

The Synthesis of Silver Salts of Halogenated and Fatty Acids, Potential Precursors for The Synthesis of Silver Nanoparticles

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Methods of synthesis of silver salts of halogenated and fatty organic acids: silver acetate, silver trifluoroacetate, silver n-butyrate, and silver monochloropropionate were reported. Silver salts can be used to obtain silver nanoparticles in non-aqueous media. Structures of these compounds were proved by means of various physical and chemical methods (IR spectroscopy, X-ray diffraction and elemental analysis). Listed methods will provide silver salts with high quality and good yield.

Key words: Silver salt, Synthesis, X-ray diffraction, IR spectroscopy, silver nanoparticles

The development of modern science in the field of nanotechnology opens up new prospects for the use of nanoparticles - objects with dimensions less than 100 nm. In such a finely divided form many compounds and individual chemical elements exhibit special chemical and physical properties. Silver nanoparticles are known for a long time as having high bactericidal activity, catalytic properties and applicability for use in the microelectronics industry to establish conductive connections.

In recent years, interest in nanoparticles and materials based on them is growing like an avalanche mainly due to their unusual physical characteristics different from the properties of the respective compact materials. Silver nanoparticles are a new class of materials with significant compared with particulates differences in physico-chemical properties, optical, electromagnetic, and catalytic properties.

In nanoscale virtually any material exhibits unique properties. Physical properties of the silver nanoparticles are different from the properties of macromolecular silver (for example, reducing the particle size leads to a decrease in its melting temperature).

Specific properties of metals in a superdispersed state (particles of a nanometer size) offer great possibilities for creation of new efficient catalysts, sensor systems, drugs of high biological activity to use in ecology, medicine, agriculture¹. Success in scientific researches and in use of metal nanoparticles mainly depend on abilities of the synthesis methods, namely, if the chosen method allows to obtain nanoparticles meeting the requirements of this scientific and practical task. Thus one of the main problems is the synthesis of sufficiently stable nanoparticles of an assigned size, preserving high chemical or biological activity for a long time.

The greatest influence on the characteristics and behavior of nanoparticles including silver nanoparticles having the ratio of surface area to volume. Reducing particle size reduces its volume and a proportional increase in

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the number of atoms on the surface of the particles. Consequently, the surface properties of the material will dominate its properties in the macrostructure. Furthermore, the structure and properties of the surface of the nanoparticles (including silver) depends on the modification of their surfaces with various components such as enzymes that can alter their toxic and biocidal properties, and changes in their catalytic activity. You also need to take into account the surface modification of silver nanoparticles components of the environment, and their ability to aggregate. These circumstances strongly affect the physical, chemical and physiological characteristics of the nanoparticles. The nanoparticles of metallic silver, typically have a shape close to spherical, and can form large aggregates.

There are methods for synthesis based on a physical impact, chemical synthesis methods are also applicable biosynthesis of silver nanoparticles. Methods for the synthesis of silver nanoparticles based on the physical effects include: photochemical reactions, sonochemical reactions, radiochemical reaction, laser ablation. These methods conventionally refers to the physical, as a result of physical and chemical processes occurring impact recovery of silver nanoparticles. Using physical methods can be initiated in condensed matter chemical reactions leading to the formation of metal nanoparticles. However, the nature of the basic process is the chemical. As reducing agents used in the synthesis of the nanoparticles, both inorganic and organic compounds. Among the inorganic reducing agents most commonly used sodium borohydride. This reaction can be carried out in a water, organic, aqueous-organic medium. Additional organic reductants commonly used sodium citrate, amines and hydrazine, aldehydes and sugars. Many high molecular weight organic compounds are also able to recover the metal cations under mild conditions.

A chemical synthesis is one of the common methods to get nanosized metal particles, characterized by unusual physical and chemical properties². It is connected with the reduction of metal ions. Colloidal solutions are formed in the synthesis under the required conditions. Stability, size and distribution by the colloidal particle size, the further changes depend on many factors, including the dispersion medium properties and the temperature.

Aqueous or nonaqueous solvents are used as the medium

To increase the stability of nano-sized state is introduced into the reaction medium further component a stabilizer. Its role is to interact with the surface atoms, which leads to a reduction of excess surface energy. As stabilizers use various materials, but often - sulfur-containing organic compounds (thiols, disulfides, sulfur-containing heterocyclic compound), a surfactant, organic compounds with polar functional group. Quite often the reducing agent or its oxidation product acts as a stabilizing agent.

The problem of stability, which is due to the high reactivity with respect to the low frequency components of the medium particles and the tendency to unite to form thermodynamically stable metal phase is achieved by creating a protective sheaths of the respective chemicals on the surface of nanosized metal particles, introducing particles into the polymer matrix and porous, binding of nanosized metal particles on solid substrates, and also due to the stabilization of the charge in polar media. In this regard, one of the most convenient and effective methods of producing a fusion of nanosized metal particles in reverse micelles¹, wherein the growth of nanosized metal particles occurs due to the chemical recovery original ionic form of the metal in the dispersed aqueous phase, solubilized in the internal cavity of the polar micelle, and protective function for particles of shell itself carries the micelles of aggregated molecules of surfactant (surfactant).

Widespread chemical synthesis method is due to its simplicity and accessibility

Silver nanoparticles have unique optical, electrical, and thermal properties and are being incorporated into products that range from photovoltaics to biological and chemical sensors. Silver nanoparticles are included in the composition of the coatings to absorb solar energy, are used as catalysts for chemical reactions as antimicrobials and disinfectants, silver nanoparticles are components of food packaging. Nanoparticles formed by dissolving silver cations have a biocidal effect against many bacteria. Additives impart antibacterial properties of nanosilver clothes, paint, enamel and other materials. Wide spectrum antimicrobial action of silver, no resistance to it in the majority of pathogenic microorganisms, low

toxicity, lack of data on the allergenic properties of silver, as well as good tolerance by patients has increased interest in silver, in many countries of the world.

Colloidal Silver

A natural antibiotic approved for use in the United States by the Federal Commission on nutrition and medicine back in 1920. In Russia Colloidal silver has also been praised doctors that contributed to its active use. The most important field of application of this material is the children's products industry due to the antibacterial effects of silver nanoparticles³. The increased interest in silver arose again in connection with the identification of its action in the body as a trace element necessary for normal functioning of organs and systems, immunokorrigirujushchej, and powerful antibacterial and antiviral properties. Efficacy of bactericidal action of colloidal silver due to the ability to suppress the work of the enzyme by which provided oxygen exchange in the simplest organisms. So simple alien microorganisms die in the presence of silver ions due to violation of the oxygen supply necessary for their livelihoods. Modern research actions colloidal silver ions have shown that they possess a pronounced ability to neutralize vaccinia virus, some strains of influenza virus, enteritis - and adenoviruses. In addition, they have a good therapeutic effect in the treatment of viral enteritis and swine in dogs. In this treatment revealed advantage colloidal silver as compared to standard therapy. Observed beneficial effects of colloidal silver ions on the healing of venous ulcers developing in circulatory disorders of the lower limbs. In neither case was not observed adverse effects of treatment with silver.

Colloidal nanosilver

A product consisting of microscopic silver nanoparticles suspended in demineralised and de-ionised water. This product is made of high scientific technology electrolytic method.

Typical silver nanoparticles have a size of 25-100 nm. They have an extremely large specific surface area, which increases the contact area of silver with bacteria or viruses, greatly improving its bactericidal action. Thus, the use of silver nanoparticle allows hundreds of times to reduce the concentration of silver retaining all bactericidal properties. Bactericidal additive based on silver

nanoparticles is one of the latest achievements of Russian science in the field of nanobiotechnology.

High chemical activity of the synthesized nanoparticles, along with their ability to spontaneous aggregation of the loss of the above properties make the actual problem of stabilizing the nanoparticles. Among the methods of stabilization are the main matrix isolation, surface functionalization of nanoparticles groups or protective layers and localization of nanoparticles on the surface of carriers of different nature. The most common method is matrix isolation in this case is used as a matrix polymer of the matrix type (organic and inorganic polymers)⁴. The second type of stabilization is to cover the functional groups of the nanoparticles of different nature. Most commonly used for these purposes, thiols, carboxylic acids, polyacrylic acid, polydimethylsiloxane, various surfactants, etc. In recent years begun to develop a third method of stabilizing the nanoparticles comprising the localization of the latter on the surface of granules of different nature having the characteristic size of the order of hundreds of nanometers. In this case objects with dimensions of tens of nanometers are localized on the surface.

A considerable number of known methods for producing silver nanoparticles due to a chemical reaction in an aqueous medium. However, for many practical applications, the silver nanoparticles is important to obtain silver nanoparticles in aqueous media such as organic solvents and polymeric matrix. Also preparation of nanoparticles of silver in non-aqueous media opens new possibilities control the shape and dimensions of the nanoparticles, and thus, influence on their biological, chemical and physical properties. During the performance will be studied patterns chemical interactions silver compounds with different reagents in a variety of non-aqueous media including polymeric matrix resulting in the formation of silver nanoparticles prescribed shapes and sizes.

Particularly important study questions introduction of silver nanoparticles in the polymeric materials by synthesizing them directly into the polymer matrix, and developing methods for producing silver nanoparticles certain predetermined size and morphological characteristics with the most pronounced

antibacterial properties and suitable for incorporation into a wide range of hydrophobic polymers to create a nanocomposite⁵.

Nanocomposite materials containing silver nanoparticles have unique properties and promising for medicine, optoelectronics, nanophotonics and catalysis. The properties of silver nanoparticles (dimension, distribution, stability, and others.) Depend essentially on the nature of the stabilizing polymer matrix, and the conditions of formation nanoparticles in the composite. Nanoparticles of metals and metal oxides - intensively developed in recent years, the area of physical chemistry of nano-sized state. Structural organization of nanoparticles - a serious problem, without which it is difficult to determine and optimize the area of their practical use. Use of polymers as stabilizers nanoscale particles is an important issue. Particularly relevant is the creation of polymer nanocomposites modified with silver nanoparticles and study their bacteriostatic and antibacterial properties.

To modify the surface of polymers with

silver nanoparticles they should be in the organic phase, therefore, it is very important to determine the possibility of the silver nanoparticle synthesis in organic solvents.

The synthesis in low-polarity organic media allows to get metallic polymeric materials of high optical transparency, and to synthesize quantum dots fixed in solid optical matrices⁶⁻⁸. The result of the synthesis is largely determined by the degree of study of colloidal systems and processes, as well as by the influence of various factors on their course.

The use for the synthesis of nanoparticles of acid salt silver with a long chain (for example, acetic, stearic, butyric acids) can be grounded by the fact that adsorbing on silver nanoparticles, long hydrocarbon radicals may stabilize the particles⁹ (Figure 1), preventing their aggregation. Nanoparticles passivated this way are stable under normal conditions either in solution¹⁰⁻¹⁴, in thin films, or powders. The powders may then be dispersed in non-polar solvents¹⁵⁻¹⁸.

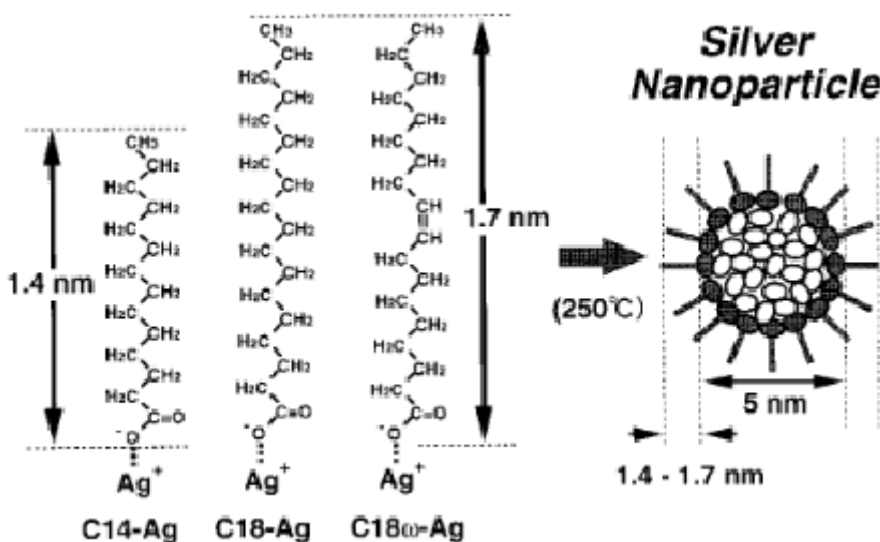


Fig. 1. Diagrammatic representation of dependences of the distance between nanoparticles using various salts of fatty acids as precursors¹⁸

We propose to use as a precursor for the silver nanoparticle synthesis both silver salts of halogenated and fatty organic acids, well-known in the literature, - silver acetate, silver trifluoroacetate, silver n-butyrate, and silver monochloroacetate not described yet.

In spite of many techniques of synthesis of silver salts of fatty acids are described in the literature. These compounds are not present in the national catalogs.

A method of silver carboxylate synthesis is known consisting of interaction of an aqueous

solution of silver nitrate and a solution of ammonium salt of organic acid¹⁹.

Organic silver salts of general formula of $!H_{x-2x-1}O_2Ag$, where $\% = 3-24$, 26, 28 were also obtained by reaction of alcoholic solution of sodium salt of the corresponding fatty acid with an aqueous solution of silver nitrate. Solution an organic acid in ethanol, was added an equivalent amount of aqueous solution of sodium hydroxide. An equivalent amount of silver nitrate was added to this alkanate solution. The precipitation was filtered off and washed with water²⁰.

Since it is known that silver monochloroacetate is used to produce a polymeric material used in surgery for the manufacture of absorbable surgical sutures in the body. This material was prepared by copolymerizing monochloroacetate silver glycolic acid by photoinduced polymerization in the solid phase.

As starting material for obtaining monochloroacetate silver commonly used inorganic silver salts, and in particular, silver nitrate. Thus, according to the well-known publications²¹, the source of silver nitrate in the first stage of the process is treated with ethanolic potassium hydroxide to form a dispersion of silver hydroxide, and then in a second stage to the resulting dispersion of silver hydroxide was added chloroacetic acid. The reaction mixture is incubated for 1 hour with stirring and at a temperature of 50°C and the precipitated title product is filtered off and recrystallized from water and dried *in vacuo*. Yield monochloroacetate silver obtained by this method is 50%. The main disadvantages of this method include uneconomic and that manifests itself in a rather low yield of the product obtained, and its inconsistency with modern environmental requirements due to the use of potassium hydroxide, which also contributes to unwanted contamination of the final product inorganic impurities.

In another known method of producing silver monochloroacetate,²², conducted in two stages, provide a first process stage to receive first sodium monochloroacetate and then receive it from monochloroacetate silver. For this process, monochloroacetic acid, aqueous sodium hydroxide solution and the reaction mixture was acidified with acetic acid and then the resulting aqueous solution of sodium monochloroacetate is poured into an

aqueous solution of silver nitrate and the resulting precipitate of silver monochloroacetate was filtered, washed with water and dried *in vacuo*. The yield of product in this case is 80-95%. A disadvantage of this process, as previously discussed analog, also is used in the synthesis process of aggressive substances such as sodium hydroxide and acetic acid, which deteriorate the environmental characteristics of the process. The use of sodium hydroxide in the process also leads to contamination of the final product by inorganic extraneous impurities and the need for additional purification steps (recrystallization), which reduces the intensity and efficiency of the process.

To increase the intensity of the process and improve its environmental and economic indicators suggest a new method of producing silver monochloroacetate comprising using as starting product monochloroacetic acid and silver nitrate in a mixture of an aqueous solution of monochloroacetic acid, and an aqueous silver nitrate solution with stirring to form a reaction mixture containing monochloroacetic acid and silver nitrate in amounts corresponding to a molar ratio, maintaining the reaction mixture at a temperature of 20-25 °C, and subsequent isolation of the precipitate by filtration, washing with water and ethanol and dried.

The main differences between the new method is known analogs of carrying out the process in one step instead of two as in prior art, and the exclusion of the use of aggressive fluids (acids and alkalis), which increases the intensity of the process, improves the environmental and economic indicators. Essentially the process of synthesis affect experimentally chosen temperature and the molar ratio of the starting monochloroacetic acid and silver nitrate (1.0-1.4: 1.0). Show additional experimental studies, with overcharge and undercharge temperature compared with the claimed mode decreases the output of the final product. Also, the output affects the molar ratio of the starting products. The advantage of the new method are softer and its conditions (compared with analogues) since the fusion process is carried out in water at room temperature (20-25 °C).

Experimental Part

Silver compound was obtained a by the below methods. All compounds were characterized

by methods of IR spectroscopy, X-ray diffraction and elemental analysis.

Synthesis of silver acetate

Solution 1.0g (0,0059m) AgNO_3 in 10 ml of H_2 in a 25 ml flask, a solution of 4 g (0.0295m) sodium acetate monohydrate was added into 20cm³ of water stirring in a magnetic stirrer. The reaction

mixture was stirred for 30 minutes, was filtered on a Schott funnel, was washed with water and was dried under vacuum. 1.5 g of silver acetate was obtained. Calc.: C-14.38%; H-1.812%. Found: C-14.69%; H-1.98%. The substance was analyzed by X-ray diffraction (figure 2).

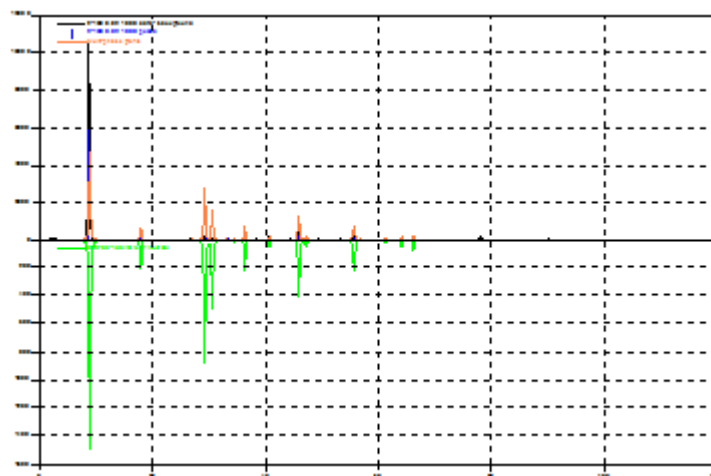


Fig. 2. X-ray pattern of silver acetate

Synthesis of silver trifluoroacetate

Solution 2.5 g (0,0147m) of AgNO_3 in 20 ml of water in 100 ml flask was added dropwise to the solution of sodium carbonate 1,715g (0.0162m) in 30cm³ of water at room temperature. The reaction mixture was stirred for 30 min, after was filtered the precipitate and washed with water and dried it

under vacuum. Trifluoroacetic acid was added to the precipitate, was stirred the solution in a magnetic stirrer and dry it under vacuum. 2.3g of silver trifluoroacetate was obtained. Calc.: C-10,859; Found: C-11,105. The substance was analyzed by X-ray diffraction (figure 3)

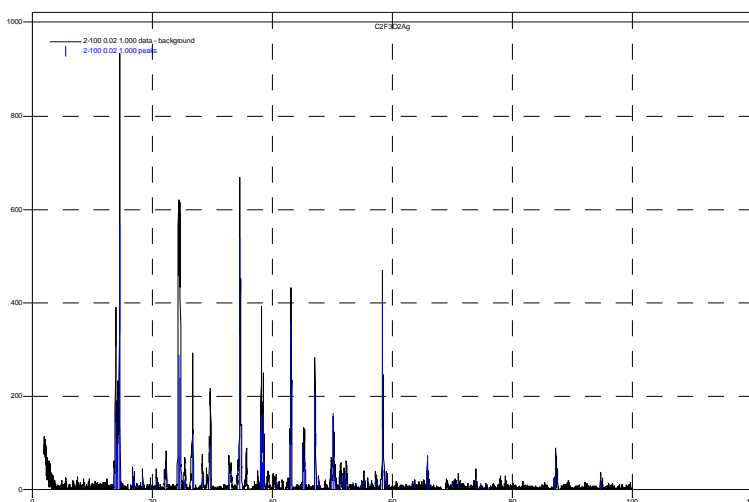


Fig. 3. X-ray pattern of silver trichloroacetate

Table 1. IR Spectroscopy Data

Peak, cm ⁻¹	Functional Group
3008, 2991, 2963	CH st
1607	(COO)-st
1401	CH ₂ δ
1248	C-Cl
767	CH ₂ γ

Table 2. IR Spectroscopy Data

Peak, cm ⁻¹	Functional Group
2955	CH st
2933	
2873	
1562	(COO)- st
1412	CH ₂ δ, CH ₃ δ as
752	CH ₂ γ

Synthesis of silver monochloroacetate

Solution 0,66g (0,007m) of chloroacetic acid in 10 ml of water in a 25 ml flask and was added 0,85g (0.005 M) of AgNO₃ in 5 ml of water to stirring. The precipitate was filtered off, was washed with water and alcohol. The product was dried to constant weight. 0,4g of silver monochloroacetate was obtained. Calc.: C-11.9%; H-0.993% Found: C-12.21%; H-1.133%. The data of IR spectroscopy are shown in table 1.

Synthesis of silver butyrate

Pour 3,6g (0,04m) of butyric (butanoic acid) into 2,8g (0,01m) of silver carbonate. The precipitate was filtered off, washed with water and alcohol. 1g silver butyrate was obtained. Calc.: C-24.63%; H-3.59% Found: C-24.177%; H-3.65%. The data of IR spectroscopy are shown in table 2

Conclusion: In order to obtain silver nanoparticles we obtained silver salts of halogenated and fatty organic acids: silver acetate, silver trifluoroacetate, silver n-butyrate, known in the literature, and silver monohlorpropionat, not described in the literature yet. The resulted compounds were characterized by IR spectroscopy, X-ray diffraction and elemental analysis. A considerable number of known methods for producing silver nanoparticles due to a chemical reaction in an aqueous medium. However, for many practical applications, the silver nanoparticles is important to obtain silver nanoparticles in aqueous media such as organic solvents and polymeric matrix. Also preparation of

nanoparticles of silver in non-aqueous media opens new possibilities control the shape and dimensions of the nanoparticles, and thus, influence on their biological, chemical and physical properties. During the performance will be studied patterns chemical interactions silver compounds with different reagents in a variety of non-aqueous media including polymeric matrix resulting in the formation of silver nanoparticles prescribed shapes and sizes. The data obtained will open the possibility of developing new materials possessing valuable practical properties, the preparation of which is difficult when using silver nanoparticles prepared in aqueous solution. Particularly important study questions introduction of silver nanoparticles in the polymeric materials by synthesizing them directly into the polymer matrix, and developing methods for producing silver nanoparticles certain predetermined size and morphological characteristics with the most pronounced antibacterial properties and suitable for incorporation into a wide range of hydrophobic polymers to create a nanocomposite .

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REFERENCES

1. Metal clusters in catalysis / Ed. by B.C. Gates, L. Guezi, H. Knosinger. Amsterdam, 1986.
2. S.N. Shtykov, T.Y. Rusanov. Nanomaterials and nanotechnologies in chemical and biochemical sensors: possibilities and application areas // *Russian Chemical Society Journal named after (D.I. Mendeleev)*. 2008; T. LII, No.2.
3. M.V. Galkin, E.V. Ageev, D.A. Nedosekin, et al. Physical properties of nanocrystalline materials, *Bulletin of Moscow University. Series 2. Chemistry*. - 2010; 51
4. A. D. Pomogailo, A.S. Rosenberg, I.E. Uflyand. Metal nanoparticles in polymers. M. Chemistry, 2000-672pg.
5. K Shameli.; M.B. Ahmad, W.M Yunus. N.A Ibrahim.; Y Gharayebi., S. Sedaghat., Synthesis of silver/montmorillonite nanocomposites using γ-irradiation. *Int. J. Nanomedicine* 2010; **5**: 1067–1077.
6. D. Donescu, C.L. Nistor, C. Purcar, C. Petcu, S.

- Serban. M.C. Corobea, M.Ghiurea, Formation and dissolution of silver nanoparticles. *J. Optoelectron. Adv. Mater.* 2009, **1**: 44–48.
7. K.G. Stamplecoskie, J.C. Scaiano, Light emitting diode can control the morphology and optical properties of silver nanoparticles. *J. Am. Chem. Soc.* 2010; **132**: 1825–1827
8. K. Shameli, M.Bin Ahmad, S. Davoud Jazayeri, S.Sedaghat, P.Shabanzadeh, H. Jahangirian, M.Mahdavi, Y. Abdollahi. Synthesis and Characterization of Polyethylene Glycol Mediated Silver Nanoparticles by the Green Method// *Int. J. Mol. Sci.* 2012; **13**: 6639-6650
9. K. Abe, T. Hanada, Y. Yoshida, N. Tanigaki, H. Takiguchi, H. Nagasawa, M. Nakamoto, T. Yamaguchi, K. Yase, Two-dimensional array of silver nanoparticles, *Thin Solid Films*, 1998 V. 327-329, 524-527
10. L.Pastoriza-Santos, M.Liz-Marzan, Self-Assembly of Silver Particle Monolayers on Glass from Ag⁺ Solutions in DMF, *Pure App. Chem.*, 2000; **83**: 72, 83
11. He X., Zhao X., Chen Y., Feng J., Sun Z. Highly controlled silica coating of PEG-capped metal nanoparticles and preparation of SERS-encoded particles. *J. Solid State Chem.*, 2007; **180**: 2262
12. I.A.Wani, S.Khatoon, A.Ganguly, J.Ahmed, A.K.Ganguli, T.Ahmad, Silver nanoparticles: Large scale solvothermal synthesis and optical properties, *Mater. Res. Bull.*, 2010; 1033
13. V.D. Buiklisky, A.V. Bepalov Synthesis of nanocomposites based on perfluorinated Sulfonated membranes with nanoscale silver particles / *worldwide scientific discoveries*. 2010; **1**(4): 50-52
14. R. Shankar, L. Groven, A. Amert, K. W. Whitesb, J. J. Kellarc. Non-aqueous synthesis of silver nanoparticles using tin acetate as a reducing agent for the conductive ink formulation in printed electronics., *J. Mater. Chem.*, 2011; **21**: 10871-10877
15. V.V.Tatarchuk, A.P.Sergievskaia, A.I. Bulavchenko, V.I.Zaikovsky, I.A.Druzhinina, T.M.Korda, G P.N.evko, A.V.Alexeyev Di-(2-ethylhexyl) dithiophosphoric acid sur-face protected gold nanoparticles: micellar synthesis, stabilization, isolation and properties // *Gold Bulletin*. 2011; **44**(4) 207-215
16. O.V. Dementieva, A.V. Malkovsky, M.A. Filippenko, Comparative study properties of silver hydrosols prepared citrate and citrate-sulfate method // *Colloid Journal*, 2008, **70**(5): 607-619.
17. I.A. Kurzina, A.S. Blokhina, , O.V. Vodyankina, Influence of the nature of the solvent on the formation of silver nanoparticles / *Bulletin of the Tomsk Polytechnic University*. 2009; **314**(3): 26-31
18. R.Chepuri, K. Rao, D.C. Trivedi, Biphasic synthesis of fatty acids stabilized silver nanoparticles: Role of experimental conditions on particle size, *Materials Chemistry and Physics* 2006; **99**: 354-360
19. L.A. Nesterova, Z.P. Bystrova, I.N. Orel, V.G. Sevastyanov, G.R. Allahverdiyev. Patent SU 1740369. Bulletin No.22 of 06.15.92
20. Chem. Mater. 2004, 16, 2021-2027 Structure and Mesomorphism of Silver Alkanoates Koen Binnemans, Rik Van Deun, Ben Thijs, Iris Vanwelkenhuysen, and Ingrid Geuens
21. M. Eppele and H. Kirschnick, The Thermally Induced Solid-state Polymerization Reaction in Halogenoacetates, , *Chem. Bev.* 1996; **129**: 1123-1129
22. TA Stromnova, Palladium nitrosyl carboxylate complexes X-ray structures of Pd4 (m-NO) 2 (m-OCOCMe3) 6 and Pd3 (NO) 2 (m-OCOCF3) 4 -2S6N5Me», *Inorganica Chimica Acta* 350 , 2003, P. 283-288.