

UDC 546.57:661.857

DOI: 10.15372/CSD2020204

Polyol Synthesis of Silver Nano- and Microplates in the Presence of an Ethoxylated Carboxylic Acid

A. I. TITKOV, T. A. BORISENKO, O. A. LOGUTENKO

*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia**E-mail: ologutenko@solid.nsc.ru*

Abstract

The reduction of silver nitrate in polyols in the presence of hydroxyethylated carboxylic acid as a stabilizer was investigated. The effect of synthesis conditions, in particular temperature, synthesis time, concentrations of silver salt, stabilizer, and sodium hydroxide, on the structural characteristics of the synthesized particles was studied by means of electron microscopy and X-ray diffraction. It was shown that large polyhedra 200–800 nm in size are formed in the system in the absence of the stabilizer, 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA). In the presence of MEEAA, silver nano- and microplates with the sizes ranging from 10–20 nm to 1 μm are formed, depending on synthesis conditions. The optimal reaction conditions were determined for obtaining silver plates 100–500 nm in size, with the dominating 200–300 nm fraction: temperature, 100 $^{\circ}\text{C}$; synthesis time, 1 h; MEEAA to Ag molar ratio, 3 : 1. The type of polyol was shown to affect both the morphology of the resulting particles and the fraction of plates and polyhedra in the final product. Thus, the fraction of polyhedra with respect to the plates increases when passing from ethylene glycol to triethylene glycol and propylene glycol. The effect of the alkaline reagent (NaOH) on the composition, size, and morphology of reduction products was studied. It was shown that the rate of silver ion reduction increases significantly in the presence of NaOH, which allows carrying out the process at room temperature. At a molar ratio of NaOH to Ag equal to 4 : 1, nanoplates 10–20 nm in size are formed. As-synthesized silver micro- and nanoplates can be used in the development of conductive materials, including pastes and inks for printed electronics.

Key words: silver, nano- and microplates, ethylene glycol, propylene glycol, triethylene glycol, 2-[2-(2-methoxyethoxy)ethoxy]acetic acid, reduction

INTRODUCTION

At present, nanomaterials based on nanoparticles of different metals are the object of intense studies because of their unique properties allowing a broad application of these materials in electronics, catalysis and medicine. With the development of digital technologies, nanoparticles of metals such as silver, gold, copper, nickel, aluminium and zinc, are actively used in pastes and ink for printed electronics [1, 2]. Special attention is attracted to micro- and nanometer silver particles, which is

due to the high conductivity of this metal and its stability to oxidation.

The methods of obtaining nanoparticles of precious metals including silver, as well as materials based on them, were considered in detail in monographs [3, 4]. These methods include a well known citrate method proposed by Turkevich, the reduction of silver ions in the aqueous medium with sodium borohydride, synthesis in two-phase organic-aqueous systems, a method involving organic reducing agents, and synthesis in reverse micelles. One of the methods to obtain

metal particles of submicron size is based on the reduction of their organic or inorganic salts in a high-boiling organic liquid. The substances used in these processes as the reducing medium are usually aliphatic polyols (ethylene glycol and its derivatives di-, tri- and tetraethylene glycols, including polyethylene glycol, as well as the compounds containing more than two hydroxyl groups, for example, glycerol) acting as stabilizers limiting the growth of particles and preventing their agglomeration [5–7]. The polyol process is relatively simple in application because it does not require complicated equipment or special conditions, and it allows controlling the size, the shape of particles and their size distribution by means of optimization of reaction conditions, for example, synthesis temperature and reagent concentration, nature of the stabilizing agent and solvent type. As a result, particles of different shapes may be obtained. Among various shapes of silver particles, plates are of special interest because they possess unique spectrum of plasmon resonance due to their geometric anisotropy [8]. It is this reason that makes them especially promising as the material for sensors and diagnostics. It has also been demonstrated that silver films obtained as a result of the deposition of ink-based on non-spherical silver particles on plastic substrates and subsequent annealing are more uniform, have lower electric resistance and improved mechanical properties in comparison with similar films formed from spherical particles [9].

In the present work, we describe the results of the investigation of silver ion reduction by polyols (ethylene glycol, triethylene glycol and propylene glycol) in the presence of methoxypolyethylene glycol modified with a carboxylic group, 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEAA). It was expected that the introduction of the end carboxyl group into polyethylene glycol would enhance its adsorption capacity with respect to silver particles and thus would improve their stabilization against aggregation [10]. In addition, the particles stabilized by oxyethylated carboxylic acids due to the presence of oxygen in the hydrocarbon chain are well dispersed in a broad range of polar solvents including alcohols and ethers of glycols, which allows obtaining stable colloid systems that may be used to prepare functional ink for jet printing, as well as glues and pastes [11].

The goal of the present studies is to develop a simple method to obtain micro- and nanoplates of

Ag, which may be used to prepare electroconductive materials including pastes and ink.

EXPERIMENTAL

Silver nitrate AgNO_3 (99.9 %, GOST 1277–75, SoyuzKhimProm, Russia), sodium hydroxide NaOH of the Kh. Ch. reagent grade, 2-[2-(2-methoxyethoxy)ethoxy]acetic acid $\text{C}_7\text{H}_{14}\text{O}_5$ (MEAA, the mass fraction of the major substance ≥ 90 %, Sigma Aldrich, USA), ethylene glycol $\text{HO}(\text{CH}_2)_2\text{OH}$ of Os. Ch. reagent grade (GOST 10164–75, the mass fraction of the major substance 99.8 %), 1,2-propylene glycol $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$ of Os. Ch. 9-5 reagent grade (TU 2634-146-44493179-11, the mass fraction of the major substance not less than 99.7 %), triethylene glycol $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$ of Os. Ch. reagent grade (GOST 10164–75, the mass fraction of the major substance 99.8 %) and ethanol (95 %, Khimmed, Russia) were used in the investigation. Solutions were prepared using distilled water.

The reduction of AgNO_3 was carried out as follows. A weighted portion of AgNO_3 was put into a heat-resistant beaker 100 mL in volume and dissolved in polyol in the presence of the sodium salt of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (the sodium form of MEAA) under mixing and heating with an oil bath to the required temperature. After synthesis, the mixture was cooled with a cold water bath, and the precipitate was separated from the settled layer of the liquid phase by decanting. The precipitate was washed with ethanol three times and dried in the air at room temperature. The size of particles and their morphology were studied with the help of transmission electron microscopy (TEM) and scanning electron microscopy (SEM), and X-ray phase analysis.

X-ray phase analysis of precipitation products was carried out using a D8 Advance diffractometer (Bruker, Germany, CuK_α -radiation, unidimensional detector Lynx-Eye with nickel filter, step 0.02° over θ , time of accumulation in a point 35.4 s). Evaluation of the average size of crystallites was made using the Rietveld method and the software for profile and structural analysis Topas 4.2 (Bruker AXS, Germany). The broadening of reflections due to crystallite size was modelled with the Double-Voigt function. Investigation of the samples by means of TEM was carried out using a JEM-2010 electron

microscope (JEOL, Japan) with accelerating voltage 200 kV and 0.14 nm resolution, SEM studies were carried out with the 3400N scanning electron microscope (Hitachi, Japan).

RESULTS AND DISCUSSION

Reduction of silver nitrate by ethylene glycol

The reduction of AgNO_3 by ethylene glycol was investigated in the presence of modified methoxypolyethylene glycol, the sodium form of MEAA, which was used as a stabilizer. The structural formula of MEAA is shown in Fig. 1. It was assumed that MEAA would bind to the surface of silver crystals more efficiently than non-modified polyethylene glycol due to the presence of end carboxylic groups in the structure. The features of MEAA coordination on the surface of silver nanoparticles were studied by us previously by means of IR spectroscopy, which allows obtaining the information on the method of carboxyl group coordination with the metal [10]. As a result, it was demonstrated that the coordination of carboxylic groups of MEAA on the silver surface does exist. Both monodentate and bridging coordination of carboxylic groups with silver occurs.

The dependence of the size and morphology of the formed particles on the conditions of their synthesis was studied, in particular the dependence on the time of the reduction, precursor concentration, alkali concentration and the relation of the stabilizer (MEAA) to silver in the solution. It was established that silver nitrate within the studied range of its concentrations forms with the sodium form of MEAA a salt soluble in polyols. So, the reduction of silver ions with the formation of metal particles proceeds in the solution according to the mechanism of homogeneous nucleation. Unlike this system, the salts of silver with fatty acids are practically insoluble in water, alcohols and polyols [12–15].

To optimize the synthesis process, silver concentration C_{Ag} in the initial solution was varied within the range 0.05–0.5 mol/L, reduction

temperature – within the range 20–170 °C, the time of reduction at a definite temperature was varied from 5 min to 4 h, and the molar ratio of MEAA/Ag was varied from 0.5 : 1 to 3 : 1.

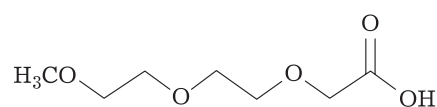
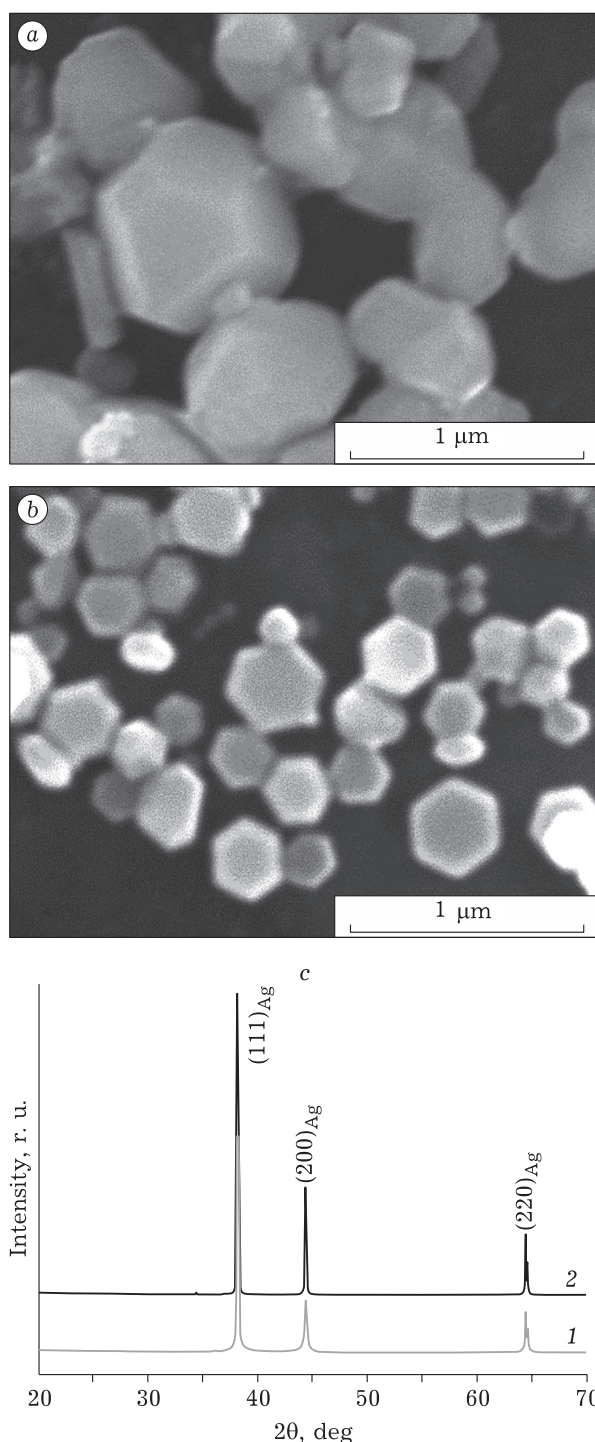


Fig. 1. The structure of 2-[(2-(2-methoxyethoxy)ethoxy)acetic acid (MEAA).

Fig. 2. Microphotographs and diffraction patterns of powders obtained as a result of the reduction of AgNO_3 by ethylene glycol in the presence of the sodium form of MEAA (b, c, curve 1) and in its absence (a, c, curve 2). Here and in Fig. 3: $T = 100$ °C, synthesis time 1 h, $\text{MEAA/Ag} = 3 : 1$, $C_{\text{Ag}} = 0.5$ mol/L.

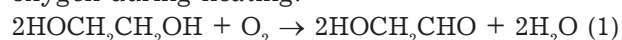
Effect of stabilizer

The effect of stabilizer on the size and morphology of the particles formed as a result of the reduction of AgNO_3 by ethylene glycol was studied at a temperature of $100\text{ }^\circ\text{C}$ and synthesis time 1 h. It was shown that in the absence of MEAA polyhedra 200–800 nm in size are formed in the system (Fig. 2, a), while in the presence of MEAA (with the molar ratio of $\text{MEAA}/\text{Ag} = 3 : 1$) nanoplates 200–500 nm in size and 10–50 nm thick are formed (see Fig. 2, b). According to the data of XPA (see Fig. 2, c), the final product of reduction under these conditions is metal silver. This is confirmed by three main characteristic diffraction maxima at $2\theta = 38.1, 44.1$ and 64.4° , corresponding to diffraction from the planes (111), (200) and (220) of the face-centred cubic structure of silver (JCPDS, [001-1164]).

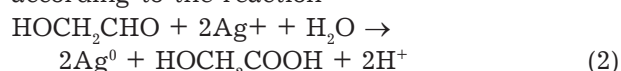
The effect of the molar ratio of MEAA/Ag on the size and morphological characteristics of the formed particles was investigated. It was demonstrated that with an increase in the amount of the stabilizer in the system, the size of particles and their polydispersity decrease; polyhedra are formed along with plates. At the molar ratio $\text{MEAA}/\text{Ag} = 0.5 : 1$, silver plates 0.5–1 μm in size are formed. So, at low MEAA concentrations the stabilization of silver particles is insufficiently efficient to protect them from aggregation, which leads to the formation of larger nano- and microparticles. An increase in the time of reduction from 1 to 4 h has practically no effect on the characteristics of the formed powders and leads only to an increase in the fraction of coarse particles in them.

Effect of the temperature of reaction medium

It is known [5, 7, 8] that the reduction of silver ions with ethylene glycol is due mainly to the presence of glycol aldehyde formed as a result of the oxidation of ethylene glycol by atmospheric oxygen during heating:



In turn, this compound reduces silver ions according to the reaction



Glycol aldehyde is formed in noticeable amounts at a temperature of $140\text{--}150\text{ }^\circ\text{C}$ [7],

however, the reduction of silver ions in our system starts even at a temperature of $80\text{ }^\circ\text{C}$. We demonstrated that under these conditions the major reducing agent is ethylene glycol itself [14]. At lower temperatures, the rate of reaction decreases, so only an insignificant part of silver is reduced. To reveal the effect of temperature on the properties of the formed particles, the reduction was carried out within the temperature range of $80\text{--}150\text{ }^\circ\text{C}$ with the molar ratio of $\text{MEAA}/\text{Ag} = 3 : 1$ and process duration 1 h. The mass ratio of the solid and liquid phases was $1 : 20$. It follows from the data obtained by means of TEM and optical spectroscopy that silver nuclei 2–5 nm in size are formed at the initial stages of the process, and then they are arranged in larger particles. It is demonstrated that the temperature of reduction affects the rate of their growth and, as a consequence, their average size and their size distribution. At a temperature of $80\text{ }^\circ\text{C}$, after 1 h the product is composed of nanoplates with a broad size distribution from 50 to 500 nm. Temperature rise to $100\text{ }^\circ\text{C}$ leads to the formation of plates 100 to 500 nm in size, but prevailing plates are those 200–300 nm in size and 10–50 nm thick (see Fig. 2, b). Further temperature rise to $120\text{ }^\circ\text{C}$ leads to the formation of a mixture composed mainly of thickened plates, polyhedra and a small number of plates 200–800 nm in size, while only coarse aggregates of particles of indefinite morphology are formed at $150\text{ }^\circ\text{C}$. So, $100\text{ }^\circ\text{C}$ is an optimal temperature for obtaining plates 100–800 nm in size, among which the major part of plates are 400–500 nm in size and about 50 nm thick as average. At a temperature above $100\text{ }^\circ\text{C}$, the rate of ion diffusion in solution and the rate of formation of silver nanoparticles and the degree of their aggregation start to increase, so it becomes almost impossible to control the growth of particles and especially the formation of anisotropic structures from them. As a result, the formation of polydisperse shapeless aggregates occurs. On the other hand, at a temperature below $100\text{ }^\circ\text{C}$, the possibility of the kinetic control of reduction and consequent anisotropic particle growth should increase, however, uniform plates are not formed under these conditions, too, which may be due to the slow reduction of silver ions and a small amount of nuclei formed at the initial stage.

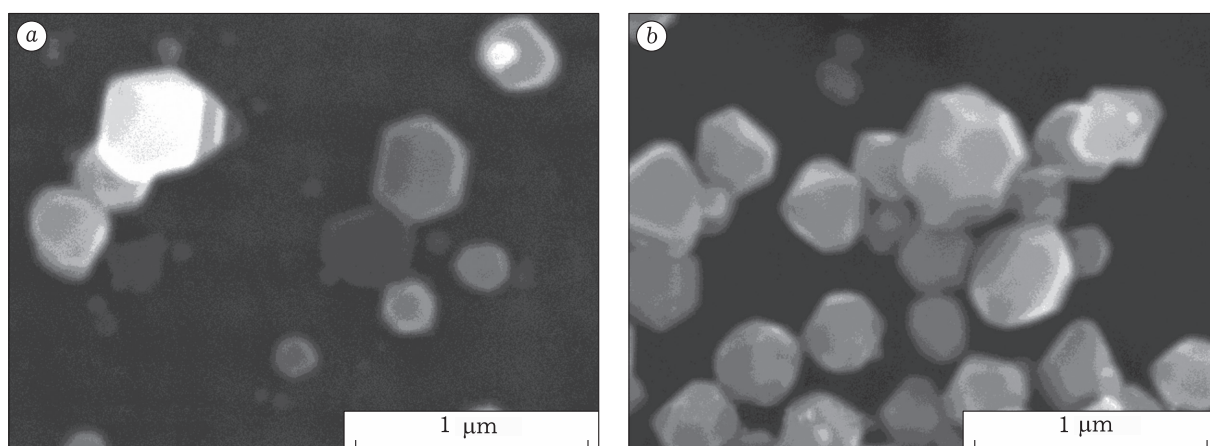


Fig. 3. Microphotographs of powders obtained as a result of AgNO_3 reduction in the presence of MEAA by triethylene glycol (a) and propylene glycol (b). For synthesis conditions, see Fig. 2.

Effect of polyol nature

It was interesting to find out how polyol structure may affect the size and morphology of the formed silver particles, as it is known that polyol may take part in stabilizing metal particles limiting their growth and preventing agglomeration. For comparison, propylene- and triethylene glycol were used as the reaction medium. The reduction was carried out at $100\text{ }^\circ\text{C}$ under the same conditions as in ethylene glycol: synthesis time 1 h, $\text{MEAA/Ag} = 3 : 1$, mass ratio of the solid and liquid phases was equal to $1 : 20$. As a result of the investigation, it was shown that the type of polyol affects the morphology of the formed particles and on the percentage of plates and polyhedra in the final product. For instance, mainly silver plates are formed under these conditions in ethylene glycol (see Fig. 2, b), while a mixture composed of plates and polyhedra is formed in triethylene glycol (Fig. 3, a), and mainly polyhedra are formed in propylene glycol (see Fig. 3, b). The size of the particles is approximately the same in all cases: $100\text{--}800\text{ nm}$. This result may be explained by the higher rate of reduction in the medium of two latter polyols in comparison with the rate of silver ion reduction in ethylene glycol. In addition, it is necessary to mention the ability of polyols to coordinate metal ions [16], in particular silver, and this ability is different for different polyols, which may affect the size and shape of the formed particles.

Effect of alkali

The activity of polyols and alcohols in alkaline media increases as reported by Gomes and co-authors [17], so it was interesting to study the effect of the alkaline reagent (NaOH) on the composition, size and morphology of reduction products. It was expected that the rate of silver ion reduction increases substantially in the presence of NaOH , which may first of all lead to the change of particle size, as well as their morphology. It was shown that, indeed, the rate of silver ion reduction increases substantially in the presence of

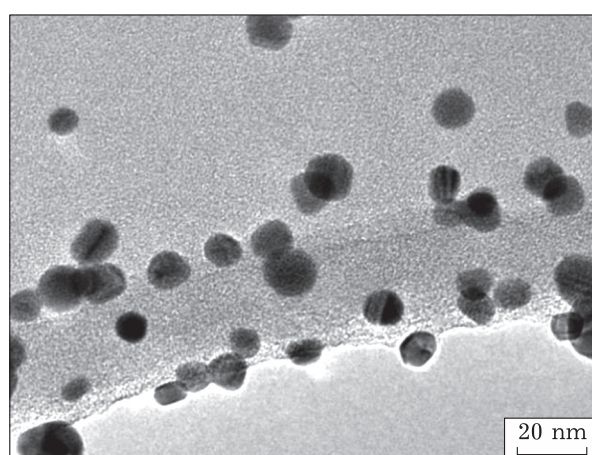


Fig. 4. TEM microphotographs of silver nanoplates obtained as a result of AgNO_3 reduction by propylene glycol in the presence of MEAA and NaOH . Conditions: $T = 25\text{ }^\circ\text{C}$, synthesis time 3 h, $C_{\text{Ag}} = 0.5\text{ mol/L}$, molar ratios $\text{MEAA/Ag} = 3 : 1$, $\text{Ag/NaOH} = 1 : 4$.

NaOH, which allows us to carry out the synthesis even at room temperature. For the molar ratio of NaOH/Ag = 4 : 1, the formed particles are nanoplates 10–20 nm in size (Fig. 4). A decrease in the concentration of the alkali in the reaction system to the molar ratio of NaOH/Ag = 2 : 1 leads to an increase in the average size of the formed particles to 20–30 nm, and with an increase in the amount of NaOH (NaOH/Ag = 8 : 1) the degree of particle aggregation increases, and correspondingly so does their size.

CONCLUSION

The reduction of silver nitrate with ethylene glycol in the presence of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid is investigated. It is shown that, depending on synthesis conditions (temperature and time of the reduction, the concentrations of silver nitrate, stabilizing agent, and sodium hydroxide), nano- and micro-sized (10–20 nm and ~1 μm) silver plates are obtained. The initial concentration of silver was 0.05–0.5 mol/L, which is 10–1000 times higher than the concentrations involved in the synthesis of nanoplates using widely known traditional methods. In the absence of MEAA stabilizer, coarse polyhedra 200–800 nm in size are formed in the system. It was shown that 100 °C is the optimal temperature for the formation of plates, their size varying from 100 to 500 nm, with the prevalence of the size fraction of plates 200–300 nm.

In the presence of NaOH at room temperature, silver nanoplates 10 to 20 nm in size were obtained. As a result of the investigation, a simple method was proposed for the synthesis of micro- and nanoplates of Ag which can be used to develop electroconductive materials, in particular pastes and inks.

Acknowledgements

The work was carried out within the State Assignment for ISSCM SB RAS (project No. 0237-2019-0002).

REFERENCES

- 1 Kamyshny A., Steinke J., Magdassi S., Metal-based inkjet inks for printed electronics, *Open Appl. Phys. J.*, 2010, Vol. 4, P. 19–36. DOI: 10.2174/1874183501104010019
- 2 Magdassi S., Bassa A., Vinetsky Y., Kamyshny A., Silver nanoparticles as pigments for water-based inkjet inks, *Chem. Mater.*, 2003, Vol. 15, P. 2208–2217. DOI: 10.1021/cm021804b
- 3 Gubin S. P., Yurkov G. Yu., Kataeva N. A., Nanoparticles of Precious Metals and Materials Based on Them, Moscow: Azbuka-2000, 2006. 156 p.
- 4 Murphy C. J., Jana N. R., Controlling the aspect ratio of inorganic nanorods and nanowires, *Adv. Mater.*, 2002, Vol. 14, No. 1, P. 80–82. [https://doi.org/10.1002/1521-4095\(20020104\)14:10::AID-ADMA803.0.CO;2-%23](https://doi.org/10.1002/1521-4095(20020104)14:10::AID-ADMA803.0.CO;2-%23)
- 5 Fiévert F., Lağier J. P., Figlarz M., Preparing monodisperse metal powders in micrometer and submicrometer sizes by the polyol method, *MRS Bull.*, 1989, Vol. 14, No. 12, P. 29–34. <https://doi.org/10.1557/S0883769400060930>
- 6 Fiévert F., Ammar-Merah S., Brayner R., Chau F., Giraud M., Mammeri F., Peron J., Piquemal J.-Y., Sicard L., Viau G., The polyol process: a unique method for easy access to metal nanoparticles with tailored sizes, shapes and compositions, *Chem. Soc. Rev.*, 2018, Vol. 47, P. 5187–5233. DOI: 10.1039/c7cs00777a
- 7 Sun Y., Xia Y., Shape-controlled synthesis of gold and silver nanoparticles, *Science*, 2002, Vol. 298, P. 2176–2179. DOI: 10.1126/science.1077229
- 8 Kelly K. L., Coronado E., Zhao L. L., Schatz G. C., The optical properties of metal nanoparticles: the influence of size, shape and dielectric environment, *J. Phys. Chem. B*, 2003, Vol. 107, No. 3, P. 668–677. <https://doi.org/10.1021/jp026731y>
- 9 Lee Y. I., Kim S., Jung S. B., Myung N. V., Choa Y. H., Enhanced electrical and mechanical properties of silver nanoplatelet-based conductive features direct printed on a flexible substrate, *ACS Appl. Mater. Interfaces*, 2013, Vol. 5, No. 13, P. 5908–5913. DOI: 10.1021/am401757y
- 10 Titkov A. I., Logutenko O. A., Gerasimov E. Yu., Shundrina I. K., Karpova E. V., Lyakhov N. Z., Synthesis of silver nanoparticles stabilized by carboxylated methoxypolyethylene glycols: The role of carboxyl terminal groups in the particle size and morphology, *J. Incl. Phenom. Macrocycl. Chem.*, 2019, Vol. 94, P. 287–295. <https://doi.org/10.1007/s10847-019-00921-x>
- 11 Titkov A. I., Logutenko O. A., Vorobyov A. M., Gerasimov E. Yu., Shundrina I. K., Bulina N. V., Lyakhov N. Z., Synthesis of ~10 nm size Cu/Ag core-shell nanoparticles stabilized by an ethoxylated carboxylic acid for conductive ink, *Colloids Surf., A: Physicochem. Eng. Asp.*, 2019, Vol. 577, P. 500–508. DOI: 10.1016/j.colsurfa.2019.06.008
- 12 Yukhin Yu. M., Titkov A. I., Kulmukhamedov G. K., Lyakhov N. Z., Synthesis of silver nanoparticles via reduction of silver carboxylates by ethylene glycol, *Theor. Found. Chem. Eng.*, 2015, Vol. 49, No. 4, P. 490–496. DOI: 10.1134/S004057951504020X
- 13 Yukhin Yu. M., Logutenko O. A., Titkov A. I., Lyakhov N. Z., Application of solvent extraction in the preparation of metal nano- and microparticles, *Theor. Found. Chem. Eng.*, 2016, Vol. 51, No. 5, P. 809–814. DOI: 10.1134/S0040579517050232
- 14 Titkov A. I., Gerasimov E. Y., Shashkov M. V., Logutenko O. A., Bulina N. V., Yukhin Y. M., Lyakhov N. Z., Specific features of polyol synthesis of silver nanoparticles with the use of solid carboxylates as precursors, *Colloid Journal*, 2016, Vol. 78, No. 4, P. 515–524. DOI: 10.1134/S1061933X16040189
- 15 Yukhin Yu. M., Titkov A. I., Logutenko O. A., Mishchenko K. V., Lyakhov N. Z., Metal extracts as precursors for the production of metal powders and coatings via the extraction-pyrolytic method, *Russ. J. Gen. Chem.*, 2017, Vol. 87, No. 12, P. 2870–2874. DOI: 10.1134/S1070363217120180
- 16 Carroll K. J., Reveles J. U., Shultz M. D., Khanna S. N., Carpenter E. E., Preparation of elemental Cu and Ni

- nanoparticles by the polyol method: an experimental and theoretical approach, *J. Phys. Chem. C*, 2011, Vol. 115, P. 2656–2664. <https://doi.org/10.1021/jp1104196>
- 17 Gomes J. F., Garcia A. C., Ferreira E. B., Pires C., Oliveira V. L., Tremiliosi-Filho G., Gasparotto L. H. S., New insights into the formation mechanism of Ag, Au and AgAu nanoparticles in aqueous alkaline media: alkoxides from alcohols, aldehydes and ketones as universal reducing agents, *Phys. Chem. Chem. Phys.*, 2015, Vol. 17, P. 21683–21693. DOI: 10.1039/C5CP02155C