of the solution obtained as a result of plasma-chemical treatment of the solution was separated, dried in the air at 25°C and then studied with the use of X-ray diffractometer Ultima IV Rigaku.

Results and discussion

To evaluate the properties of colloidal solutions of nanoparticles, the method of optical spectroscopy [12] is widely used. According to the Mie-Drude theory, the optical properties of colloidal solutions of silver nanoparticles are characterized by the presence of the pronounced resonance absorption band of the surface plasmon resonance (SPR) in the range of 395–465 nm [13].

The effect of concentration of the stabilizer on the efficiency of preparation of silver nanoparticles under action of CNP discharge was studied. Fig. 1 represents the absorption spectra of dispersions with silver particles obtained both without stabilizer and in the presence of sodium alginate at concentrations of 5.0 to 10.0 g/l, the concentration of silver nitrate being constant (0.5 g/l) and plasma-chemical treatment being performed during 5 minutes.

The analysis of obtained data showed that the nanoparticles are formed without using sodium alginate (Fig. 1,a) as a result of plasma discharge action on the solution of silver nitrate. The colloidal solutions of silver are characterized by the presence of maximum of absorption SPR (λ_{max}) at 440 nm. When sodium alginate is introduced into the reaction mixture before its treatment with CNP (Fig. 1,b curves 1–4), the peak with λ_{max} within 400–440 nm is observed in the spectrum; it characterizes formation

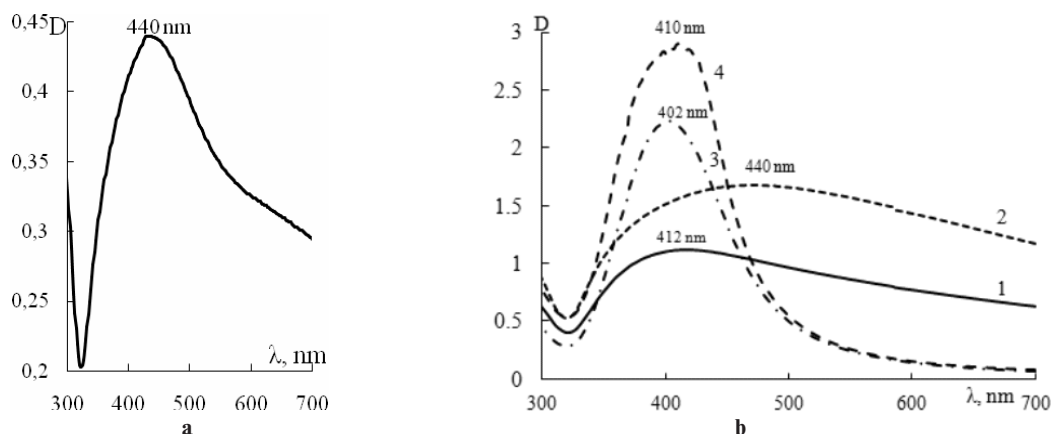


Fig. 1. Dependence of absorbance (D) of plasma-chemically prepared colloidal solution of silver on the wavelength (λ) without using sodium alginate (a) and at various concentrations of sodium alginate, g/l (b): 1.25 (1); 2.5 (2); 5.0 (3); 10 (4)

of silver nanoparticles. Growing intensity of the peak, compared with the data without introduction of alginate, indicates that the latter, probably, acts as a stabilizing and reducing agent simultaneously. An increase in the concentration of sodium alginate from 2.5 to 5.0 g/l (Fig. 1, b curves 2–3) contributes to sharp increase in the SPR peak intensity and its noticeable shift (~ 40 nm) to the short-wave region. This can be explained by the formation of more silver nanoparticles and/or reduction of their size [13]. The possible reason is that the increase in quantity of carboxyl and hydroxyl groups of sodium alginate assists in complexation between Ag^+ and molecular matrix of the polymer, apart from the fact that the higher quantity of hydroxyl groups promotes the reduction of Ag^+ [14]. An increase in the concentration of sodium alginate from 5.0 g/l to 10.0 g/l (Fig. 1, b curve 4) contributes to splitting and insignificant shifting of SPR peak to long-wave region along with the increase of its intensity. It can be caused by the aggregation and formation of nanoparticles of the larger size; at 5.0 g/l of sodium alginate we observed the narrow and symmetric peak of SPR, typical of particles of similar diameter, accordingly, close to ± 15 nm [13].

Therefore, an increase in the polymer concentration may cause an ambiguous effect on the size of particles. With the higher polymer concentrations the larger number of polymer molecules is capable of “closing” the particles by reducing their size, while the polymer acting as a reducing agent accelerates the formation of nucleation centers and the growth of nanoparticles, forming the particles of larger size. With the growth of concentration of sodium alginate, the stabilizing effect of molecules of sodium alginate increases. However, it is likely that its role as a reducing agent is dominant at relatively high concentrations and

promotes the formation of large-sized particles, as a result of their formation and growth. Taking into account the above, it should be noted that the content of sodium alginate in the reaction medium (5.0 g/l) is sufficient for nanoparticle stabilization. According to [5,6], the duration of contact nonequilibrium low-temperature plasma treatment is one the most important factors of plasma-chemical action towards aqueous solutions. The influence of the treatment duration of reaction medium with plasma discharge on the formation of silver particles in the presence of sodium alginate was studied. The conditions of experiment were as follows: the concentration of silver nitrate was 0.5 g/l and the concentration of sodium alginate was 5.0 g/l.

Fig. 2. gives the spectra of silver nanoparticles obtained after various time intervals of the reaction medium treatment with plasma discharge.

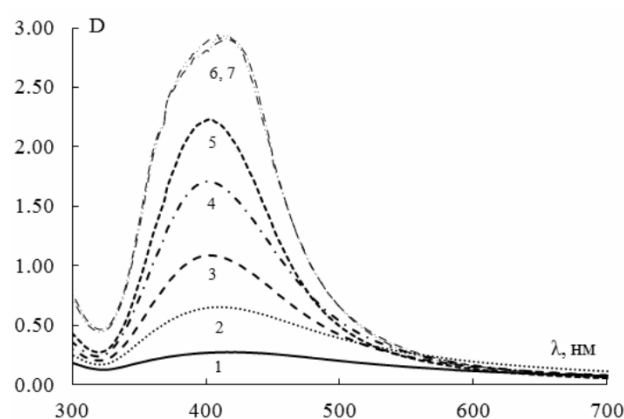


Fig. 2. Dependence of absorbance (D) of plasma-chemically prepared colloidal solution of silver on the wavelength (λ) at various duration of treatment with plasma discharge (minutes): 1 (1), 2 (2), 3 (3), 4 (4), 5 (5), 6 (8), 7 (12)

When the duration of solution treatment is less than 2 minutes, plasmon band is wide and weak, evidencing the low degree of Ag^+ reduction to nanoparticles of silver at this duration of exposure. When the treatment continues for 2–5 minutes, a gradual increase in absorbance is observed without any change in peak wavelength, which indicates that the content of silver nanoparticles increases with the growth of treatment duration. The average diameter of the formed particles is almost the same and, according to data of [13], is equal to 15–30 nm. An increase in the exposure time to 8–12 minutes is accompanied by the shift of absorption band toward longer wavelength (~ 420 nm) which can be explained by silver nanoparticles' size growth.

X-ray diffraction study was carried out to confirm the crystalline phase of plasma-chemically obtained nanoparticles of silver. Fig. 3 shows X-ray pattern of silver nanoparticles obtained in the presence of sodium alginate under action of CNP during 5 minutes. The conditions of experiment were as follows: concentration of silver nitrate was 0.5 g/l and concentration of sodium alginate was 5.0 g/l.

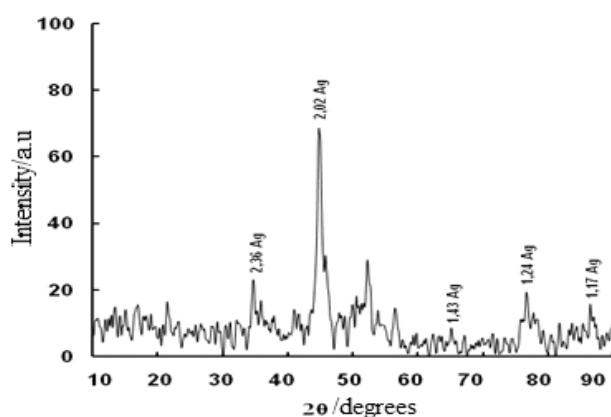
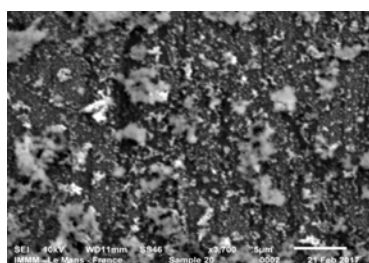


Fig. 3. X-ray diffraction pattern of plasma-chemically prepared nanoparticles of silver in the presence of sodium alginate



a

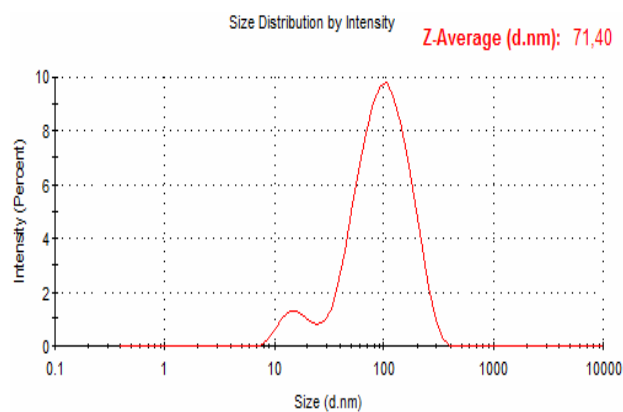
A number of different diffraction peaks at approximately 38.1° , 44.2° , 64.3° and 77.4° correspond to reflexes from (111), (200), (220) and (311) silver crystal planes, respectively, which confirms the presence of crystalline silver with the boundary-cubic structure of silver.

Dimensional characteristics of plasma-chemically prepared silver nanoparticles in the presence of sodium alginate were investigated by the method of scanning electron microscopy (Fig. 4,a). The results showed the presence of agglomerated and non-agglomerated particles. The average particle size of silver is up to 100 nm.

One of the important parameter in terms of the further practical application of colloidal solutions is their aggregative stability. The degree of aggregation of the metal nanoparticles can be effectively estimated by changing the absorption characteristics as follows: displacement of SPR peak in the spectrum and its intensity. The analysis of spectra of silver colloids after aging during 4 weeks (Fig. 5) passing from the date of obtaining showed no significant changes in the structure and intensity of SPR bands, thus evidencing the absence of noticeable (quick) aggregative processes in silver dispersions.

In order to evaluate the stability of colloidal systems, the pH value of freshly obtained solutions of silver were investigated during storage (Fig. 6). Colloidal solutions are characterized by the absence of explicit pH change during storage.

Zeta potential of plasma-chemically obtained nanoparticles of silver in the presence of various concentrations of sodium alginate was determined (Table).



b

Fig. 4. SEM-image(a) and size distribution (b) of colloidal solution of silver obtained by plasma-chemical method with addition of sodium alginate. The content of silver nitrate is 0.5 g/l, the content of sodium alginate is 5.0 g/l, $I=120$ mA, $P=0,08$ MPa, and $t=5$ minutes

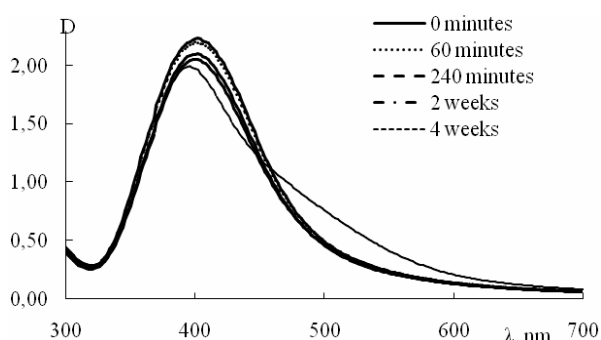


Fig. 5. Dependence of intensity of absorbance (D) of plasma-chemically prepared colloidal solution of silver on wavelength (λ) at various duration of storage after action of plasma (at sodium alginate concentration of 5.0 g/l)

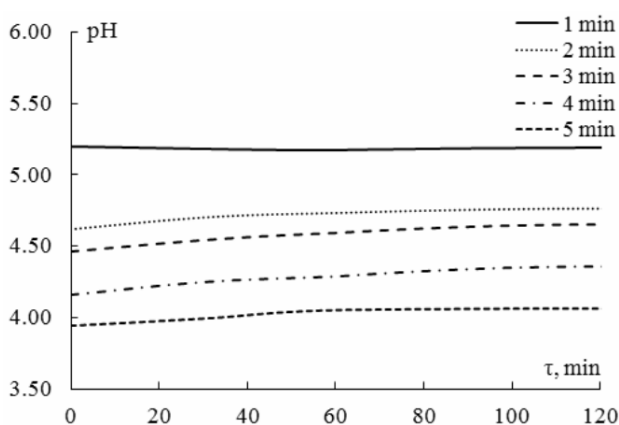


Fig. 6. Dependence of the acidity of solutions with various time of treatment with plasma discharge on storage time

Characteristic of plasma-chemically obtained nanoparticles of silver in the presence of sodium alginate

Concentration of sodium alginate, g/l	Zeta potential, mV
–	–14.2
1.25	–32.8
2.5	–33.4
5.0	–34.6
10.0	–39.3

Depending on the concentration of stabilizer, the obtained solutions of silver nanoparticles are characterized by the average value of zeta potential in the range from -32.8 to -39.3 mV, which is typical of the stable colloidal systems.

Conclusions

In this study a facile and efficient method for the green synthesis of well-distributed spherical AgNPs was developed. The synthesis was carried out in an aqueous medium treated by the discharge of contact nonequilibrium low-temperature plasma in the presence of sodium alginate as a stabilizer. According to the results of our findings, the introduction of stabilizer promotes an increase in the intensity of formation of silver nanoparticles. The effects of the concentration of sodium alginate and the duration of treatment with plasma discharge on the characteristics of silver nanoparticles as well as the aggregative stability of silver nanoparticles obtained using plasma-chemical method were studied. It was shown that the use of sodium alginate leads to an increase in the aggregative stability of plasma-chemically prepared solutions of silver nanoparticles. Zeta potential of plasma-chemically prepared colloidal solutions at various concentrations of introduced stabilizer was determined. The silver nanoparticles prepared in this way are uniform and stable in solution over a period of months at room temperature (25°C) and show no signs of aggregation. The utilization of environmentally benign and renewable materials like sodium alginate for the synthesis of AgNPs in an aqueous medium offers numerous benefits, including eco-friendliness and compatibility with biomedical, pharmaceutical, and textile applications.

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PREPARATION OF SILVER NANOPARTICLES BY CONTACT NONEQUILIBRIUM LOW-TEMPERATURE PLASMA IN THE PRESENCE OF SODIUM ALGINATE

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