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# Study of electrical conductivity of the coatings of bimetallic Au-Ag nanoparticles

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#### ABSTRACT

The "metallic" temperature variation of the electrical resistance of chemical coatings of starlike gold-silver nanoparticles with a silver content of 6.6% at. to 13.1% at. is carefully analyzed in the temperature range 4.2–300 K. Features of low-temperature measurements of the resistance of nanocoatings were found and explained. The possibility of the superconductivity appearance in such structures is discussed.

# 1. Introduction

In recent years, one of the main directions in physical research of solids has been the study of the properties of formations (ensembles) of nanoparticles (NPs) of various materials (metals, semimetals, semiconductors and dielectrics). These properties turned out to be significantly different from the properties of the same materials in the form of solids with macroscopic dimensions. The reason for these features was the increased contribution of surface energy to the total energy of NPs, as well as quantum-size effects [1]. This led not only to a change in the physical properties of the materials themselves, but also to a change in their interaction with the environment. For example, it became possible to create highly sensitive and miniature gas sensors in the form of nanocomposites based on liquid crystals and carbon nanotubes [2], as well as on the basis of nanocontacts between two metals [3]. An unusual effect of gold (Au) nanoparticles on the biological environment was discovered, which allows to create new types of medicines for the fight against cancer [4]. One example of the effect of particle sizes on their physical properties was the discovery of the nonlinear optical susceptibility of Au nanoparticle coatings [5]. The peculiarity of obtaining coatings in these experiments was the use of chemical low-temperature technologies. Such technologies ensure high purity of coatings and eliminate the appearance of mechanical stresses [6].

Gold nanoparticles are most of all applied in medicine because of high biocompatibility and chemical firmness. On the other hand it is known, that silver has most great among metals a factor of absorption in a region of plasmon resonance frequencies. Thus, the bimetallic system gold-silver can have positive properties of gold and silver [7]. Recent researches of optical properties of coatings of bimetallic nanoparticles (NPs), containing gold, have confirmed, that they are improving significantly at chemical association of gold and silver in one nanoparticle (NP). Thus properties (in particular, stability in relation to silver oxidation) bimetallic Au-Ag NPs above if a core of the NP is gold, and silver to be on its periphery [8–10].

The important role is played also by morphology and size of the NPs. At optical researches resolution of Raman spectroscopy of substances on substrates with a coating of bimetallic starlike NPs repeatedly increases in comparison with a coating of round NPs [11–14]. Substrates with such coatings are known as surface-enhanced Raman scattering (SERS) substrates. On tips of the starlike NPs is collected electrons and form the big local intensity of electric field providing additional splitting of quantum levels of investigated substances. SERS-substrates find application for diagnostics of cancer diseases, the analysis of pesticides, detection of explosives, in research of other difficult chemical compounds [11]. The best optical properties SERS-substrates are received at the sizes starlike NPs, equal 55–73 nm [15,16]. In too time the value of electric conductivity of starlike coatings and its influence on optical properties SERS-substrates were not studied.

Regarding the study of conductive properties of coatings of round Au-Ag NPs outstanding results are here too reached. Researches of

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conducting properties of coatings of round bimetallic Au-Ag NPs, executed by scientists from India in 2018–2019, have allowed to find out their dependence on percentage of silver in these NPs and even superconductivity signs at the temperatures close to room (nearby 300 K) [17, 18]. Acknowledgement of superconducting properties of coatings of such NPs in journal publications of other authors while is absent.

The purpose of our work is studying electrical conductivity of coatings, consisting of starlike Au-Ag NPs in the sizes 40–70 nm at various silver contents, and check of possibility of occurrence in them super-conductivity in a range of temperatures 4.2–300 K.

## 2. Samples preparation method

To obtain coatings based on bimetallic Au-Ag starlike nanoparticles (NPs), we used chloroauric acid HAuCl<sub>4</sub> 3H<sub>2</sub>O ( $\geq$ 99.9%); trisodium citrate Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> ( $\geq$ 98.0%); hydrochloric acid HCl ( $\sim$ 38.0%); silver nitrate AgNO<sub>3</sub> ( $\geq$ 99.8%); ascorbic acid C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> ( $\geq$ 99.0%); (3-aminopropyl) triethoxysilane (APTES) C<sub>9</sub>H<sub>23</sub>NO<sub>3</sub>Si ( $\geq$ 99.0%); sulfuric acid H<sub>2</sub>SO<sub>4</sub> ( $\sim$ 98.0%); hydrogen peroxide H<sub>2</sub>O<sub>2</sub> ( $\sim$ 38.0%); ethyl hydroxide C<sub>2</sub>H<sub>6</sub>O  $\sim$  96% purchased from Sigma-Aldrich, Germany. All chemicals were used without further purification.

Aqueous NPs colloidal solutions were obtained by a two-step method on Au nucleating seeds by reduction of chloroauric acid and silver nitrate by ascorbic acid. In [16] we describe the Au-Ag NPs synthesis in detail. The Au-Ag NPs coatings were obtained by self-assembly method [19,20], based on multistage NPs absorption from the colloidal solution onto the substrate. In order to improve the first NPs layer absorption, the substrate surface was chemically modified by APTES molecules [20]. After that substrates were immersed into a fresh prepared colloidal solution of NPs and soaked for 24 h at a temperature of  $20 \pm 2$  °C to form Au-Ag NPs coating, then repeatedly flushed out and air-cured. To increase the surface thickness the second and third cycles of NPs deposition onto the substrate were processed analogously (the thickness of the NPs layer after the third cycle was 800 nm).

Morphology and structure of Au-Ag NPs were studied by transmission electron microscopy (TEM) with the use of electron microscope TEM-125 (Selmi, Ukraine) with accelerating voltage of 100 kV and highresolution transmission electron microscopy (HRTEM) with the use of the microscope JEM-2100F (JEOL). The statistical analysis of NPs sizes obtained by the electron microscopy was processed, and the NPs size distribution histograms were constructed. For every NPs size obtained in the process the diameter of at least 300 particles was measured. Morphology and surface profile of NPs coatings were studied by the high-resolution scanning electron microscope (HR-SEM) (Hitachi S-5500, Hitachi High-Technologies Corporation, Japan) and the atomic force microscope (AFM) (SPM-9600, Shimadzu Corp., Japan) in noncontact mode with frequency of 0.2 Hz using PPP-NCHR cantilever. Sample composition was analyzed by the scanning electron microscope JSM-6390LV with the X-ray chemical analysis system INCA Energy 350. Localness of energy dispersive X-ray analysis was  $\sim 1 \,\mu m$ , concentration accuracy was 1-5 rel. %. Sample uniformity was verified using a pointto-point analysis method.

Stable colloidal solutions of starlike Au-Ag NPs with the average particle size of 55–73 nm were obtained. Silver ions presence is an important condition for forming and growth of sharp tips of "star"-shaped NPs along certain crystallographic faces of Au nucleating seeds with size 20–30 nm. We suppose that silver is adsorbed onto the surfaces of seeds faces with the largest surface energy, after that silver forms monolayers [21,22], selectively stabilizes faces {110}, {310}, {720} and prevents further growth of Au on the surface of these faces. Anisotropic growth of NPs leads to the forming of side tips on faces with lower surface energy. After the stabilization of faces {110} Au is adsorbed on faces {111}, that leads to the forming of gold tips. Increase of the silver ions concentration in the growth solution leads to an increase of the average NPs size.

(Fig. 1a), as well as a TEM image of nanoparticles array (Fig. 1b) show that the obtained Au-Ag nanoparticles have a developed surface due to the peculiarities of their preparation method.

The study of Au-Ag NPs chemical composition indicates that the detection limit of analysis does not allow identifying the dopant gradient of Ag on the surface of Au-Ag NP at such a low Ag concentrations. Fig. 1c demonstrates the distribution map of gold as a matrix element. It can be seen that developed surfaces cause the observed inhomogeneous signal of gold.

The chemical composition of Au-Ag NPs samples was determined by using the scanning electron microscope JSM-6390LV equipped with the X-ray chemical analysis system INCA Energy 350. It was determined that the silver content in the obtained NPs is 6.6, 10.8 and 13.1 at.% for Au-Ag NPs with the average particle size of 55, 68 and 73 nm, respectively.

In Fig. 2 electron microscope image and size distribution histograms of Au-Ag NPs with tips morphology are represented. NPs with average size of 55 and 68 nm have  $\sim$ 20% size dispersion (Fig. 2a and b), and NPs with average particle size of 73 nm have  $\sim$ 10% size dispersion (Fig. 2 c).

Obtained starlike Au-Ag NPs are nanocrystals, and the existence of distinctive reflexes, corresponding to the faces {111}, {200}, {220}, {311}, indicate a face-centered cubic lattice of Au-Ag NPs (Fig. 2d).

Using self-assembly method, stable coatings with different Ag concentration were obtained (Fig. 3). Produced coatings are characterized by a frame work (arc) structure defined by a starlike shape of Au-Ag NPs. Analysis of films surfaces by the AFM method showed that the average thickness of NPs coating is 800 nm (Fig. 4).

# 3. Method of electrical conductivity investigation

The study of the electrical conductivity of rectangular samples with a coating of Au–Ag NPs on glass consisted in measuring their temperature dependences of the resistance using four probe method in temperature range 300–4.2 K. The connection of current and potential wires with the sample was carried out in one of two ways. In the first method, thin film strips of indium-tin alloy or strips of indium melted in air were applied on the coating across the entire width of a sample. Gold wires with a diameter of 0.05 mm were glued to the contact areas of the strips with silver paste (inserts in Figs. 5 and 6). In the second method, the current and potential wires were glued with silver paste directly on the edge of the coating (insert in Fig. 7).

The typical length of the samples was 5 mm with a width of 1-2 mm. The distance between potential contacts ranged from 0.1 to 1 mm. Measurement of the resistance (R) of the sample as a function of temperature (T) was carried out automatically by recording the currentvoltage characteristics I(V) of the sample at different temperatures and converting them into R(T). The maximum measuring direct current in various experiments was from 50 to 800  $\mu$ A. Dependencies I(V) and R(T)were linear in the entire range of measuring currents and temperatures when using the first method of forming current and potential contacts (details are provided below). The magnetic properties of the samples were controlled in two ways. In the first of them, a permanent magnet was located above the surface of the sample, creating magnetic field of 0.05 T in the coating zone. Then, the temperature dependence of the sample resistance was recorded in the temperature range 4.2-300 K. After that the dependencies obtained with and without a magnet were compared. In the second method, the substrate with coating could be placed on a flat coil with a diameter close to the size of the sample coating. After that, measurement and comparison of the inductance of the coil with and without of a substrate with coating was performed. The inductance was measured using a high-frequency digital inductance meter type E7-12 at a frequency of 1 MHz. The resolution of the meter was 100 nH.

### 4. Research results and discussion

The HRTEM micrograph of an individual Au-Ag nanoparticle

Typical temperature dependences of the relative value of resistance



Fig. 1. HRTEM image of single Au –Ag NP (a); TEM image of Au-Ag NPs sample with Ag concentration 6.6 at. % (b); and EDS elemental mapping of Au-Ag NPs of the sample in Fig. 1b (c).

 $R/R_{273K}(T)$  of samples with different silver contents in the temperature between the room temperature and 100 K are shown in Fig. 5.

The common property of all curves is the almost linear ("metallic") dependence of the resistance  $R/R_{273K}(T)$  in a wide temperature range with different values of the temperature coefficient of resistance (TCR). It is seen that the relative TCR of the samples increases with increase of silver percentage. It is established (Fig. 5) that relative TCR of this Au-Ag coatings (from  $10^{-3}$ /K to  $0.5 \times 10^{-3}$ /K) is 1.5–2 times less than TCR of pure gold ( $1.5 \times 10^{-3}$ /K) and silver ( $10^{-3}$ /K) [23]. We suggest that this feature of the TCR is due to the size effect. The mean free path of electrons (MFPE) in these NPs and the nanocontacts between them is limited by their small size. The golden core (seed) size of the NPs is two times smaller than the mean free path of an electron in massive gold. Accordingly, this leads to an increase in the resistance of nanocontacts between the Au-Ag NPs.

All these dependences are obtained using the first method of forming current and potential contacts. Potential and current contacts of InSn melt strips applied to coatings across the direction of the transport current (and along the sample width) were used. The dependences  $R/R_{273K}(T)$  for sample No. 2, taken with an interval of two weeks, are presented in Fig. 6. Reproducible results with multiple repetitions of the cooling-heating process can obtain only with this method of forming contacts. The investigated coatings were not protected from the moisture of the surrounding air.

Experience of researches of optical properties of not protected coatings of stars like Au-Ag NPs with the content of silver from 6.6 to 13.1% made by co-authors of article [15,16,20], has shown, that parameters of such SERS-substrates do not vary within several months. Besides, repeating electrical resistance values of the same conductive coatings, received by us within two weeks (Fig. 6), also speak about high stability of their properties in laboratory conditions. Stability of similar coatings proves to be true also other authors [8,11,12]. It has formed the basis not to subject the coatings to additional influence for the purpose of their protection against an atmospheric moisture.

Optical studies of samples showed that they are very heterogeneous in area and have poor adhesion to glass. NPs of the coatings have poor contact not only with the substrate, but also with each other. This means that the coating is a heterogeneous in conductivity and weakly bound in the volume of the grid of contacting with each other NPs. Photomicrographs in Figs. 3 and 4 confirm this idea of the electrical properties of coatings. The current flow in such structures is percolation. Contacts between NPs can change or even break, changing the configuration and number of parallel current paths with decreasing temperature due to different thermal expansion coefficient of glass and coating. These features are more often observed under the second method of connecting current contacts. The dependence, similar to a sharply non-linear temperature dependence of resistance with a superconducting transition at a temperature of 230 K, is shown in Fig. 7.

For this sample, potential contacts were located on the bottom edge of the sample. However, the detected independence of R(T) curves on the magnetic field and the absence of the expected decrease in the inductance of the measuring coil due to the suggested diamagnetic effect on the inductance of the sample do not confirm the presence of a superconductivity. Thus, a nonlinear temperature decrease in resistance to zero on one of the Au-Ag coating samples, not indicate the appearance of high-temperature superconductivity. At the same time, the results we obtained (Fig. 7) is an experimental proof of the assumption made in [24] that the shape of the experimental R(T) curves may not always be a criterion for the appearance of a superconducting transition. Really, in the case of Fig. 7, there is likely a percolation flow of the measuring current through the areas of the sample with a significantly lower local resistance than the areas adjacent to the location of the potential contacts. As a result, these areas are actually isolated from the measuring current and there is no voltage on them. This can be mistakenly perceived as the decrease of the resistance of the sample to zero and the occurrence of superconductivity.

The nonlinear dependences R(T) can be explained by a change in the mechanical stresses in the coating with a change in temperature, which causes a change in the total electrical conductivity of the nanocontacts between the NPs of the coating.

The potential contacts completely overlap the measuring current paths with the first method of measuring the  $R/R_{273K}(T)$  dependences (Figs. 5 and 6), which makes it impossible to disconnect the potential contacts from the transport current. As a result, the dependences  $R/R_{273K}(T)$  in most cases do not have nonlinear sections. Only in rare cases, weak nonlinearities were observed. Their appearance can be explained by the same processes of both thermal compression (upon cooling) and expansion (upon heating) of a weakly bound NPs forming the coating. This causes an irreversible decrease or increase in contact resistance between the NPs located in the area between the potential contacts.

Regarding the nature of the electrical conductivity of the samples, the following can be noted. A linear decrease in resistance R with decreasing temperature indicates their metallic conductivity. Hence a contribution to the conductivity of possible semiconductor layers between the NPs is unlikely. In this regard it can be assumed that the total resistance (R) of the sample consists of the resistance ( $R_1$ ) of the NPs itself and the resistance ( $R_2$ ) of the metal point nanocontacts between them. The following model technique is used to estimate the value of  $R_1$ .

Let's consider the rectangular modeling sample in the form of a gold film, at which mass (*m*), length *l* and width *w* (0.5 × 5 mm) same as at the experimental Au-Ag coating sample. The difference between specific gravity of gold and Au-Ag particle with the small silver content is very little for the approached calculation of  $R_1$  value. The mass (*m*) this coating is defined experimentally by weighing. Approximate value of resistance  $R_1$  can be calculated if the *m*, *l* and *w* of the sample, as well as the specific gravity ( $\sigma$ ) and the specific resistance ( $\rho$ ) of gold are known.



Fig. 2. TEM of starlike Au-Ag NPs with average size: (a) 55 nm, (b) 68 nm, (b) 73 nm and the corresponding NPs size distribution histograms; (d) electric micro diffraction of NPs.

Fig. 3. TEM of coatings surfaces of NPs with different Ag concentration: (a) 6.6 at. %, (b) 10.8 at. %, (c) 13.1 at. %.



Fig. 4. Surface profile of NPs coating with Ag concentration of 6.6 at. %; coating thickness is 800 nm.



**Fig. 5.** Dependencies of the relative resistance  $R/R_{273K}(T)$  of the coating samples with different silver contents: 1–6.6% Ag (black line), 2–10.8% Ag (dark gray line), 3–13.1% Ag (light gray line). The inset shows the layout of the contacts on the samples.

Thickness of the modeling sample in the form of the gold film it is designated as *d*. In our case  $\sigma \approx \sigma_{Au} = 19.3 \text{ g/cm}^3$ ,  $\rho \approx \rho_{Au} \approx 10^{-6}$  Ohm-cm and  $m \approx 0.001$  mg. The value of  $R_1$  can be calculated from two ratios:

$$R_1 \approx \rho[l/(wd)],\tag{1}$$

 $m \approx \sigma \times l \times w \times d. \tag{2}$ 

From (1) and (2) we get:



**Fig. 6.** Dependences of the relative resistance  $R/R_{273K}(T)$  of coating sample No. 2 (see Fig. 5) in the temperature between the room temperature and 4.2 K, taken at time intervals of 2 weeks (black line — 1st experiment, gray triangles — 2nd experiment). Contacts — In-Sn strips. The inset shows the layout of the contacts on the sample.



**Fig. 7.** Dependences R(T) of sample resistance with Ag concentration 6.6% during cooling (black triangles) and heating (gray triangles) obtained using the second method of forming contacts with a sample similar to the one used by the authors of [17]. Current contacts were prepared by gluing the wires by silver paste along the edge of the sample. The inset in Fig. 7 shows the layout of contacts.

$$R_1 = \frac{\rho \sigma \ l^2}{m}.$$
 (3)

For the above numerical parameters from formula (3), we get  $R_1 \approx 6 \times 10^{-2}$  Ohm. From a comparison of the resistance values (from 10 to 100 Ohm) experimentally measured Au-Ag samples at room temperature and the calculated value of  $R_1$ , it follows that the nanocontacts resistance  $R_2$  makes the main contribution to the resistance of the sample of starlike Au-Ag coating. The thickness (*d*) of the model sample, based on relationship (2), is about 20 nm. If we take into account the thickness of the studied coatings (800 nm), we can be deduced that its specific density is 40 times less than the density of its NPs, i. e. half the water density. This also indicates a very large number of nanosized electrical nanocontacts between the coating NPs. The average specific resistance 10–100 Ohm ranges from  $3 \times 10^{-5}$  to  $3 \times 10^{-4}$  Ohm-cm.

#### 5. Conclusions

The electrical conductivity of coatings of starlike nanoparticles (NPs) Au-Ag at silver content of 6.6–13.1% was first determined by measuring of their electrical resistivity in the temperature range 4.2–300 K.

The coating samples were obtained by the chemical deposition of an Au–Ag colloid on glass substrates. The complexity of the cryogenic measurements of the electrical resistance of these samples is due to the weak and non-uniform adhesion of the coating to the substrate, as well as the low and non-uniform density of the coating. The original way of reception of repeated temperature dependences of electric resistance of chemical coatings of star like NPs by means of four probe method is developed.

It is established that the temperature dependence R(T) has a metallic character, i.e. the resistance decreases linearly with decrease of temperature up to the minimum its value (4.2 K). This suggests that between the nanoparticles there are mainly metallic nanocontacts without oxides and dielectric inclusions. Wherein resistance of the coatings decreases with increase in the maintenance of silver in the NPs. Measurements also showed that the relative value of temperature coefficient of resistance (TCR) of the coatings is 1.5–2 times less than TCR of pure gold and silver. This can be explained by the size effect associated with the small size of NPs compared to the mean free path of electrons in pure bulk gold and silver. It was also established that the average value of the electrical resistivity of the coatings was several orders of magnitude greater than the resistivity of bulk gold and silver. The difference in the resistances is explained by the predominant contribution to the resistance of coatings of numerous nanocontacts between NPs.

The linear temperature dependences of the resistance of the coatings obtained using the original design of current and potential contacts with the sample, and the negative result of Meissner effect observation indicate the absence of superconductivity in them.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

A.G. Sivakov: Investigation, Validation. R.P. Yavetskiy: Supervision, Project administration. N.A. Matveevskaya: Investigation, Writing - original draft. T.G. Beynik: Investigation. A.V. Tolmachev: Investigation. S.I. Bondarenko: Supervision, Project administration, Writing - original draft, Formal analysis, Methodology, Conceptualization. A.S. Pokhila: Visualization, Investigation. A.V. Krevsun: Investigation, Resources. V.P. Koverya: Investigation, Writing - review & editing. A.S. Garbuz: Investigation.

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#### References

- M.I. Baraton, Shintesis, Functionalization, Surface Treatment of Nanoparticles, Am. Sci., Los- Angeles, 2002.
- [2] N. Lebovka, T. Dadakova, L. Lisetskiy, O. Melezhik, G. Puchkovskaya, T. Gavrilko, Ya. Baran, M. Drozd, Percolation properties, phase transformations and electrical conductivity of nanocomposites based on liquid crystals and carbon nanotubes, in: Abstracts of scientific Conference "Nanoscale Systems" (NANCIS 2007), Kiev, Ukraine, 2007, p. 464.

- [3] G.V. Kamarchuk, A.P. Pospelov, A.V. Savytskyi, A.O. Herus, Yu.S. Doronin, V. L. Vakula, E. Faulques, Conductance quantization as a new selective sensing mechanism in dendritic point contacts, SN Appl. Sci. 1 (2019) 244, https://doi.org/ 10.1007/s42452-019-0241-x.
- [4] A.P. Shpak, P.P. Gorbyk, Nanomaterials and Supramolecular Structures, Physics, Chemistry, and Applications, Springer Science+Business Media B.V., Springer, Dordrecht, 2010, https://doi.org/10.1007/978-90-481-2309-4.
- [5] Yu.V. Ermolaeva, M.V. Dobrotvorskaya, S.V. Dukarov, A.V. Tolmachev, A. A. Borsch, V.I. Volkov, V.R. Lyakhovetsky, 2D ensembles of gold nanocrystals on glass substrates, in: Abstracts of the scientific conference "Nanoscale Systems" (NANCIS 2007), Kiev, Ukraine, 2007, p. 185.
- [6] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, Synthesis of thiolderivatised gold nanoparticles in a two-phase Liquid–Liquid system, J. Chem. Soc., Chem. Commun. 7 (1994) 801–802, https://doi.org/10.1039/C39940000801.
- [7] Yong Yang, Jianlin Shi, Go Kawamura, Masayuki Nogami, Preparation of Au–Ag, Ag–Au core-shell bimetallic nanoparticles for surface-enhanced Raman scattering, Scripta Mater. 58 (2008) 862–865, https://doi.org/10.1016/j. scriptamat.2008.01.017.
- [8] Li Yuan, Weihong Qi, Baiyun Huang, WenhaiJi, Mingpu Wang, Size- and composition-dependent structural stability of core-shell and alloy Pd-Pt and Au-Ag nanoparticles, J. Phys. Chem. C 117 (2013) 15394–15401, https://doi.org/ 10.1021/jp404422y.
- [9] Derrick M. Mott, Dao Thi Ngoc Anh, Prerna Singh, Cheshta Shankar, Shinya Maenosono, Electronic transfer as a route to increase the chemical stability in gold and silver core-shell nanoparticles, Adv. Colloid Interface Sci. 185–186 (2012) 14–33, https://doi.org/10.1016/j.cis.2012.08.007.
- [10] Yanlin Feng, Guorui Wang, Yun Chang, Yan Cheng, Bingbing Sun, Liming Wang, Chunying Chen, Haiyuan Zhang, Electron compensation effect suppressed silver ion release and contributed safety of Au@Ag Core–Shell nanoparticles, Nano Lett. 19 (2019) 4478–4489, https://doi.org/10.1021/acs.nanolett.9b01293.
- [11] A. Guerrero-Martínez, S. Barbosa, I. Pastoriza-Santos, L.M. Liz-Marzán, Nanostars shine bright for you: colloidal synthesis, properties and applications of branched metallic nanoparticles, Curr. Opin. Colloid Interface Sci. 16 (2011) 118–127, https://doi.org/10.1016/j.cocis.2010.12.007.
- [12] H. Yuan, C.G. Khoury, H. Hwang, C.M. Wilson, G.A. Grant, T. Vo-Dinh, Gold nanostars: surfactant-free synthesis, 3D modelling, and two-photon photoluminescence imaging, Nanotechnology 23 (2012), 075102, https://doi.org/ 10.1088/0957-4484/23/7/075102.
- [13] K. Saha, S.S. Agasti, C. Kim, X. Li, V.M. Rotello, Gold nanoparticles in chemical and biological sensing, Chem. Rev. 112 (2012) 2739–2779, https://doi.org/10.1021/ cr2001178.
- [14] P.H.B. Aoki, L.N. Furini, P. Alessio, A.E. Aliaga, C.J.L. Constantino, Surfaceenhanced Raman scattering (SERS) applied to cancer diagnosis and detection of pesticides, explosives, and drugs, Rev. Anal. Chem. 32 (2013) 55–76, https://doi. org/10.1515/revac-2012-0019.
- [15] V. O Yukhymchuk, O.M. Hreshchuk, V.M. Dzagan, M.A. Skoryk, S.R. Lavoryk, G. Yu. Rudko, N.A. Matveevskaya, T.G. Beynik, M.Ya. Valakh, Experimental studies and modeling of "starlike"plasmonic nanostructures for SERS application, Phys. Status Solidi B 256 (2019), 1800280, https://doi.org/10.1002/pssb.201800280.
- [16] T.G. Beynik, N.A. Matveevskaya, M.V. Dobrotvorskaya, A.S. Garbuz, D. Yu. Kosyanov, V.I. Vovna, A.A. Vornovskikh, S.I. Bogatyrenko, Synthesis and characterization of branched gold nanoparticles, Funct. Mater. 24 (2017) 21–25, https://doi.org/10.15407/fm24.01.021.
- [17] D.K. Thapa, A. Pandey, Evidence for Superconductivity at Ambient Temperature and Pressure in Nanostructures, 23 Jul 2018. arXiv:1807.08572 [cond-mat.suprcon].
- [18] M.K. Hooda, P. Kumar, ViswanathBalakrishnan, C.S. Yadav, Observations of Zero Electrical Resistance of Au-Ag Thin Films Near Room Temperature, 3 Jun 2019. arXiv:1906.00708 [cond-mat.supr-con].
- [19] O. Bibikova, J. Haas, A.I. López-Lorente, A. Popov, M. Kinnunen, I. Meglinski, B. Mizaikoff, Towards enhanced optical sensor performance: SEIRA and SERS with plasmonicnanostars, Analyst 142 (2017) 951–958, https://doi.org/10.1039/ C6AN02596J.
- [20] T.G. Beynik, N.A. Matveevskaya, D.Yu. Kosyanov, A.A. Vornovskikh, V. G. Kuryavyi, V.O. Yukhymchuk, O.M. Hreshchuk, Nanostructured films based on branched gold particles, J. Nanophotonics 12 (2018), 036001, https://doi.org/ 10.1117/1.JNP.12.036001.
- [21] P. Ndokoye, X. Li, Q. Zhao, T. Li, M.O. Tade, S. Liu, Gold nanostars: benzyldimethylammonium chloride-assisted synthesis, plasmon tuning, SERS and catalytic activity, J. Colloid Interface Sci. 462 (2016) 341, https://doi.org/ 10.1016/j.jcis.2015.10.007.
- [22] T.G. Beynik, N.A. Matveevskaya, M.V. Dobrotvorskaya, P.V. Matejchenko, M. I. Danilenko, T.A. Cheipesh, D. Yu. Kosyanov, A.A. Vornovskikh, V.G. Kuryavyi, Fabrication and properties of gold nanostars and film structures based on them, Nanosist. Nanomater. Nanotekhnol 15 (2017) 417–429.
- [23] M.P. Malkov, Handbook of Physical and Technical Fundamentals of Cryogenic Engineering, 1973. M.:Energiya.
- [24] D. Pekker, J. Levy, A Comment on Percolation and Signatures of Superconductivity in Au/Ag Nanostructures, 17 Aug 2018 [cond-mat.supr-con], arXiv:1808.05871.