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Chemistry

SYNTHESIS OF SILVER NANOPARTICLES AND SILVER-GOLD BINARY SYSTEM BY GALVANIC REPLACEMENT IN AN ULTRASONIC FIELD

Galyna Zozulya[1,✉], Orest Kunty[1], Mariana Shepida[1], Vasyl Kordan[2]

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Abstract. The conditions for the synthesis of colloidal solutions of silver nanoparticles by galvanic replacement in an ultrasonic field and the AgAuNP binary system by galvanic replacement have been studied. It has been shown that colloidal solutions of stabilized nanoparticles with absorption maxima at 410 nm (AgNPs) and 540–560 nm (AgAuNPs) are formed in solutions of sodium polyacrylate and metal precursors of $AgNO_3$ and $H[AuCl_4]$. The synthesized AgAuNPs are spherical in shape and their size does not exceed 20 nm.

Keywords: galvanic replacement, silver nanoparticles, silver-gold binary systems, ultrasound, magnesium, sodium polyacrylate.

1. Introduction

In recent decades, significant progress has been observed in the production of metal nanoparticles[1, 2]. The greatest attention is paid to the research of silver (AgNPs)[3–7] and gold (AuNPs)[8–11] nanoparticles since they are characterized by unique physical, physicochemical, and chemical properties. Accordingly, they have a wide range of applications in high-tech scientific and technological fields. Thus, the antibacterial and optical properties of AgNPs determine their use in the biological and biomedical fields, optoelectronics, and wastewater treatment[12–14]. AuNPs have high catalytic activity, unique thermal, electronic, and optical properties, affinity, biocompatibility, and non-toxicity. They are used to develop photoelectronic devices, highly sensitive sensors, efficient catalysts for chemical and electrochemical processes, biomedical preparations, and therapeutic agents for drug delivery[15, 16]. Recently, special attention has been paid to binary nanoparticles M_1M_2NPs, which are characterized by a synergistic combination of the properties of M_1NPs and M_2NPs[17, 18]. In particular, the AgAuNPs system, in which the synergistic combination of silver and gold in a bimetallic nanostructure, effectively enhances their catalytic properties and significantly expands their applications[18, 19].

The functionality of nanoparticles is determined by their morphological features (size, shape), homogeneity, and chemical composition (in the case of binary nanoparticles). These features, accordingly, depend on the production method. To tune specific functional properties, the main focus is on the controllability of the synthesis of MNPs. One of the prospective methods in nanotechnology is a galvanic replacement (GR), which serves as a simple and effective way to obtain mono- and bimetallic nanoparticles with controlled morphology[20, 21]. GR is a spontaneous oxidation-reduction process that occurs through an electrochemical mechanism. This process involves the electricity-generating half-reaction of the oxidation of the sacrificial metal M_2 on the anode area (1) and the half-reaction of the reduction of the metal M_1 on the cathode area (2). This is reflected by the generalized equation (3). In this case, the equilibrium electrode potential value of the sacrificial metal should be lower than that of the restored metal.

$$nM_2 \rightarrow nM_2^{m+} + me \quad (1)$$

$$mM_1^{n+} + ne \rightarrow mM_1 \quad (2)$$

$$mM_1^{n+} + nM_2 \leftrightarrow mM_1 + nM_2^{m+} \quad (3)$$

By using surfactant-containing solutions, galvanic replacement in an ultrasound field (sonogalvanic replacement) produces stabilized metal nanoparticles in the bulk of the solution (Fig. 1). This is a relatively new and little-studied area of GR[22–24], characterized by the technological efficiency of synthesizing colloidal solutions of stabilized nanoparticles of noble metals, particularly silver and gold. The peculiarity of sonogalvanic replacement is that reaction (3) occurs only during the stages of nucleation and formation of M_1NPs. Subsequently, surfactant molecules

[1] Lviv Polytechnic National University, 12, S. Bandery Str., Lviv, 79013, Ukraine
[2] Ivan Franko National University of Lviv, 6, Kyryla i Mefodiya Str., Lviv, 79005, Ukraine
✉ *gzozula@ukr.net*

are adsorbed on the surface of nanoparticles, forming surface complexes. This process slows down the growth of M1NPs, prevents agglomeration, and ensures stability. Under the influence of ultrasound, the synthesized nanoparticles are detached from the surface of the sacrificial metal M_2. Additionally, in the ultrasonic field, the dissolution rate of M_2 according to reaction (1) increases. Consequently, the reduction of M_1^{n+} ions according to reaction (2) and the nucleation process accelerates, promoting the formation of nano-sized particles.

The purpose of this study was to determine the conditions for synthesizing colloidal solutions of silver nanoparticles by galvanic replacement in an ultrasonic field and a binary system of AgAuNPs by galvanic replacement in aqueous solutions of metal precursors and a surfactant using magnesium as a sacrificial metal.

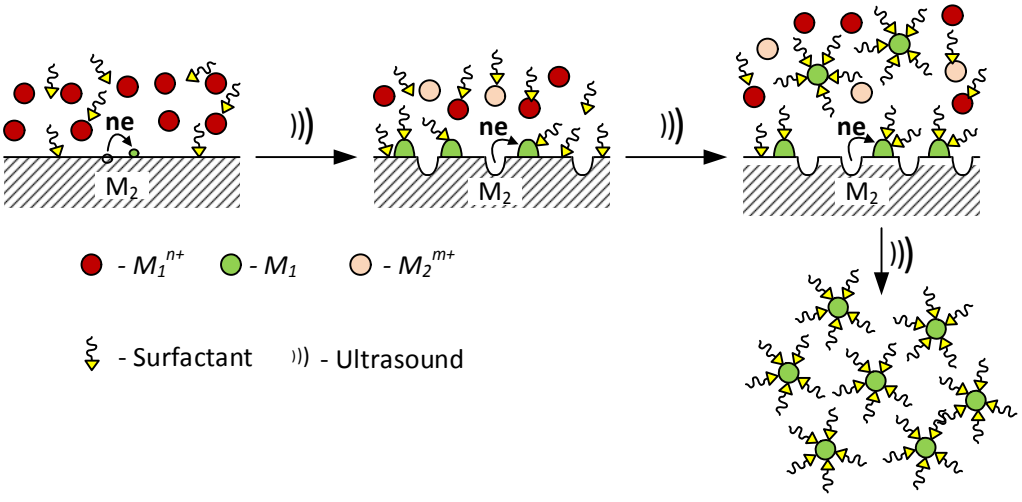


Fig. 1. Scheme of the galvanic replacement process with the formation of metal nanoparticles (M_1) of the surface of the sacrificial metal (M_2)

2. Experimental

2.1. Materials

For the synthesis of AgNPs by galvanic replacement in an ultrasound field and AgAuNPs by galvanic replacement, the following materials were used: metal precursors $AgNO_3$ (99.9 %, Alfa Aesar) and $H[AuCl_4]\cdot 3H_2O$ (99.99 %, Alfa Aesar), magnesium scrap (99.5 %, Alfa Aesar) with a fractional composition of 0.75–1.0 mm as a reducing agent for silver ions, and sodium polyacrylate (NaPA) with MW = 1000 (45 % aqueous solution, Sigma – Aldrich) as a surfactant. The magnesium scrap was etched in a 1M acetic acid solution before the experiments to remove oxide from the surface, then washed with isopropanol, and dried in an airstream at 60 °C.

2.2. Methods

The research was carried out in the following directions: 1) synthesis of solutions of silver nanoparticles stabilized with a polyacrylate anion by galvanic replacement in an ultrasound field; 2) synthesis of solutions of silver-gold binary system nanoparticles by galvanic replacement; 3) study of their main characteristics, including absorption spectra, nanoparticle sizes, and uniformity of distribution.

The synthesis of AgNPs by sonogalvanic replacement was performed using an ultrasonic emitter of the magnetostrictive type, specifically the Bandelin Sonopuls HD 2200.2 (Germany), at a power of 20 W and a frequency of 20 kHz. The detailed technique has been described in previous studies[24, 25]. The main synthesis parameters were as follows: precursor concentrations of 0.5 mM $AgNO_3$, 5 $g\cdot L^{-1}$ NaPA, magnesium scrap mass of 0.25 g, and a reaction solution temperature ranging from 20 to 40 °C.

The synthesis of AgAuNPs by galvanic replacement involved the following steps: 50 cm^3 of a presynthesized 0.5 mM solution of AgNPs was placed in a glass thermostated container with a volume of 100 cm^3, and a solution of $HAuCl_4$ was added. Simultaneously, a magnetic stirrer and a stopwatch were turned on. Samples of the solution were periodically taken for spectroscopic studies. The obtained AgAuNPs solutions were stored in glass flasks placed in containers. The studies were conducted at initial molar ratios of Ag and Au in the bimetallic compositions of 10:1, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5,

and 1:10, with a temperature interval of the reaction solution of 20–40 °C.

The samples of solutions were analyzed using the UV-3100PC UV-Vis-spectrophotometer (Shanghai Mapada Instruments Co., Ltd. (China)) in quartz cuvettes with a thickness of 1 cm in the wavelength region from 190 to 1100 nm. The comparison solution was distilled water. TEM images of the samples were recorded using a JEM-I230 (JEOL, Tokyo, Japan) operating at an accelerating voltage of 80 kV. TEM grids were preliminarily supplied with a formvar film, which was then fixed by carbon using a JEE-4X vacuum evaporator (JEOL, Tokyo, Japan). Small drops (0.01–0.05 μL) of the gold compositions were applied to grids under a light microscope and dried in air at room temperature. The size of the obtained AgNPs and AgAuNPs was determined using TEM images by comparing the sizes of individual particles with the scales presented in the images. SEM examination of the samples was carried out using the electron microscope Tescan Vega 3 LMU equipped with an X-MaxN 20 silicon drift detector. Overall compositions were investigated by energy-dispersive X-ray spectroscopy (EDX) using energy-dispersive integral maps analysis.

3. Results and Discussion

The formation of AuAgNPs by galvanic replacement occurs in two stages: 1) synthesis of AgNPs in solutions of $AgNO_3$ and sodium polyacrylate using magnesium as a sacrificial metal through galvanic replacement in an ultrasound field; 2) synthesis of AuAgNPs by galvanic replacement of pre-obtained AgNPs with an $H[AuCl_4]$ solution.

$AgNO_3$ in NaPA surfactant solutions forms $[Ag_mPA]^{(n-m)-}$ complexes, due to the electron-donating properties of the polymer anion PA^{n-}. The deposition of silver on the surface of magnesium in $AgNO_3$ + NaPA solutions can be described by the generalized equation of galvanic replacement (4):

$$[Ag_mPA]^{(n-m)-} + m/2Mg \rightarrow \rightarrow [Ag(0)_mPA]^{n-} + m/2Mg^{2+} \quad (4)$$

Due to the electrons generated as a result of the anodic dissolution reaction of the sacrificial magnesium metal (5), the complex ions $[Ag_mPA]^{(n-m)-}$ are reduced at the cathode areas, leading to the formation of $[Ag(0)_mPA]^{n-}$ (6) and subsequent formation of AgNCs@PA nanoclusters and stabilized silver nanoparticles AgNPs@PA (7).

$$m/2Mg \rightarrow m/2Mg^{2+} + me \quad (5)$$

$$[Ag_mPA]^{(n-m)-} + me \rightarrow [Ag(0)_mPA]^{n-} \quad (6)$$

$$[Ag(0)_mPA]^{n-} \rightarrow AgNCs@PA \rightarrow AgNPs@PA \quad (7)$$

Magnesium, as an active sacrificial metal-reductant ($E^0Mg^{2+}/Mg = -2.36$ V), provides a significant difference between the standard electrode potentials of half-reactions (5) and (6). This causes a high reaction rate (4) and, accordingly, and promotes the nucleation process of silver on the surface of magnesium scrap. Mg and Ag are characterized by significant differences in crystal structures (hexagonal for Mg and face-centered cubic for Ag) and have different lattice parameters (a = 0.321 and c = 0.521 nm for Mg and a = 0.409 nm for Ag). This results in the formation of an island-type precipitate consisting of discrete AgNPs on the substrate, that is, according to the Volmer – Weber growth mode[26–28]. The significant difference (6.4 %)[26] in the interplanar distance between the crystal structures of Mg and Ag causes weak binding of silver nanoparticles to the magnesium surface. In an ultrasonic field, AgNPs are easily detached from the substrate and move into the volume of the surfactant solution. Molecules of surfactant (PA^-) are adsorbed on the surface of silver nanoparticles and provide their stabilization with the formation of yellow-brown colloidal solutions, which have an absorption maximum of 410 nm (Fig. 2). In this case, during sonogalvanic synthesis, the value of the maximum practically does not change. It also does not change during the long-term storage (90 days) of synthesized colloidal solutions. The nature of the absorption spectra of AgNPs solutions indicates the monodispersity of the synthesized silver nanoparticles[29].

The sonogalvanic synthesis of AgNPs is characterized by certain features, which are explained by the action of the ultrasonic field in solutions. These features include: 1) a significant increase in mass transfer at the magnesium surface, which provides the acceleration of reactions (5) and (6); 2) sonolysis of water with the formation of radicals (H·, ·OH, HO_2·) and their interaction products (H_2O_2)[30, 31].

The latter causes the sonoreduction of $[Ag_mPA]^{(n-m)-}$ ions (8–10).

$$[Ag_mPA]^{(n-m)-} + H\cdot \rightarrow [Ag(0)_mPA]^{n-}. \quad (8)$$

$$[Ag_mPA]^{(n-m)-} + R\cdot \rightarrow [Ag(0)_mPA]^{n-}. \quad (9)$$

$$[Ag_mPA]^{(n-m)-} + H_2O_2 \rightarrow [Ag(0)_mPA]^{n-}. \quad (10)$$

So, the reduction of $[Ag_mPA]^{(n-m)}$ ions simultaneously occurs on the surface of the sacrificial magnesium by reaction (4) and chemical reduction in the solution by the products of water sonolysis.

During the synthesis of AgNPs by sonogalvanic replacement, spherical nanoparticles of small sizes (10–15 nm) are formed with a small spread in diameter (Fig. 3). However, no significant changes in their size and shape are observed with the increasing concentration of $AgNO_3$ in the working solution and the temperature of galvanic replacement.

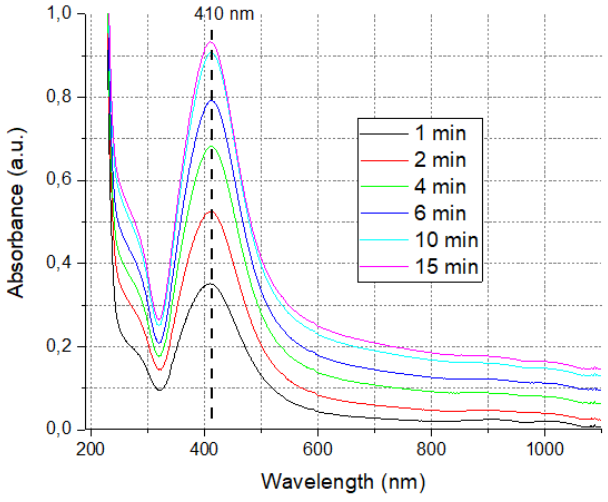


Fig. 2. UV-Vis absorption spectrum of AgNPs solutions in 5 g·L^{-1} NaPA solution after sonogalvanic replacement by magnesium scrap for 15 min, with 0.5 mM $AgNO_3$, at 20 °C

Silver nanoparticles obtained by sonogalvanic replacement of magnesium in sodium polyacrylate solutions were used as sacrificial templates for the synthesis of AgAu bimetallic nanostructures in $H[AuCl_4]$ solution by the galvanic replacement reaction (11).

$$[AuCl_4]^- + 3Ag \rightarrow Au + 3Ag^+ + Cl^- \quad (11)$$

At a stoichiometric ratio of Ag:Au = 1:3, three Ag atoms are ionized for each Au atom deposited. The formed Ag(+) ions pass into the solution, leading to the formation of vacancies at the interface. These vacancies significantly simplify the migration of Au and Ag atoms in the near-surface layer. As the concentration of vacancies increases, they unite, forming holes on the surface. These holes serve as centers for further ionization of Ag, transitioning into the solution. Silver and gold are characterized by close parameters of the crystal lattice (0.408 nm and 0.409 nm, respectively), which facilitates the easy formation of binary compounds between these metals according to the Frank-van der Merwe (layer) growth mode[26, 28].

At initial molar ratios of Ag:Au = 10:1, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5, and 1:10 during galvanic replacement, according to equation (11), the solutions of AgNPs change color from yellow to red (Fig. 4) with an absorption maxima ranging from approximately 410 to 560 nm.

In the absorption spectra, the maxima of the bands of localized surface plasmon resonance (LSPR) of silver and gold are located in the visible region of the spectrum at 410 and 560 nm, respectively. For bimetallic silver-gold nanoparticles, the maxima of the LSPR bands lie between the maxima of the individual metals and depend on their content in the particle. These maxima gradually shift to the region of longer wavelengths as the molar ratio of Ag:Au metals in the bimetallic system decreases (Fig. 4). This shift is accompanied by a successive color change from yellow to red.

The formation of bimetallic nanosystems was confirmed by scanning microscopy and EDX analysis. A uniform distribution of silver and gold was revealed (Fig. 5). It is shown that the metal content in AgAuNPs, synthesized through galvanic replacement in a $HAuCl_4$ solution at an Ag:Au molar ratio of 1:3, is 55.36 % silver and 44.64 % gold.

The effect of $H[AuCl_4]$ concentration and temperature, as the main parameters of galvanic replacement, on the synthesis rate and geometry of AgAuNPs was studied. Colloidal solutions of AgAuNPs with an absorption maximum at ~560 nm are formed in the range of 0.2–0.4 mM $H[AuCl_4]$ at 20–40 °C. The maximum practically does not change with increasing concentration and temperature, while the synthesis rate of binary AgAuNPs nanoparticles increases proportionally (Fig. 6).

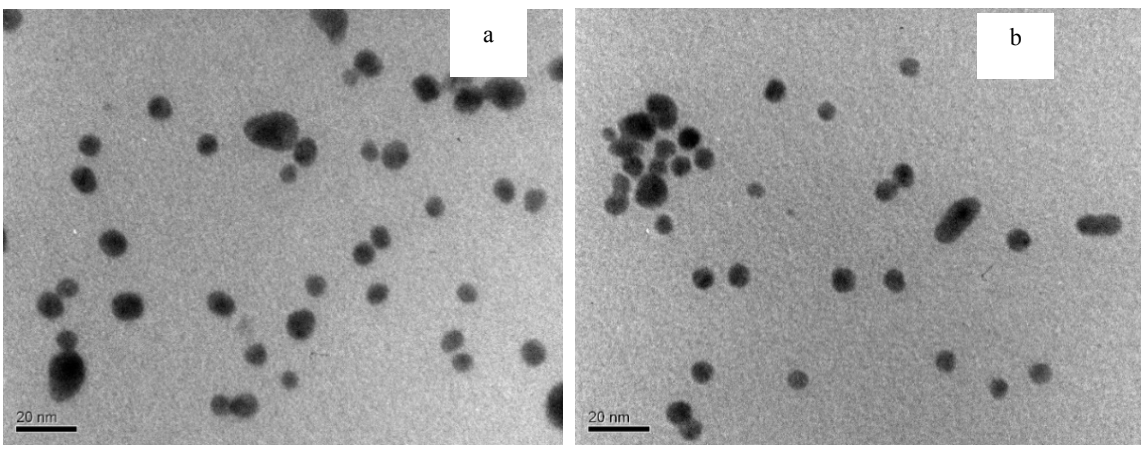


Fig. 3. TEM images of AgNPs synthesized in solutions of 0.5 mM $AgNO_3$ and 5 g·L^{-1} NaPA at temperatures of 20 (a) i 40 (b) °C

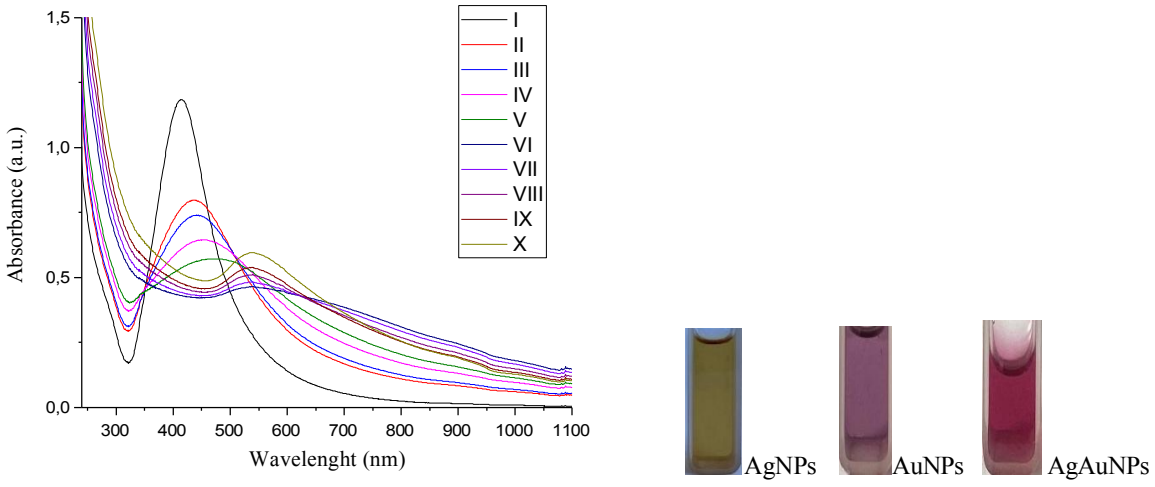
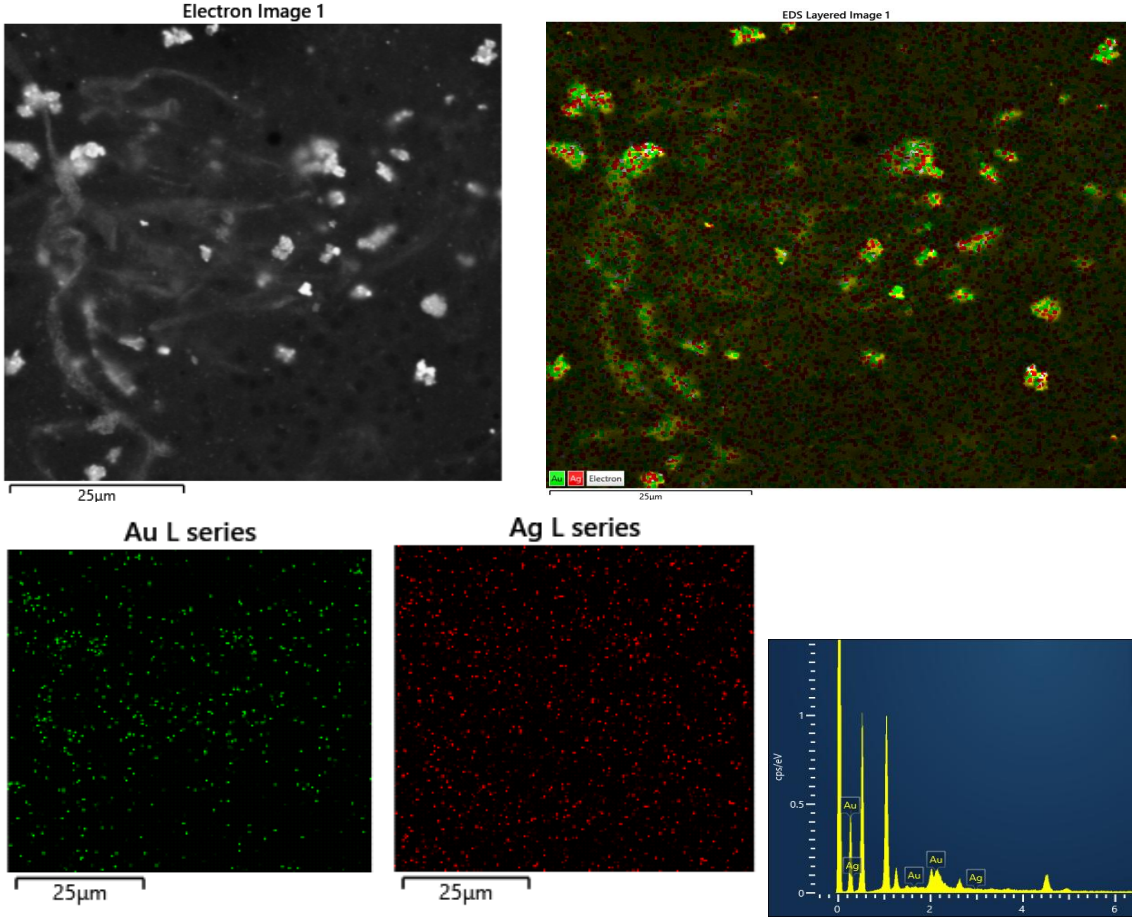


Fig. 4. UV-Vis absorption spectrum of nanoparticles solutions before (I) and after (II–X) galvanic replacement in $H[AuCl_4]$ at different Ag:Au molar ratios: 10:1, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5 and 1:10, respectively, and images of solutions containing Ag, Au, and AgAu nanoparticles synthesized by galvanic replacement



Map Sum Spectrum	Atomic %
Ag	55.36
Au	44.64
Total	100.00

Fig. 5. EDX mapping of the surface of Ag-AuNPs nanoparticles synthesized by galvanic replacement at a molar ratio of Ag:Au = 1:3 and a temperature of 20 °C

Small spherical AgAuNPs with a diameter of 15–20 nm are formed by galvanic replacement (Fig. 7). It was found that the size of the formed AgAu nanoparticles depends on the initial size of AgNPs and slightly increases after the formation of the bimetal. As the temperature increases, AgAuNPs tend to aggregate (Fig. 7, *c*). This can be explained by a decrease in the binding strength of polyacrylate anions (PA^-), as a stabilizer, to the surface of the nanoparticles.

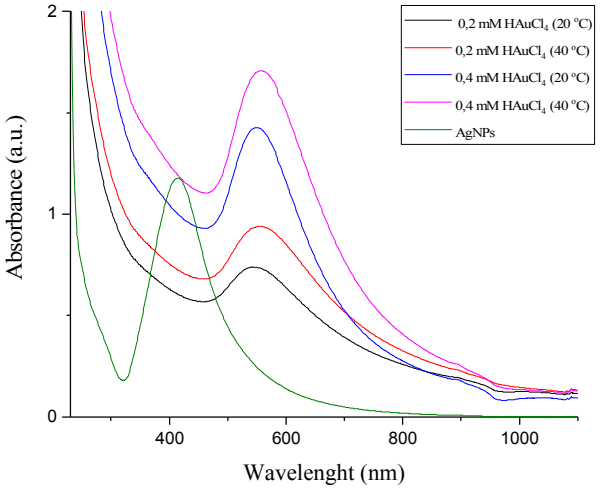


Fig. 6. UV-Vis absorption spectrum of Ag-AuNPs nanoparticles synthesized by galvanic replacement at concentrations of $H[AuCl_4]$ 0.2 mM, 0.4 mM for 1 min at temperatures of 20 °C and 40 °C

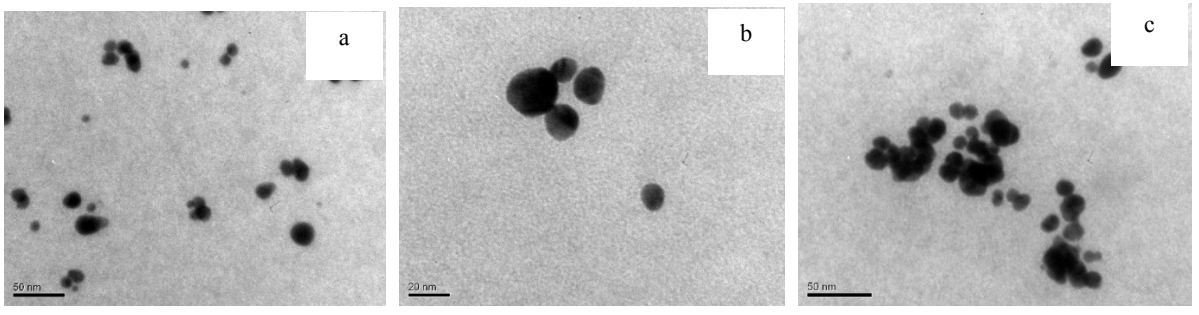


Fig. 7. TEM images of AuAgNPs synthesized by galvanic replacement in solutions of AgNPs in NaPA + $H[AuCl_4]$, for 1 min at temperatures of 20 °C (*a, b*) and 40 °C (*c*)

4. Conclusions

Galvanic replacement is an effective method for synthesizing monometallic AgNPs and bimetallic AuAgNPs systems. Stable and monodisperse nanoparticles are obtained by galvanic replacement in an ultrasound field using metal precursors and surfactants. The use of magnesium as an active sacrificial metal-reducing agent provides a high rate of galvanic replacement and the formation of nano-sized particles.

The process of obtaining AuAgNPs by galvanic replacement occurs in two stages: 1) the synthesis of AgNPs in solutions of $AgNO_3$ and sodium polyacrylate using magnesium as a sacrificial metal by galvanic replacement in an ultrasonic field, and 2) the synthesis of AuAgNPs by galvanic replacement of the synthesized AgNPs with an $H[AuCl_4]$ solution.

Stable colloidal solutions of AgNPs with an absorption maximum at 410 nm are formed in solutions containing 0.5 mM $AgNO_3$ and polyacrylate in an ultrasonic field (20 kHz). The sizes of AgNPs synthesized through sono-galvanic replacement are 10–15 nm and remain unchanged with increasing temperature up to 40 °C.

The synthesis of AuAgNPs occurs due to the galvanic replacement of AgNPs in solutions containing 0.2–0.4 mM $H[AuCl_4]$ at 20–40 °C. The AgAuNPs solutions are characterized by an absorption maximum at approximately 560 nm wavelength, and by particles with a diameter of 15–20 nm. The latter depends on the size of

the sacrificial AgNPs. As the temperature increases, there is a tendency for the AgAuNPs to aggregate.

Nanoparticles of the AgAu binary system, synthesized using the galvanic method, are characterized by stability over time, monodispersity, and small sizes. These nanoparticles have great potential for various biomedical applications and sensing technologies.

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References

[1] Habibullah, G.; Viktorova, J.; Ruml, T. Current Strategies for Noble Metal Nanoparticle Synthesis. *Nanoscale Res. Lett*. **2021**, *16*, 47. https://doi.org/10.1186/s11671-021-03480-8

[2] Rodrigues, T.S.; Da Silva, A.G.M.; Camargo, P.H.C. Nanocatalysis by Noble Metal Nanoparticles: Controlled Synthesis for the Optimization and Understanding of Activities. *J. Mater. Chem. A* **2019**, *7*, 5857–5874. https://doi.org/10.1039/c9ta00074g

[3] Naganthran, A.; Verasoundarapandian, G.; Khalid, F.E.; Masarudin, M.J.; Zulkharnain, A.; Nawawi, N.M.; Karim, M.; Abdullah, C.A.C.; Ahmad, S.A. Characterization and Biomedical Application of Silver Nanoparticles. *Materials* **2022**, *15*, 427. https://doi.org/10.3390/ma15020427

[4] Wahab, M.A.; Luming, L.; Matin, M.A.; Karim, M.R.; Aijaz, M.O.; Alharbi, H.F.; Abdala, A.; Haque, R. Silver Micro-Nanoparticle-Based Nanoarchitectures: Synthesis Routes, Biomedical Applications, and Mechanisms of Action. *Polymers* **2021**, *13*, 2870. https://doi.org/10.3390/polym13172870

[5] Parmar, S.; Kaur, H.; Singh, J.; Matharu, A.S.; Ramakrishna, S.; Bechelany, M. Recent Advances in Green Synthesis of Ag NPs for Extenuating Antimicrobial Resistance. *Nanomaterials* **2022**, *12*, 1115. https://doi.org/10.3390/nano12071115

[6] Kuntyi, O.I.; Kytsya, A.R.; Mertsalo, I.P.; Mazur, A.S.; Zozula, G.I.; Bazylyak, L.I.; Topchak, R.V. Electrochemical Synthesis of Silver Nanoparticles by Reversible Current in Solutions of Sodium Polyacrylate. *Colloid Polym. Sci*. **2019**, *297*, 689–695. https://doi.org/10.1007/s00396-019-04488-4

[7] Kuntyi, O.; Shepida, M.; Sozanskyi, M.; Mazur, A.; Kytsya, A.; Bazylyak, L. Sonoelectrochemical Synthesis of Silver Nanoparticles in Sodium Polyacrylate Solution. *Biointerf. Res. Appl. Chem*. **2020**, *11*, 12202–12214. http://doi.org/10.33263/briac114.1220212214

[8] Anik, M.I.; Mahmud, N.; Masud, A.A.; Hasan, M. Gold Nanoparticles (GNPs) in Biomedical and Clinical Applications: A Review. *Nano Select*. **2022**, *3*, 792–828. https://doi.org/10.1002/nano.202100255

[9] Ielo, I.; Rando, G.; Giacobello, F.; Sfameni, S.; Castellano, A.; Galletta, M.; Drommi, D.; Rosace, G.; Plutino, M.R. Synthesis, Chemical–Physical Characterization, and Biomedical Applications of Functional Gold Nanoparticles: A Review. *Molecules* **2021**, *26*, 5823. https://doi.org/10.3390/molecules26195823

[10] Timoszyk, A.; Grochowalska, R. Mechanism and Antibacterial Activity of Gold Nanoparticles (AuNPs) Functionalized with Natural Compounds from Plants. *Pharmaceutics* **2022**, *14*, 2599. https://doi.org/10.3390/pharmaceutics14122599

[11] Mazur, A.; Shepida, M.; Zozulya, G.; Kuntyi, O. Synthesis of Gold Nanoparticles by Sonogalvanic Replacement in Sodium Polyacrylate Solutions. 2023 IEEE 13th International Conference Nanomaterials: Applications & Properties (NAP),10-15 September, Bratislava, 2023. https://doi.org/10.1109/NAP59739.2023.10310801

[12] Gherasim, O.; Puiu, R.A.; Bîrcă, A.C.; Burdușel, A.C.; Grumezescu, A.M. An Updated Review on Silver Nanoparticles in Biomedicine. *Nanomaterials* **2020**, *10*, 2318. https://doi.org/10.3390/nano10112318

[13] Shabaninezhad, M.; Ramakrishna G. Theoretical Investigation of Plasmonic Properties of Quantum-Sized Silver Nanoparticles. *Plasmonics*, **2020**, *15*, 783–795. https://doi.org/10.1007/s11468-019-01102-9

[14] Znak, Z.; Kochubei V. Influence of Natural Clinoptilolite Modification with Ions and Zero-Valent Silver on Its Sorption Capacity. *Chem. Chem. Technol*. **2023**, *17*, 646–654. https://doi.org/10.23939/chcht17.03.646

[15] Datta, D.; Deepak, K.S.; Das, B. Progress in the Synthesis, Characterisation, Property Enhancement Techniques and Application of Gold Nanoparticles: A Review. *MRS Commun.* **2022**, *12*, 700–715. https://doi.org/10.1557/s43579-022-00216-2

[16] Sengani, M.; Grumezescu, A.M.; Rajeswari, V.D. Recent Trends and Methodologies in Gold Nanoparticle Synthesis - A Prospective Review on Drug Delivery Aspect. *Open Nano* **2017**, *2*, 37–46. https://doi.org/10.1016/j.onano.2017.07.001

[17] Idris, D.S.; Roy, A. Synthesis of Bimetallic Nanoparticles and Applications-An Updated Review. *Crystals* **2023**, *13*, 637. https://doi.org/10.3390/cryst13040637

[18] Loza, K.; Heggen, M.; Epple, M. Synthesis, Structure, Properties, and Applications of Bimetallic Nanoparticles of Noble Metals. *Adv. Function. Mater.* **2020**, *30*, 1909260. https://doi.org/10.1002/adfm.201909260

[19] Fu, J.; Wang, S.; Zhu, J.; Wang, K.; Gao, M.; Wang, X.; Xu, Q. Au-Ag Bimetallic Nanoparticles Decorated Multi-Amino Cyclophosphazene Hybrid Microspheres as Enhanced Activity Catalysts for the Reduction of 4-Nitrophenol. *Mater. Chem. Phys*. **2018**, *207*, 315–324. https://doi.org/10.1016/j.matchemphys.2018.01.002

[20] Silva, A.G.M.; Rodrigues, T.S.; Haigh, S.J.; Camargo, P.H.C. Galvanic Replacement Reaction: Recent Developments for Engineering Metal Nanostructures Towards Catalytic Applications. *Chem. Commun*. **2017**, *53*, 7135−7148. https://doi.org/10.1039/C7CC02352A

[21] Cheng, H.; Wang, C.; Qin, D.; Xia, Y. Galvanic Replacement Synthesis of Metal Nanostructures: Bridging the Gap between Chemical and Electrochemical Approaches. *Acc. Chem. Res*. **2023**, *56*, 900−909. https://doi.org/10.1021/acs.accounts.3c00067

[22] Wu, C.; Mosher, B.P.; Zeng, T. Chemically-mechanically Assisted Synthesis of Metallic and Oxide Nanoparticles in Ambient Conditions. *J. Nanosci. Nanotechnol*. **2008**, *8*, 386–389. https://doi.org/10.1166/jnn.2008.18144

[23] Kuntyi, O.; Zozulya, G.; Kytsya, A. "Green" Synthesis of Metallic Nanoparticles by Sonoelectrochemical and Sonogalvanic Replacement Methods. *Bioinorg Chem Appl.* **2021**, *2021*, 9830644. https://doi.org/10.1155/2021/9830644

[24] Zozulya, G.; Kuntyi, O.; Mnykh, R.; Kytsya, A.; Bazylyak, L. Synthesis of Silver Nanoparticles by Sonogalvanic Replacement on Aluminium Powder in Sodium Polyacrylate Solutions. *Ultrason Sonochem.* **2022**, *84*, 105951. https://doi.org/10.1016/j.ultsonch.2022.105951

[25] Zozulya, G.; Kuntyi, O.; Mnykh, R.; Sozanskyi, M. Synthesis of Antibacterially Active Silver Nanoparticles by Galvanic Replacement on Magnesium in Solutions of Sodium Polyacrylate in an Ultrasound. *Chem. Chem. Technol.* **2021**, *15*, 493–499. https://doi.org/10.23939/chcht15.04.493
[26] Niu, K.-Y.; Kulinich, S.A.; Yang, J.; Zhu, A.L.; Du, X.-W. Galvanic Replacement Reactions of Active-Metal Nanoparticles. *Chem. Eur. J.* **2012**, *18*, 4234–4241. https://doi.org/10.1002/chem.201102544
[27] Asselin, J.; Boukouvala, C.; Wu, Y.; Hopper, E.R.; Collins, S.M.; Biggins, J.S.; Ringe, E. Decoration of Plasmonic Mg Nanoparticles by Partial Galvanic Replacement. *J. Chem. Phys.* **2019**, *151*, 244708. https://doi.org/10.1063/1.5131703
[28] Kuntyi, O.I.; Zozulya, G.I.; Shepida, M.V. Nanoscale Galvanic Replacement in Non-Aqueous Media: A Mini-Review. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2020**, *4*, 5–15. https://doi.org/10.32434/0321-4095-2020-131-4-5-15
[29] Bastús, N.G.; Merkoçi, F.; Piella, J.; Puntes V. Synthesis of Highly Monodisperse Citrate-Stabilized Silver Nanoparticles of up to 200 nm: Kinetic Control and Catalytic Properties. *Chem. Mater.* **2014**, *26*, 2836–2846. https://doi.org/10.1021/cm500316k
[30] Znak, Z.O.; Sukhatskiy, Yu.V.; Mnykh, R.V.; Tkach, Z.S. Thermochemical Analysis of Energetics in the Process of Water Sonolysis in Cavitation Fields. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2018**, *3*, 64−69.
[31] Pollet, B.G. The Use of Ultrasound for the Fabrication of Fuel Cell Materials. *Int. J. Hydrogen Energy* **2010**, *35*, 11986–12004. https://doi.org/10.1016/j.ijhydene.2010.08.021

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СИНТЕЗ НАНОЧАСТИНОК СРІБЛА ТА БІНАРНОЇ СИСТЕМИ СРІБЛО–ЗОЛОТО ГАЛЬВАНІЧНИМ ЗАМІЩЕННЯМ В УЛЬТРАЗВУКОВОМУ ПОЛІ

Анотація. *Досліджено умови синтезу колоїдних розчинів наночастинок срібла гальванічним заміщенням в ультразвуковому полі та бінарної системи AgAuNPs гальванічним заміщенням. Показано, що в розчинах натрію поліакрилату та прекурсорів металів* $AgNO_3$ *і* $H[AuCl_4]$ *утворюються колоїдні розчини стабілізованих наночастинок з максимумами поглинання 410 нм (AgNPs) й 540–560 нм (AgAuNPs). Синтезовані AgAuNPs мають сферичну форму, їхні розміри не перевищують 20 нм.*

Ключові слова: *гальванічне заміщення, наночастинки срібла, бінарні системи срібло–золото, ультразвук, магній, натрію поліакрилат.*